total molecular concentration both of the undissociated molecules and of the molecules of the products of the dissociation.

Summary.

The dissociation pressures of calomel for temperatures between 309° and 384° are given. The pressure, 760 mm., is reached at 383.7°.

The Kirchoff-Rankin-Dupré equation represents the results satisfactorily.

The entropies of vaporization to constant molecular concentration for eight dissociating substances are recorded.

Confining liquids are discussed.

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THE OXIDES OF IRON. I. SOLID SOLUTION IN THE SYSTEM FE₂O₃–FE₃O₄[1].

BY R. B. SOSMAN AND J. C. HOSTETTER.

CONTENTS.—Introduction. State of Knowledge of the Oxides of Iron. Apparatus Employed. Materials: Ferric Oxide; Merck's "Reagent Iron Oxide;" Oxide from Electrolytic Iron; Sibley Ore; Magnetite; Oxygen. Special Problems: Optical Properties of the Oxides of Iron; Reduction of Iron Oxides by Platinum; Disappearance of Oxygen in Furnace; Adsorption of Gases. Questions of Equilibrium: Reproducibility of Dissociation Pressures; Accuracy of Temperature and Pressure; Pressures from Ferric Oxide from Different Sources; Effect of Temperature Gradient in Furnace; Comparison of Rising and Falling Temperatures; Pressures Obtained by Oxidation of Magnetite. The System Fe₂O₃–Fe₃O₄: Experimental Results: General Plan; Methods of Analysis; Total Iron; Pressure-composition Isotherm at 1200°; Pressure-composition Isotherm at 1100°; Form of Dissociation-pressure Curve near Fe₂O₃; Optical Properties. Comparison with Previous Investigations. Summary.

Introduction.

The silicate systems which have hitherto been the subjects of study in this laboratory have all been made up of oxides which are apparently unaffected by atmospheric oxygen at temperatures below 1600°. They could therefore be melted in platinum-wound furnaces in the open air. The oxides which can be so treated include silica, alumina, magnesia, lime, and the alkalies. But iron, which is one of the most important constituents of natural silicates, changes its form of combination and the properties of its compounds according to the amount of oxygen which is combined with it, and, furthermore, the amount of oxygen so combined is constantly changing, especially at high temperatures. It becomes necessary, then, to take account of oxygen as one of the components in any silicate system containing iron.

[1] Presented in abstract at the Seattle Meeting of the American Chemical Society, Sept. 1, 1915.

Early in the work on the iron-bearing silicates, it became evident that we must know something about the dissociation pressures and chemical relationships of the iron oxides, in order to explain complications arising in the silicate systems. We found the published information too incomplete for our purpose, and have therefore devoted some time to the study of the system iron-oxygen.

This paper will deal with the equilibrium conditions that must be met in the study of the dissociation of Fe_2O_3, and with the information obtained on the series Fe_2O_3-Fe_3O_4 by measurement of the dissociation pressures, that is, the oxygen pressures in equilibrium with the oxides.

State of Knowledge of the Oxides of Iron.

Three principal (anhydrous) oxides of iron have long been familiar in chemical literature: ferric oxide, Fe_2O_3, occurring in nature as the mineral hematite; ferroso-ferric oxide, Fe_3O_4, occurring as magnetite; and ferrous oxide, FeO, which is not known to occur in nature. A less common mineral form is martite, which has a somewhat variable composition intermediate between Fe_2O_3 and Fe_3O_4. It is commonly described as "hematite pseudomorph after magnetite," as it usually lies nearer hematite than magnetite in composition, but has the external octahedral form of magnetite. In addition to these natural oxides, many other oxides have been prepared and described by various investigators. Some of these are listed below in the order of their oxygen content (Table I).

It would be too long a task to review completely the history of the many researches upon the iron oxides. It must suffice for the present to say that as most of these have been conducted at ordinary temperatures and in connection with water solutions, with attending complications in the formation of colloidal hydroxides, they have not yielded the information necessary to an understanding of the equilibrium relationships in silicate mixtures at higher temperatures. Some of the investigations on dissociation pressures of the iron oxides will be discussed in connection with our own conclusions later in this paper.

TABLE I.

Principal Oxides of Iron Described in Chemical Literature.

Formula.			Described by	Percentage of the iron which is in the ferrous state.
Fe_2O_3, hematite				0.00
Fe_7O_{10}	or	$(FeO).3(Fe_2O_3)$	Kohlmeyer	14.29
$Fe_{13}O_{18}$	or	$3(FeO).5(Fe_2O_3)$	Kohlmeyer	23.08
Fe_8O_{11}	or	$2(FeO).3(Fe_2O_3)$	Haber and Kaufmann	25.00
$Fe_{11}O_{15}$	or	$3(FeO).4(Fe_2O_3)$	Kohlmeyer	27.27
Fe_3O_4	or	$(FeO).(Fe_2O_3)$, magnetite		33.33
Fe_4O_5	or	$2(FeO).(Fe_2O_3)$	Gregory	50.00
Fe_5O_6	or	$3(FeO).(Fe_2O_3)$	Döbereiner	60.00
Fe_6O_7	or	$4(FeO).(Fe_2O_3)$	Hauser	66.67
FeO				100.00

Apparatus Employed.

Our furnace and accessory apparatus are shown in somewhat dia-
grammatical section in Fig. 1.[1] In principle, the furnace is similar to
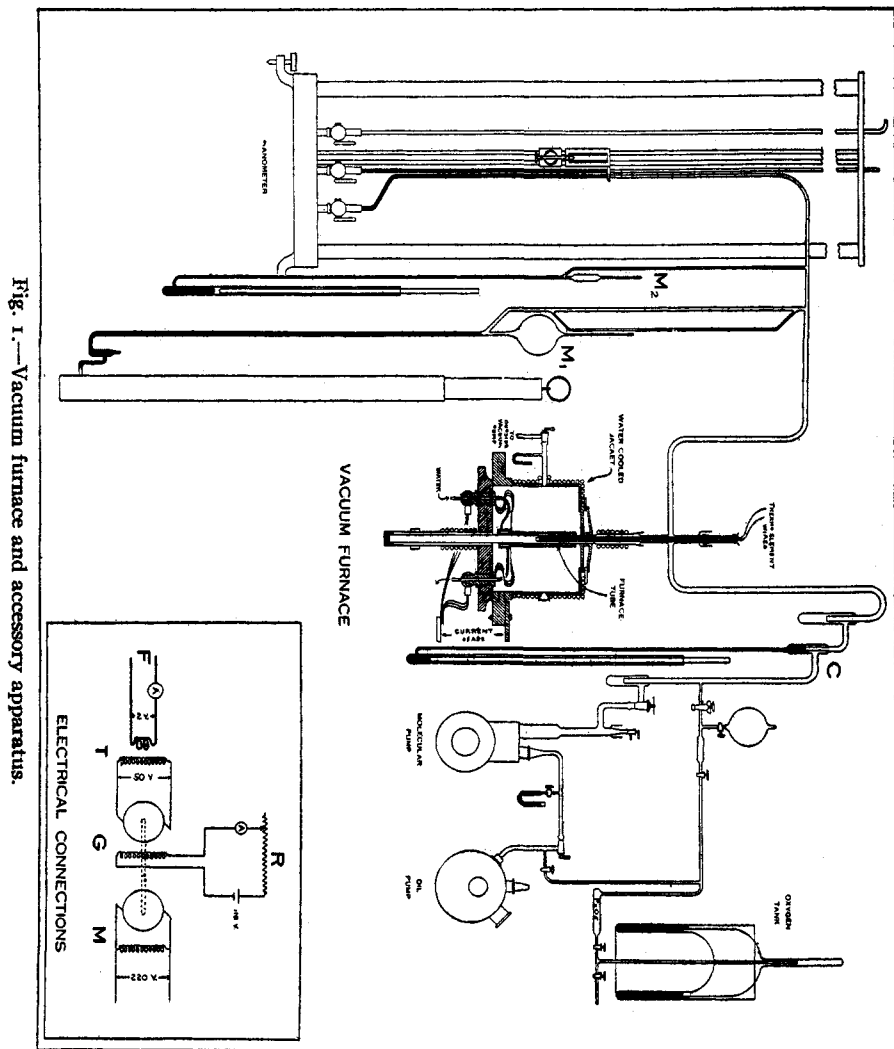that of Slade.[2] It consists essentially of two parts: (1) the furnace tube,

Fig. 1.—Vacuum furnace and accessory apparatus.

which serves both as the furnace wall inclosing the "inside vacuum"
and as the heating element; (2) the water-cooled jacket, which surrounds
the furnace tube and incloses the "outside vacuum."

[1] A more detailed description than that here given has been published in *J. Wash.
Acad. Sci.*, **5,** 277–285 (1915).

[2] R. E. Slade, "An Electric Furnace for Experiments *in vacuo* at Temperatures
up to 1500°," *Proc. Roy. Soc. London*, (A) **87,** 519–524 (1912).

An alternating current at low voltage is sent through the furnace tube, which is made of an alloy of 80 parts platinum and 20 rhodium.[1] The tube is 15 mm. inside diameter and 200 mm. long, with walls 1 mm. thick. The current is carried in by water-cooled terminals; the upper terminal is fixed to the furnace jacket, while the lower terminal moves with the expansion and contraction of the furnace tube. The cooling water is led into the lower terminal by lead pipes, and the current is carried by a sheaf of flexible copper strips. The lower leads are insulated from the furnace jacket by the stone base of the jacket, and are prevented from accidentally touching the walls by mica sheets around the inside of the jacket.

The lower end of the platinrhodium tube is extended by a steel tube, capped with a screw cap and sealed with kollolith.[2] The upper end is likewise extended by a steel tube into which a glass tube is sealed.

Branches from the glass tube connect with the Gaede molecular vacuum pump, on the one hand, and with the pressure gages on the other. The interior of the furnace and gages is kept dry by a tube of P_2O_5 in the bottom of the steel extension of the furnace tube.

The charges are contained in a small platinum crucible suspended by two platinum wires sealed into a glass cap, which is attached to a ground glass conical joint at the top of the tube above the furnace. The two wires of the platinum-platinrhodium thermoelement are also sealed through this glass cap, and the four wires are insulated from one another by transparent fused silica or Marquardt porcelain capillaries. The two suspension wires may also be used as the leads for the determination of melting points, et cetera, by the quenching method.

There are three pressure gages: (1) a McLeod vacuum gage of 500 cc. capacity from Leybold (shown at M_1); (2) a similar gage of 50 cc. capacity made here (M_2); (3) a mercury manometer read to 0.01 mm. by means of parallel knife edges and a vernier. The latter is the manometer used in previous work on the nitrogen thermometer.[3] It has an excellent scale, calibrated throughout its length to 0.01 mm. by the Normal-Aichungs-Kommission in Charlottenburg. The three gages, compared against one another at various pressures within their ranges, agreed within the error of their readings. We have in this combination of gages a range of pressure measurement from 0.000001 mm. mercury up to about 2.5 atmospheres.

[1] The tube was made by Dr. Heraeus of Hanau, to whom we have several times had occasion to express our indebtedness for his interest in the forwarding of high-temperature investigations.

[2] A Canada balsam substitute of constant "melting point" and low vapor pressure, made by Voigt & Hochgesang.

[3] Day and Clement, Am. J. Sci., [4] 26, 415 (1908); Publ. Carnegie Inst. Washington, No. 157, p. 19.

The furnace jacket is an inverted iron pot, closed at the bottom by a disk of Alberene stone through which pass (1) the two conductors in parallel which carry the current to the lower end of the platinrhodium tube, together with the tubes for the cooling water, and (2) the steel extension of the platinrhodium tube. The latter is surrounded by a water-jacketed steel tube and cap.

The jacket is evacuated independently of the inside vacuum by means of a May-Nelson pump. There is no connection between the inside high vacuum and the outside "ordinary" vacuum. No insulation or refractory material is used excepting a magnesia tube surrounding the platinrhodium tube. The outside vacuum removes any danger of collapsing the hot furnace tube at high temperatures, and also provides an efficient heat insulation. The furnace jacket is cooled by a coil of lead pipe on the outside carrying cold water. An observation window permits optical temperature measurements to be made from without.

The current is supplied to the furnace from the secondary of a small 25 : 1 transformer. The primary of the transformer is supplied by a motor generator of 60 cycles and a voltage range from 0 to about 300 volts. The generator voltage is regulated by means of its field current, which is supplied by a 110 volt storage battery and passes through rheostats alongside the potentiometer. By regulation of the field current the furnace current can be regulated without any waste of electrical energy, and if the voltage applied to the motor of the motor generator is reasonably constant, the temperature can be held constant without difficulty to one degree at 1500°. This degree of constancy is very often necessary for accurate measurements of the dissociation pressures of iron oxides, as these pressures change quite rapidly with temperature.

Materials.

Ferric Oxide.—Ferric oxide is rather difficult to prepare pure, and not many preparations of the required purity can be found on the market. We have used several different preparations in the course of the work.

Kahlbaum's "Eisenoxyd zur Analyse mit Garantieschein" is said by the manufacturer to contain 99.60% Fe_2O_3, 0.40% moisture, no manganese and no alkalies. Its color is between raisin-black and dark slate-purple, 65''' l, of Ridgway's color system.[1] Our analysis of this oxide gives: Fe_2O_3, 99.70; FeO, 0.09; SiO_2, 0.01; Na_2O, 0.04; TiO_2, less than 0.01; MnO, less than 0.01; P_2O_5, less than 0.005; water-soluble, 0.02; total, 99.85. The remainder of 0.15% may be moisture.

Merck's "Reagent Iron Oxide."—No analysis is given by the manufacturer. It is stated in the catalog that this oxide is made according to the method of Brandt (ignition of nitrate made from pure iron).[2] Ac-

[1] Robert Ridgway, "Color Standards and Color Nomenclature," 1912.

[2] L. Brandt, *Chem. Ztg.*, **32**, 812, 830, 840, 851 (1908).

cording to the tests which it is supposed to pass, this oxide should contain, at the most: 0.1% water and volatile substances, 0.01 water-soluble substances, 0.005 Cl, 0.0032 N_2O_5, 0.035 SO_3, 0.033 SiO_2, 0.003 FeO, 0.01 substances insoluble in HCl, 0.02 Al_2O_3, 0.007 Ca, 0.0002 Mg. Its color is quite different from that of Kahlbaum's oxide, and is between Prussian-red and ocher-red $5''$ $l.$ Our analysis of Merck's oxide gives: Fe_2O_3, 99.30; FeO, 0.07; SiO_2, 0.01; Na_2O, 0.05 (as Na_2SO_4, 0.11); MnO, less than 0.01; TiO_2, less than 0.01; P_2O_5, less than 0.005; water-soluble, 0.02; H_2O at $100°$, 0.34; H_2O (and adsorbed gases?) lost in vacuum at $500°$, 0.50. Total, 99.82 to 99.98.

Oxide from Electrolytic Iron.—Pure electrolytic iron made about 1907, by C. F. Burgess,[1] was dissolved in nitric acid (J. T. Baker's C. P.), filtered, evaporated to form the basic nitrate, and ignited in small portions over the blast lamp in a platinum crucible. No analysis was made of the product. The original metal contains no manganese and only traces of sulfur, phosphorus, and silicon.

Sibley Ore.—This is one of the purest natural ferric oxides available in large quantity, although, of course, selected hematite crystals are much purer. It is standard sample No. 27 of the Bureau of Standards, and contains, according to the Bureau's certificate and its Circular No. **26:** 69.2% total iron, 0.036% phosphorus, 0.78% SiO_2, no Mn and no Ti. Ferrous iron does not seem to have been looked for in the analyses which have been published, but we find a surprisingly large percentage of FeO in this sample. Four analyses, on two different bottles, gave 2.27, 2.24, 2.34 and 2.25%; mean 2.28%. On the basis of 69.2% total iron, as reported by the Bureau, the calculated composition in terms of oxides is: 96.41 Fe_2O_3, 2.28 FeO, 0.78 SiO_2, 0.09 P_2O_5, 0.01 V_2O_3;[2] total, 99.57.

Magnetite.—Probably the purest and best crystallized magnetite ever obtained in large quantity was from the "Lovers' Pit" of the Barton Hill mines at Mineville, N. Y. We collected a number of specimens from this mine in 1914. The sample (No. 3g) used for the present work consisted of clean crystals from a pillar in the Lovers' Pit, taken about 3 ft. below the hanging wall or 10 ft. above the foot wall.[3] This magnetite contains by our analysis 30.72% FeO, 72.08% total iron, and 0.01% moisture coming off at $100°$. It therefore contains 99.00% pure Fe_3O_4,

[1] For this we are indebted to Professor C. F. Burgess, of the University of Wisconsin.

[2] Cain and Hostetter, *J. Ind. Eng. Chem.*, **4**, 254 (1912). *Bur. Standards Tech. Paper*, No. 8.

[3] We are greatly indebted to Mr. Rigby and the officials of Witherbee, Sherman & Co., for assistance in collecting a series of magnetite specimens, concerning which we hope to report more in detail at a later date.

0.63% excess Fe_2O_3, and 0.37% impurities. This 0.37% consists chiefly of insoluble quartz.

Oxygen.—Oxygen was made from sodium peroxide, dried and passed over copper oxide in a resistance furnace heated to 650° to oxidize any hydrogen that might be present, again dried over $CaCl_2$ and P_2O_5 and stored over mercury. For use it was drawn out through another P_2O_5 tube. Its purity is shown by the fact that less than 0.01% remained unabsorbed by magnetite when the amount of oxygen was insufficient to completely oxidize the magnetite to Fe_2O_3.

Special Problems.

Optical Properties of the Oxides of Iron.—A few of the difficulties peculiar to the study of the iron oxides deserve mention. The first of these is the opacity of the oxides. In the study of the silicates the microscope is an almost indispensable tool; by its aid one can tell at once how many and what phases are present in a given preparation. But in the present work we have had to fall back upon the chemical analysis of each charge in order to secure the information that the microscope would have yielded if the oxides had possessed easily measurable optical properties. This feature has made the work much slower than it would otherwise have been.

By the use of his immersion glass of selenium and tellurium, Dr. H. E. Merwin, of this Laboratory, has, however, succeeded in contributing a great deal of assistance. It is possible by these means to get some light through the oxides of compositions lying between pure Fe_2O_3 and a point midway in composition between Fe_2O_3 and Fe_3O_4; the refractive indices and double refraction can then be determined. His detailed results will be presented later in the paper.

Reduction of Iron Oxides by Platinum.—Another difficulty peculiar to the study of the iron oxides is their reduction by platinum. The charges were heated in small platinum crucibles 18 mm. deep and 8 to 10 mm. in diameter. These crucibles almost always gained in weight from 0.1 to 1.0 mg. during a series of measurements. As we have already shown in a recent publication,[1] this gain in weight is due partly to iron reduced by the platinum and taken up in solid solution. The rest of the gain in weight consists of rhodium and platinum from the furnace tube.

Platinum acts on both hematite and magnetite at 1200° under low pressures of oxygen, absorbing iron and giving off oxygen. It also reacts with magnetite in the same way at 1600° and at the usual atmospheric pressure of oxygen. On the other hand, it is well known to analysts

[1] Sosman and Hostetter, "Reduction of Iron Oxides by Platinum with a Note on the Magnetic Susceptibility of Iron-bearing Platinum," *J. Wash. Acad. Sci.*, **5**, 293–303 (1915).

that platinum crucibles in which Fe_2O_3 is ignited in air for weighing in analytical procedures take up no such amounts of iron as we have found taken up under the above-mentioned conditions. The reason for these differences of behavior is apparent from the relations of iron and platinum in their alloys, as interpreted by the phase rule.

The system contains 3 components: platinum, iron, and oxygen. Iron and platinum form a continuous series of solid solutions.[1] The oxidation of the iron causes it to separate from the platinum as an oxide. If we now have present the three phases, iron-platinum alloy, solid oxide, and gaseous oxygen, and assume a certain concentration of iron in the platinum (say 0.01%), and a certain temperature (say 1200°) then there must be a definite oxygen pressure in equilibrium with this system. If the existing pressure of oxygen is less than this equilibrium pressure, the oxide will dissociate and metallic iron will be absorbed by the platinum. If the pressure of oxygen be greater, on the other hand, iron from the platinum solution will be oxidized, the oxide will separate on the surface of the metal, and the concentration of the iron in the platinum will be reduced.

It is evident from the fact that melted magnetite is reduced by platinum in air that at 1600° the oxygen pressure of the air (about 152 mm.) is less than the oxygen pressure in equilibrium with dilute solutions of iron in platinum. Similarly, at 1200°, it is found that 18 mm. oxygen is less than the equilibrium oxygen pressure, and at this temperature and pressure iron is absorbed by platinum from all oxides between Fe_2O_3 and Fe_3O_4. 152 mm. oxygen, however, is greater than the oxygen pressure of any but the most extremely dilute solution of iron in platinum at 1200°, and at this temperature, which is seldom exceeded in igniting iron oxide precipitates for analysis, there is no appreciable reduction of Fe_2O_3 by platinum in the open air.[2]

These considerations explain the very common occurrence of small amounts of iron in platinum, since platinum will exercise its reducing action on any material containing iron oxides with which it comes in contact, provided that the temperature is above, say, 1000°. At lower temperatures, on the other hand, and with abundant access of atmospheric oxygen, no appreciable reduction is to be expected.

Disappearance of Oxygen in Furnace.—In many of the measurements a gradual decrease of pressure was observed at 1200° and higher, and a calculation of the final composition of the charge, from the original composition and from the amount of oxygen removed, showed that more

[1] Isaac and Tammann, Z. anorg. Chem., **55**, 63–71 (1907).

[2] This kind of contamination of platinum by iron is to be distinguished from the contamination caused by the reducing action of incompletely burned gases during the ignition of ferric oxide over a gas flame.

ferric and less ferrous iron should be present than was actually obtained by analysis. A series of measurements made with oxygen alone showed that oxygen was in fact disappearing at the higher temperatures. No change occurred at 500° or lower, showing that the loss was not due to ordinary leakage. On the other hand, a very small, although measurable and apparently constant evolution of gas was observed at 1450° when the furnace was completely evacuated; this evolution seemed to be unaffected, however, when the pressure in the "outside vacuum" was allowed to rise. A possible explanation of these phenomena is that when the furnace is heated to a high temperature the silver-soldered joint between platinum and steel is warmed sufficiently to allow the diffusion of oxygen through the silver, which is known to occur at a relatively low temperature. It has not been possible as yet to prove this explanation. As the rate of disappearance of oxygen is too small to affect appreciably the results reported in this article, this source of loss has been neglected for the present.

Adsorption of Gases.—The pressure within the vacuum apparatus always rises slowly on standing. We have ascribed this to the slow escape of gases from the surface of the glass. As the apparatus must be opened to the air for the insertion and removal of oxide charges, there is abundant opportunity for oxygen or other gases to be taken up by the glass.

On one occasion the apparatus stood unused for 27 days, and there was opportunity to observe the slow rise of pressure due presumably to gases from the glass. The measurements are plotted in Fig. 2. After

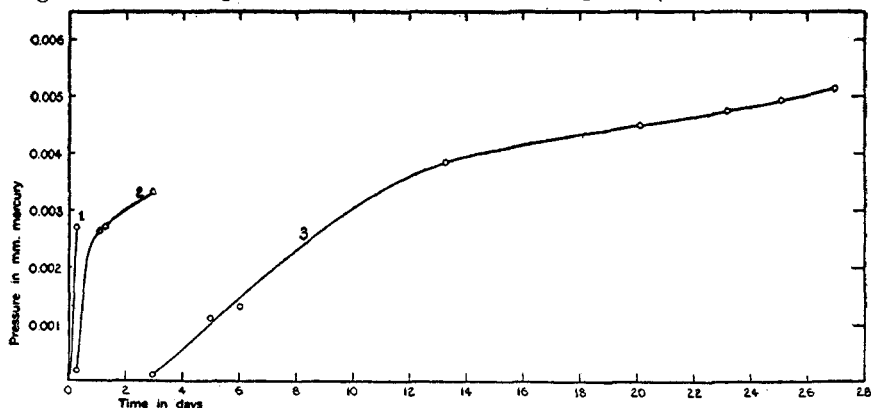Fig. 2.—Evolution of gases from walls of apparatus.

the initial pumping the pressure rose in 11 minutes from 0.00060 mm. to 0.00270 mm. (Curve 1). It was immediately pumped out a second time, after which the pressure rose in 2 days and 17 hours from 0.00016 mm. to 0.00332 mm. (Curve 2). This gas was then pumped out, following which the pressure rose still more slowly, taking 24 days to rise from

0.00010 mm. to 0.00515 mm. (Curve 3). The mercury cut-off (C in Fig. 1) was closed during the entire time, so that no gas could have been furnished by stopcock grease.[1]

Some gas may also be held on the surface of the platinum tube. A small amount was always obtained when the furnace was heated without a crucible or charge in position. It is possible, however, that some of this comes from minute amounts of Fe_2O_3 which has been blown out of crucibles or which may even have been volatilized and deposited on the furnace walls on cooling. The amounts of gas in question were too small to have an appreciable effect on the pressures reported in this article.

Questions of Equilibrium.

Reproducibility of Dissociation Pressures.—Before it can be assumed that a given experimental procedure is yielding results that represent conditions of true chemical equilibrium, there are several questions to be answered experimentally. The first of these concerns the reproducibility of the pressures under given experimental conditions. In general, we have found that, using equal weights of the same initial oxide, we obtained at a given temperature pressures which in most cases agreed within the limits of error. In some cases, however, the pressures differed by amounts considerably larger than the errors of reading temperature and pressure, especially in the case of Merck's oxide. These results will be specifically discussed later. An example of the reproducibility of pressure measurements made under similar conditions is to be found in the second, third, fourth and fifth measurements in Table II.

Accuracy of Temperature and Pressure.—The temperature can be regarded as certain within 2°, since calibrations by the thermal curve method, with a charge of diopside ($MgSiO_3.CaSiO_3$) in place of the iron oxide charge, gave 1389.4° and 1390.3°, as against 1391.2°, the original nitrogen thermometer value. The degree of accuracy of the pressure measurements varies widely, according to the degree of compression on the McLeod gages and the magnitude of the pressure. 1 mm. on the large McLeod gage corresponds to 0.0004 mm. in 0.1500 mm. at the lowest compression, or to 0.000004 mm. in 0.000100 mm. at the highest compression. Pressures above 3.00 mm. were read directly, with an accuracy of 0.02 mm.

Pumping for different lengths of time before heating had no considerable effect on the pressures. Holding the temperature constant produced a gradual change, and yielded a constant value in from 10 to 20 minutes, if the effects of by-reactions (reduction by platinum and absorption of oxygen) were taken into account.

[1] At this time the cap which carried the thermoelement wires was sealed to the furnace tube with kollolith.

Pressures from Ferric Oxide from Different Sources.—Preliminary tests showed that oxide from different sources gave pressures of the same order, when equal amounts were heated at the same temperature, but that there were some differences considerably larger than could be accounted for experimentally. Later measurements showed rather unsatisfactory results for Merck's oxide, which gave at 1200°, on 0.5 and 1.0 g. samples, pressures of from 1.39 to 1.95 mm., a rather large variation for which no cause is known. Kahlbaum's oxide gave 2.07 mm., a slightly higher pressure than Merck's highest, but still somewhat lower than that obtained by oxidation of magnetite. Pure ferric oxide, on the other hand, made from nitrate from electrolytic iron, and heated in oxygen at 1200°, gave pressures in exact agreement with those obtained by the oxidation of magnetite. Natural hematite ore (Sibley), and pure oxide from nitrate ignited in air, gave pressures differing by only 0.02 mm., but were not directly compared with the other oxides.

In general, therefore, it may be said that the oxides from different sources are in fairly good agreement, with the exception of Merck's, which is rather low and variable. Measurements on products which have not been ignited are subject to uncertainties from the presence of moisture and adsorbed gases of all kinds, and further work would be necessary to completely explain these variations in the commercial products.

Effect of Temperature Gradient in Furnace.—Shortly after the preliminary experiments, a series of tests was made to determine the effect of temperature gradient in the furnace. The uniformity of temperature could not well be tested by direct measurement, as a complicated arrangement of apparatus would have been necessary to permit of moving the thermoelement up and down in the completely sealed furnace. An equally sensitive test was made, however, by taking a series of measurements of the oxygen pressures produced by 0.5 g. charges of Merck's ferric oxide, heated under exactly similar conditions as to rate and time of heating but at various levels in the furnace. In our preliminary measurements of dissociation pressures the thermoelement junction was always placed 3 to 5 mm. above the top of the charge of oxide, so that the change in weight of the charge could be determined without uncertainty due to oxide adhering to the wires. It is obvious that near the top of the furnace the thermoelement, under these conditions, will be colder than the bottom of the charge, whereas near the bottom of the furnace the reverse will be true. Hence if the temperature of the thermoelement is set to the same value in both positions, the temperature of the charge, and therefore the pressure obtained, will be greater near the top than near the bottom of the furnace. If two or more pressures obtained near the middle of the furnace agree within the range of reproducibility of these pressures proof is afforded that there is a space of uniform tem-

perature equal to the distance between the highest position of the thermo-
element and the lowest position of the bottom of the charge. Measure-
ments can therefore be made on charges set in this part of the furnace
with the assurance that the temperature of the charge is uniform and is
represented accurately by the temperature of the thermoelement. This
condition is further assured by packing deep charges into the crucible
with a polished steel plunger which shapes the surface in such a way
that there is a central well, in which the thermoelement is inserted, so
that it is actually within, but not in contact with, the charge.

The result of the uniformity tests is shown in Table II. The distance
from the top of the furnace tube to the top of the crucible in millimeters
is given in the third column, and the pressure in millimeters of mercury
in the fourth column. The degree of reproducibility of the pressures is
shown by the second, third fourth and fifth measurements. The pressures
at depths of 85, 92 and 95 mm. are practically constant. Since the depth
of the crucible is 18 mm. there seems therefore to be a range of about 25–30
mm. in which the temperature is uniform within one degree, judging from
the variation of pressure, which is of the order of magnitude of 0.01 mm.
per degree under the conditions of the tests. For subsequent measure-
ments the crucible was always placed in the middle of this zone, and the
thermoelement brought near the center of gravity of the charge as ex-
plained above. The charges varied in depth from 5 to 10 mm.

TABLE II.

Temperature Distribution in Furnace, as Indicated by Pressures Obtained at Various
Levels at 1100°.

No.	Weight oxide. Mg.	Distance from top. Mm.	Pressure. Mm.
1345	493.3	65	0.610
1347	502.9	75	0.330
1349	504.0	75	0.305
1351	502.9	75	0.320
1355	503.8	75	0.315
1358	501.8	85	0.215
1362	501.6	92	0.210
1360	507.1	95	0.195
1361	499.6	107	0.120

Comparison of Rising and Falling Temperatures.—True equilibrium
can be assured only if the same pressure is obtained both by the addition
and by the removal of oxygen. One method of changing the amount of
oxygen in the charge is to change the temperature. If it is raised, oxy-
gen is removed from, if lowered, oxygen is added to, the charge. If the
temperature is then brought back to its original value, the same pressure
should be obtained as before.

The results of a series of tests with Merck's oxide are presented in
Fig. 3, and show that, on the same charge of oxide, substantially the

same pressures are obtained at 1100° with rising and with falling temperatures. The pressures at 1100° and 1200° are also shown to be uninfluenced by heating the charge at 750°, 850°, or 950°. The unab-

Fig. 3.—Reproducibility of dissociation pressures of Fe₃O₄ at 1100° and 1200° with rising and falling temperature.
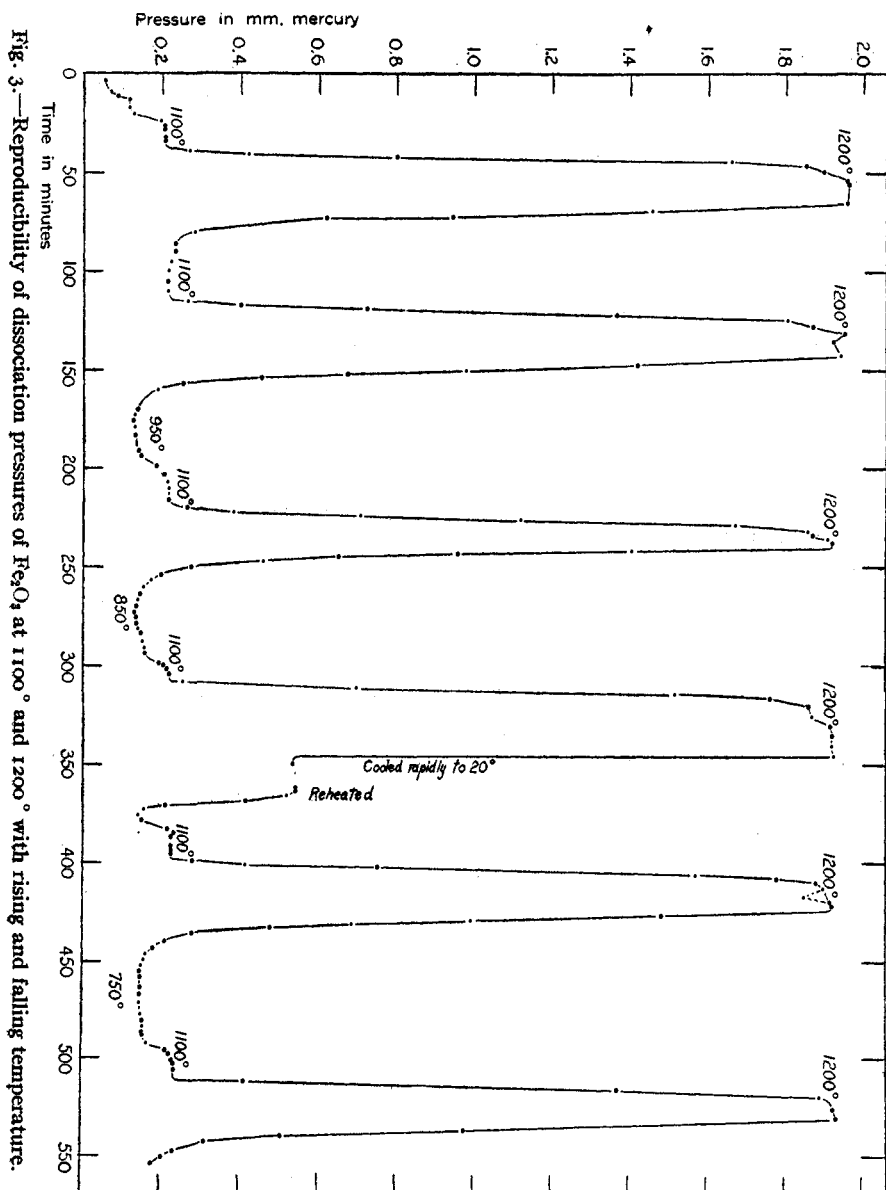
sorbed or slowly absorbing residue of 0.15 mm. which appears at 750° and 850° probably represents in part nitrogen or air adsorbed in the finely powdered oxide; the rapid drop to lower temperatures from 1200° also

leaves part of the original oxygen of the oxide unabsorbed, because of the slowness of diffusion and reaction at the lower temperatures.

Pressures Obtained by Oxidation of Magnetite.—A second method of comparing the effects of adding and removing oxygen is to use Fe_3O_4 as the initial solid, and add various amounts of oxygen, comparing the pressures at a given temperature with those obtained by starting with Fe_2O_3.

The results obtained with pure Fe_2O_3 made from Burgess electrolytic iron through the nitrate, and heated beforehand in a current of oxygen at 1200°, are in exact agreement with the pressures of oxidized magnetite, as is evident from Fig. 5. In addition to the single points, one series was run in which oxygen was added in excess at the start, and then withdrawn in steps as in the case of oxidized magnetite. These results also are in excellent agreement with the oxidized magnetite.

The pressures obtained by heating Kahlbaum's and Merck's Fe_2O_3 are somewhat lower than the pressures, at a corresponding composition of the solid, obtained by oxidizing magnetite. Nevertheless, each gives every appearance of being in equilibrium. The pressure from Merck's oxide, as shown in Fig. 3, returns repeatedly to the same value after heating at various lower temperatures. The magnetite, in the course of being heated up to 1200°, was sometimes held at 1100° until completely oxidized to the composition of Fe_3O_4, yet the pressures obtained on further heating and dissociating the oxide so formed were no lower than those obtained by heating directly to 1200°.

Whatever may be the cause of the low results obtained with Merck and Kahlbaum oxides, it is not evident in the optical properties of the products, for the crystals not only appear optically as a single phase, but the product formed by oxidation of magnetite has the same optical properties as the pure artificial oxides, and also the same as pure natural hematite.

The System Fe_2O_3–Fe_3O_4: Experimental Results.

General Plan.—In general, our preliminary measurements showed clearly that the oxygen pressure depends not only upon the temperature, but also upon the weight of the charge and the volume of the gas space—in other words, upon the composition of the charge of oxide at the time of measurement. This can have only one meaning, namely, solid solution between the original Fe_2O_3 and some lower oxide.

The existence of a solid solution series is best demonstrated by a pressure-composition isotherm. The temperature of 1200° seemed most favorable for our purpose. On the one hand, the pressures obtained are high enough so that the by-reactions (page 813) are of small effect; on the other, the pressures are not so high that the amount of oxygen in the gas space forms too large a proportion of the oxygen in the charge.

For our final series, we preferred to start with magnetite and add oxygen, for the following reasons: Ferric oxide, Fe_2O_3, always contains some moisture and adsorbed gas, which cannot be removed by pumping alone; the charge must be heated to a high temperature in order to drive them off. This heating dissociates the oxide, so that it must be reoxidized by slow cooling, and also sinters it into a solid cake; so that the initial conditions of the charge are rendered uncertain. Magnetite, on the other hand, can be heated up for a few minutes initially, cooled, and the residual adsorbed gas pumped out. Its own dissociation pressure is so very low that its composition is not changed to any measurable extent by this treatment, and the charge is furthermore not sintered.

The procedure was as follows: The apparatus was first evacuated to o.oo1 mm. or lower. The mercury cut-off C was closed, and the charge was heated to 1200° for a few minutes and then cooled. This heating drives off water and adsorbed gases, and converts the small excess of Fe_2O_3 present almost completely into Fe_3O_4. The residual gas was pumped out, and a known amount of pure oxygen was admitted. The charge was again heated at a definite rate. The magnetite began to oxidize at an observable rate at 300°. In some cases the temperature was held at 1100° until the pressure came to equilibrium; in others, the temperature was carried steadily up to 1200°.

The removal of oxygen in steps at 1200° was accomplished by closing the cut-off C, and pumping out the oxygen from the space between cut-off and stopcock. The quantity removed was known from the pressure and temperature of the gas in this space. The cut-off was then again opened and equilibrium reëstablished by further dissociation of the iron oxide of the charge.

At the end of such a series the temperature was lowered at a definite rate, sometimes with a halt at 1100° for an additional measurement. The charge was removed at room temperature, weighed, and the ferrous oxide determined. The difference between the percentage of FeO so found and that calculated from the known amounts of oxygen removed was in nearly all cases less than o.4%, and a correction for this difference was distributed among the calculated intermediate values for the composition of the oxide. The difference was probably brought about by small constant errors in the data for the volume or the temperature of the gas.

Methods of Analysis—Ferrous Oxide.—In the determination of ferrous oxide we have followed the method described by Blair[1] but with some details slightly modified. Blair's method consists essentially in the solution of the oxide in hydrochloric acid in an atmosphere of carbon dioxide, with subsequent titration with permanganate after the addition of zinc

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[1] "The Chemical Analysis of Iron," 7th edition, p. 239.

sulfate. We would have preferred to use sulfuric acid as the solvent for the oxide, but the rate of solution of the oxides in this acid, even when crushed to pass 200 mesh, was so small as to exclude its use. This stability of otherwise readily soluble oxides is developed by the action of high temperatures.

Our apparatus in which the solution of the oxide is effected in an atmosphere of carbon dioxide is shown in Fig. 4. The flask has a capacity of about 110 cc. The inlet tube for carbon dioxide is ground into the funnel tube and this joint serves as a valve for the introduction into the flask of liquid held in the funnel tube. The funnel tube is graduated at 10 and 25 cc. The advantages of an all-glass apparatus for this determination where all reducing substances must be rigorously excluded are evident.
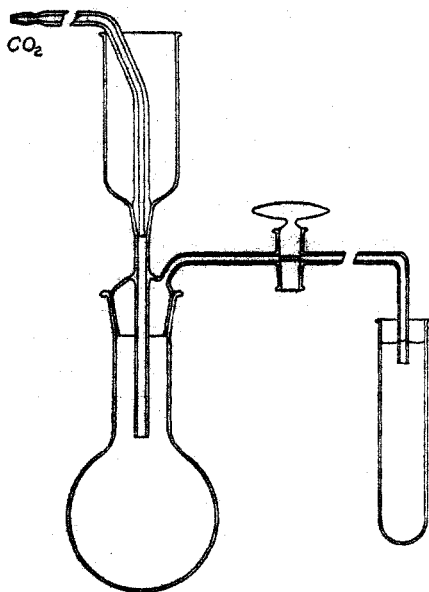

Fig. 4.—Apparatus for determination of FeO.

While Blair uses zinc sulfate to eliminate the action of permanganate on the hydrochloric acid during titration we have preferred to use the ordinary "titrating mixture" of manganese sulfate, phosphoric acid and sulfuric acid.[1] For small amounts of ferrous oxide we used 0.01 N permanganate in volume burets while for larger amounts we weighed the 0.1 N permanganate used. All the solutions were standardized against Bureau of Standards sodium oxalate.

Total Iron.—Total iron was determined by reductions with zinc sulfur dioxide, and also with stannous chloride, the resulting ferrous iron being titrated with 0.1 N permanganate. When the reductions were made with zinc and with sulfur dioxide the sodium oxalate titer of the permanganate was employed; but this titer gave slightly high results with the stannous chloride reduction. Consequently, for the latter reduction, Bureau of Standards Ore No. 27 with total iron content of 69.2% was used as an empirical standard. The values for total iron reported in this paper are averages of a series of determinations by all three methods of reduction.

Using the convention, the results of analysis have been reported in the text as percentages of FeO on total weight of the oxide. This must

[1] *Bur. Standards Circ.* **26**, 3d ed., p. 12.

not be understood as implying any opinion regarding the form of combination of ferrous iron in the solid phase. What is actually determined is of course the amount of iron which goes into solution in a form which will reduce permanganate. Whether or not FeO can actually exist free, whether or not FeO exists within the crystalline oxide, and whether or not there is any atomic distinction between ferrous and ferric iron inside of a crystal, are questions on which we have at present no information. For the present, therefore, the reporting of ferrous iron as FeO is to be considered simply as a convention.

Pressure-composition Isotherm at 1200°.—In Table III are recorded the results of numerous measurements of the oxygen pressure at 1200°, obtained (1) by heating Fe_2O_3; (2) by heating Fe_3O_4 with varying amounts of oxygen; (3) by withdrawing oxygen in known amounts from the oxide-oxygen system of (2); and (4) by withdrawing oxygen similarly from Fe_2O_3 with excess oxygen added.

The first column of the table contains the reference number of the series; the second gives the original weight of the charge in mg.; the third, the amount of oxygen added, in mg., calculated from the pressure, temperature, and volume of the furnace and gages.

The fourth column gives the equivalent volume of the apparatus at 1200° under the conditions of measurement. Since that portion of the gas which is within the furnace tube is heated to 1200°, its density is correspondingly diminished. In calculating the amount of gaseous oxygen this is allowed for by subtracting from the volume at room temperature the amount which the heated gas would contract if cooled to room temperature. This correction was calculated from the approximately known temperature distribution and was checked by measuring the actual increase of pressure produced in oxygen when the furnace was heated to various temperatures. Other smaller corrections to the volume were also made to allow for changes in level of the mercury columns caused by changes in barometer height and in the internal pressure.

The amount of oxygen present as gas was calculated from the volume corrected as above and the temperature of the apparatus. The latter was measured by means of six mercury thermometers hung at different points over the apparatus.

The fifth column contains the equilibrium pressure as measured, in mm. of mercury at 0°. The last column gives the percentage of the total iron which is in the "ferrous condition." This is calculated as follows: From the original weight and composition of the charge, the original amount of oxygen added, and the amount of oxygen remaining as gas in the apparatus, the amount actually combined in the charge can be calculated. A certain quantity of oxygen would have to be added to bring the charge up to the composition of Fe_2O_3. The proportion of this

oxygen to the total in Fe_2O_3, multiplied by 3, gives the "per cent. ferrous." For instance, the removal of 11.11% (one-ninth) of the total oxygen of Fe_2O_3 yields magnetite, in which the "per cent. ferrous" is 33.33

TABLE III.
Oxygen Pressures at 1200°.

No	Initial wt. charge. Mg.	Oxygen added. Mg.	Gas volume. cc.	Pres-sure. Mm.	Per cent. ferrous.
		Magnetite.			
1562	1006.0	0	1265	0.041[1]	33.43
1545	1000.3	5.46	1462	1.00	30.60
		5.13	2023	0.770	30.96
		4.12	2023	0.590	31.29
		3.35	2023	0.460	31.56
		2.75	2023	0.360	31.77
1558	1003.3	13.26	1462	1.44	24.06
		12.79	2063	1.27	25.29
		11.13	1267	1.29	25.32
		9.63	1266	1.17	26.49
		8.27	1266	1.065	27.60
		8.27	2023	0.965	28.59
		7.01	2023	0.865	29.49
		5.88	2023	0.750	30.18
1516	1999.9	19.64	1454	1.355	25.41
1551	1000.1	21.25	1461	1.855	17.27
		20.65	1266	1.895	17.33
		18.41	1266	1.75	19.19
		18.41	2022	1.605	20.90
		16.33	2022	1.46	22.43
1554	1002.5	21.13	1462	1.79	17.31
		20.55	1267	1.825	17.35
		20.55	2023	1.68	19.18
1548	1002.6	26.22	1460	1.86	12.60
		25.62	2021	1.69	14.32
		21.34	1265	1.595	16.04
		19.45	1265	1.49	17.58
		17.66	1265	1.395	19.06
		17.66	2021	1.30	20.45
1556	994.9	21.17	1462	1.56	16.56
		20.67	2023	1.45	18.11
		18.79	2023	1.37	19.64
		17.01	2023	1.275	20.98
1509	593.4	19.97	1451	2.43	10.50
1512	996.6	20.09	1452	2.50	19.83
1519	1001.5	40.03	1451	4.12	4.56
1523	1126.5	39.60	1451	2.885	5.36
1539	1000.5	41.85	1463	3.86	2.19
		43.01	2024	3.21	2.73

No.	Initial wt. charge. Mg.	Oxygen added. Mg.	Gas volume. cc.	Pres-sure. Mm.	Per cent. ferrous.
		35.37	1267	2.68	4.86
		32.25	1267	2.48	7.44
		29.29	1267	2.285	9.90
1536	999.4	42.43	1464	3.98	1.93
		41.15	1464	3.59	2.23
		40.09	1464	3.37	2.75
		39.01	1464	3.13	3.23
		38.00	1464	3.03	3.99
		37.03	1464	2.87	4.81
1532	1000.5	44.95	1461	4.76	1.43
		67.26	1463	13.09	0.61
		63.05	1462	11.38	0.61
		59.38	1462	9.92	0.63
		56.18	1462	8.62	0.58
		53.40	1461	7.48	0.53
		50.99	1461	6.56	0.66
		48.88	1461	5.78	0.85
		47.02	1461	5.08	1.08
		45.38	1461	4.50	1.32
		43.93	1461	3.99	1.53
		42.65	1461	3.61	1.92
1529	1002.4	59.10	1455	10.23	0.97
1521	1000.8	80.46	1455	18.31	0.24
		Fe_2O_3 from electrolytic iron.			
1595	1000.2	....	1271	2.54	5.64
1596	501.3	....	1271	2.055	9.00
1598	999.3	6.86	1396	3.64	1.94
		6.09	1950	2.76	3.22
		2.81	1950	2.38	5.20
		—0.01	1950	2.18	7.34
		—2.59	1950	2.08	9.58
		—5.06	1950	1.99	11.74
		Fe_2O_3 Merck.			
1390	507.8	....	758	1.95	5.57
1391	497.0	....	758	1.385	3.88
1392	497.5	....	758	1.65	4.63
1394	499.6	....	758	1.61	4.53
1398	489.2	....	758	1.95	5.37
		Fe_2O_3 Kahlbaum.			
1503	504.0	....	758	2.07	5.46

[1] The larger part of this pressure is due to oxygen released by the reducing action of the platinum (see p. 813).

(one-third). The removal of 33.33% of the total oxygen of Fe_2O_3 would yield FeO, in which the "per cent. ferrous" is 100.

The data of Table III are shown graphically in Fig. 5. The form of the curve shows clearly that the dissociation pressure varies with the

Fig. 5.—Pressure-composition isotherm at 1200°.

composition of the solid. Since this is a two-component system (iron and oxygen), there can be only one solid phase; in other words, there is a continuous solid solution series from Fe_2O_3 to Fe_3O_4, or at least to a point very near Fe_3O_4.

Fortunately this conclusion can be demonstrated optically for at least half the distance from Fe_2O_3 to Fe_3O_4, as is shown later in more detail by Merwin's report.

This type of solid solution system, in which one of the two components is volatile while the two compounds which mix with one another differ only in the proportion of volatile component which is combined with the nonvolatile component, has few representatives among the systems that have been studied. One which is quite analogous is the series $CoCl_2.-6NH_3–CoCl_2.2NH_3$.[1] The ammonia pressures of this system fall continuously with diminishing content of NH_3, following a reversed curve like that of the iron oxides, but less pronounced; near $CoCl_2.2NH_3$ the pressure drops rapidly, as it does near Fe_3O_4.

Pressure-composition Isotherm at 1100°.—Table IV contains the results of measurements at 1100°. These were, for the most part, made either in the course of heating a charge to 1200°, or during cooling from

TABLE IV.

Oxygen Presures at 1100°.

No.	Initial wt. charge. Mg.	Oxygen added. Mg.	Gas volume. cc.	Pressure. Mm.	Per cent. ferrous.
		Magnetite.			
1562	1006.0	0	1265	0.010[2]	33.36
1545	1000.3	2.75	2023	0.100[3]	30.99
1558	1003.3	4.90	1266	0.068	28.71
1516	1999.9	19.64	1455	0.075	23.85
1551	1000.1	14.44	1265	0.094	19.49
1548	1002.6	15.96	1264	0.084	18.73
1554	1002.5	18.36	1268	0.102	15.79
1512	996.6	20.09	1452	0.142	14.01
1556	994.9	21.17	1465	0.084	12.93
		15.36	1265	0.081	18.40
1509	593.4	19.97	1452	0.248	1.65
1523	1126.5	39.60	1449	0.710	0.66
1519	1001.5	40.03	1452	2.35	0.23
1529	1000.5	59.10	1458	10.04	0.30
1521	1000.8	80.46	1456	18.24	0.12
		Fe2O3 from electrolytic iron.			
1598	999.3	6.86	1398	2.95	0.29

No.	Initial wt. charge. Mg.	Oxygen added. Mg.	Gas volume. cc.	Pressure. Mm.	Per cent. ferrous.
		—5.06	1953	0.139[3]	5.53
1595	1000.2	....	1273	0.425	0.95
1596	501.3	....	1273	0.290	1.26
		Fe2O3 Kahlbaum.			
1503	504.0	....	760	0.200	0.60
		Fe2O3 Merck.			
1394	499.6	....	760	0.196	0.62
1398	489.2	....	760	0.208	0.63
1369	204.9	....	760	0.120	0.85
1370	299.8	....	760	0.141	0.70
1374	295.4	....	760	0.120	0.60
1371	402.9	....	760	0.130	0.50
1373	407.1	....	760	0.140	0.52
1375	497.7	....	760	0.170	0.51
1376	501.0	....	760	0.165	0.51
1362	501.6	....	760	0.213	0.63
1365	1007.3	....	760	0.235	0.38
1367	1506.0	....	760	0.265	0.42

[1] Biltz and Fetkenheuer, "Ammoniakverbindungen der Halogenide des zweiwertigen Kobalts," Z. anorg. Chem., 89, 97–133 (1914).

[2] The larger part of this pressure is due to oxygen released by the reducing action of the platinum.

[3] Pressure still falling.

1200°, the temperature being held at 1100° long enough for equilibrium to be established. The results are less reliable than those at 1200°, because the pressures are so much smaller that the effect of by-reactions becomes a much larger factor of uncertainty. Nevertheless, the pressures
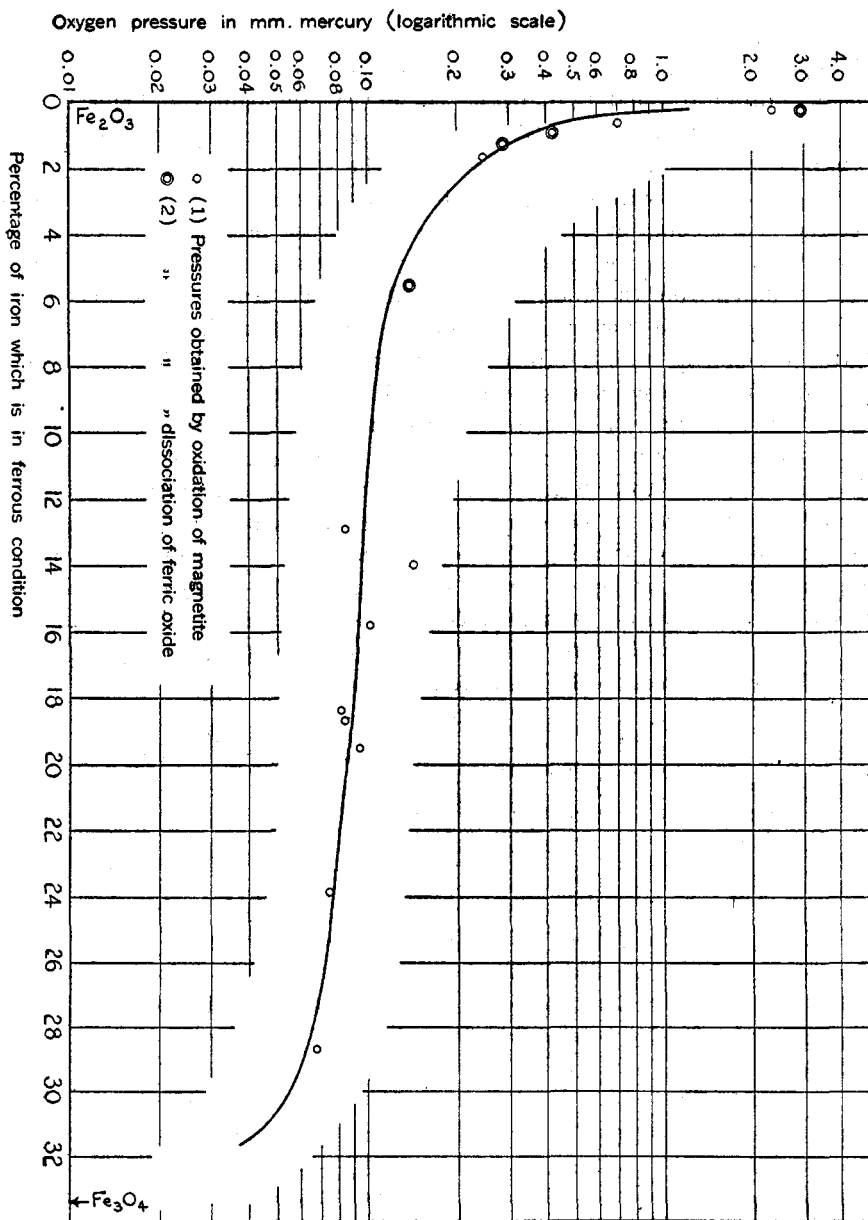

Fig. 6.—Pressure-composition isotherm at 1100°.

confirm in a general way the form of curve at 1200°, as may be seen from Fig. 6.

Form of Dissociation-pressure Curve near Fe₂O₃.—The form of the dissociation-pressure curve near the ferric oxide side of the diagram is of interest. The evidence all points to a rapid rise of pressure near pure Fe_2O_3; in other words, the initial dissociation pressure of pure Fe_2O_3 is high, but drops rapidly as a small percentage of FeO appears in the oxide.

In addition to the data in Tables III and IV, the figures in Table V support this interpretation. These are data on approximately one-gram charges, all cooled from 1200° at about the same rate. The second column gives the amount of oxygen in the system in excess of the original Fe_3O_4 at the last reading at 1200°; the third gives the pressure at 1200°; the fourth, the amount of oxygen absorbed in cooling to room temperature, as calculated from the known volumes and temperatures of the gas space: and the fifth, the percentage of FeO found in the charge by analysis after its removal from the furnace. In every case a small amount of FeO is found in the charge after cooling. This indicates that there was at least this amount of FeO in the charge at 1200°. It might be supposed that the FeO was in the interior of some of the grains, to which oxygen had not had time to penetrate; but on lowering the temperature to 1100°, and then to room temperature, we found that a prompt absorption of oxygen took place, showing that some at least of the ferrous iron was in equilibrium with oxygen at 1200°, but immediately began to be oxidized when the temperature was lowered. It is significant that the amount of FeO left, as well as the amount of oxygen absorbed, is roughly inversely proportional to the pressure at 1200°.

TABLE V.

No.	Oxygen added. Mg.	Pressure at 1200°. Mm.	Oxygen absorbed in cooling from 1200° to 20°. Mg.	Percentage of FeO in product at 20°.
1521	80.46	18.31	0.27	0.14
1529	59.10	10.23	0.54	0.185
1532	42.65	3.61	1.76	0.24
1536	37.03	2.87	4.55	0.41

It is not surprising that on cooling to room temperature some of the ferrous iron did finally escape oxidation, for as the temperature is lowered the rates of diffusion and of oxidation rapidly diminish.

An observation by Baxter and Hoover during their work on the atomic weight of iron[1] is of interest in this connection. They ignited their oxide at a temperature which is estimated to be between 1000° and 1100°, both in air and in pure oxygen. The weight after ignition in oxygen was consistently 0.2 mg. (in 5 grams) higher than after ignition in air. This

[1] Baxter and Hoover, "A Revision of the Atomic Weight of Iron. V. The Analysis of Ferric Oxide," This JOURNAL, 34, 1657–1669 (1912).

was confirmed by repeated heating of the same charge, and again on another series of ignitions. Although the value for the atomic weight of iron, calculated from the oxygen ignition, is 55.840 as against 55.838 from $FeBr_2$, whereas the air ignition yields the high value 55.847, nevertheless the authors ascribe the difference to "occlusion" of oxygen at the higher oxygen pressure. A more probable explanation, in view of our results, is that even under an oxygen pressure of 152 mm. (pressure of oxygen in air) there is a small amount of dissociation forming a very dilute solid solution of Fe_3O_4 in Fe_2O_3; this is driven back practically to zero by a full atmosphere of oxygen. The amount of FeO produced, if all the difference in weight observed is due to dissociation at the lower pressure, would be 0.036 per cent.; an amount which could hardly be detected analytically.

Optical Properties.[1]—The synthetic Fe_2O_3 of Merck and of Kahlbaum consists in each case of aggregates of exceedingly small doubly refracting crystals. After being heated to 1200° in the vacuum furnace, under the oxygen pressure produced by its own dissociation, it is much more coarsely crystalline; the grains reach a maximum diameter of about 0.02 mm. Grains of magnetite of about this size may be oxidized to apparently homogeneous single grains of hematite.

The structure of similar grains which are not yet fully oxidized is shown in Fig. 7. Extinction is parallel to the structure. The dark or opaque skeleton consists presumably of a portion of the oxide which contains enough FeO to render it opaque in the thickness in which it is found in the grains. Such skeletons were found in Samples 1548, 1512, 1310 and 1536. In all these cases the amount of oxygen present was insufficient to oxidize the sample to Fe_2O_3. Hence the rapid cooling from high tem-

Fig. 7.—Skeletons of opaque oxide in transparent oxide, oxidized magnetite.

peratures was all the more likely to produce a certain amount of inhomogeneity, shown by the skeletons, as a result of the lack of opportunity for diffusion and reaction.

The observable optical properties[2] of the crystals of completely oxidized magnetite are not distinguishable from those of pure natural hematite, namely: uniaxial, negative, ϵ for $700\mu\mu = 2.74$, double refraction greater than 0.21, absorption of ω very slightly greater than that of ϵ. The products obtained by heating mixtures of Fe_2O_3 and Fe_3O_4 agree in optical characters with products having a similar content of FeO but made by other methods.

[1] Measurements by H. E. Merwin.
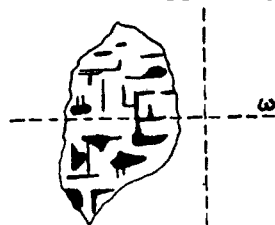[2] Amorphous mixtures of selenium and tellurium were used as embedding materials for this series of preparations.

Preparations having compositions between pure Fe_2O_3 and a solution of the composition FeO 22% : Fe_2O_3 78% appear optically as a single phase. A progressive darkening and a progressive lowering of the index ϵ accompany increasing FeO. Beyond 18% FeO the absorption is so strong that optical study is not feasible. Oxide with 28% FeO (No. 1545), for instance, is completely opaque even in strong sunlight.

The results of the optical study are shown in Table VI.

TABLE VI.

Optical Properties.

No.	Material.	Treatment.	Final per cent. FeO.	ϵ at 700 $\mu\mu$.	$\omega - \epsilon$.
1503	Kahlbaum Fe_2O_3	Heated at 1200°	0.58	2.74	>0.21
1314	{ 5% Fe_3O_4 { 95% Merck Fe_2O_3	Heated at 1200°	5.60	2.73	....
1512	$Fe_3O_4 + O_2$	Heated at 1200°	12.99	2.72	....
1548	$Fe_3O_4 + O_2$	Heated at 1200°	16.11	2.71	>0.16
1310	{ 50% Fe_3O_4 { 50% Merck Fe_2O_3	Heated at 1200°	17.79	2.71	....

The refractive index of magnetite has been determined by a reflection method by Loria and Zakrzewski,[1] who found n to be 2.42 for a wave length of 700 $\mu\mu$. The refractive indices of hematite should therefore be lowered by dissolved Fe_3O_4, as is found to be the case. The observed lowering, however, is far from being proportional to the amount of Fe_3O_4 in solution. The optical properties, therefore, confirm the existence of solid solution between hematite and magnetite over the range, within which the products are reasonably transparent (0–18% FeO), and unless the curve of index against composition changes direction rapidly, would indicate a separation into two phases at some point between 18% FeO and pure Fe_3O_4. The pressure-composition isotherm indicates that solid solution continues at least as far as 31.8% ferrous. If there is a break, then, it must be expected between 31.8 and 33.33% ferrous, that is, within 1.5% of pure magnetite.

Comparison with Previous Investigations.

Since the dissociation pressure depends upon the composition of the solid phase, it is easy to see why there has been so much uncertainty about the value of the dissociation pressure of Fe_2O_3. The pressure obtained depends not only upon the temperature, but also upon the relation of weight of charge to volume of gas space. The data of Walden,[2] for instance, which are frequently quoted, have very little quantitative significance because the weight of charge and volume of gas are not stated, and the oxide whose pressure is being measured is different for each temperature. Hilpert[3] suspected some years ago, after many unsatisfac-

[1] Loria and Zakrzewski, *Anz. Akad. Wiss. Krakau*, **1910**, 278–286.

[2] P. T. Walden, THIS JOURNAL, **30**, 1350–1355 (1908).

[3] S. Hilpert, *Ber.*, **42**, 4893–4895 (1909).

tory experiments by the kinetic (gas-current) method, that the difficulty lay in the formation of intermediate compounds between Fe_2O_3 and Fe_3O_4. He found that the dissociation pressure varied with the source and condition of the Fe_2O_3 employed. This is to be expected when the pressure is determined kinetically in a solid solution system, for the result will depend to a large extent upon the fineness of the powder and the condition of the surface of the grains.

Kohlmeyer[1] has made cooling curves on Fe_2O_3 heated rapidly to its "melting point" and interprets the results as indicating the existence of compounds $FeO.3Fe_2O_3$, $3FeO.5Fe_2O_3$, and $3FeO.4Fe_2O_3$, as well as inversion points[2] in Fe_2O_3 at $1028-1035°$ and $1250-1350°$. We have found no direct thermal or other evidence either of compounds or inversion points above $1000°$.

Differential heating curves on Kahlbaum's and Merck's pure Fe_2O_3 do, however, show a sharp inversion point at $678°$, and a barely detectable irregularity between $755°$ and $785°$. The latter may be due to an inversion point corresponding to the A2 point in pure iron. The A2 point has been shown by electrical resistance measurements on pure iron[3] to occur at $757°$, and by thermal curves on the same iron,[4] at $768°$. These points are in the temperature region in which iron becomes practically non-magnetic. If there is in fact an inversion in Fe_2O_3 which corresponds with that in pure iron, the inversion would seem to have some atomic basis, and would not, as suggested by Burgess and Crowe,[5] depend entirely upon a crystallographic change of the type of A3 (at $898-909°$).

The only remaining oxide indicated between Fe_2O_3 and Fe_3O_4 is the Haber-Kaufmann oxide[6] $2FeO.3Fe_2O_3$. This is said to be a well-defined compound when prepared at ordinary temperatures and can be dried at $180°$, but according to Chandra[7] it is unstable at higher temperatures. We find no indication of its existence at $1100°$ and $1200°$.

Further investigations are under way on the magnetic properties of the $Fe_2O_3-Fe_3O_4$ series, the inversions in Fe_2O_3 and Fe_3O_4, and the melting points and oxygen pressures in the system Fe_3O_4-Fe. The geological and mineralogical application of these data will be presented in a later paper.[8]

[1] E. J. Kohlmeyer, *Met. u. Erz*, 1, 447–462 (1913).
[2] E. J. Kohlmeyer, *Metallurgie*, 6, 323–325 (1909).
[3] Burgess and Kellberg, *Bull. Bur. Standards*, 11, 457–470 (1914).
[4] Burgess and Crowe, *Ibid.*, 10, 315–370 (1913).
[5] *Op. cit.*, 1913, p. 367.
[6] Kaufmann, *Z. Elektrochem.*, 7, 733–741 (1901).
[7] H. Chandra, *Inaug. Diss.*, Berlin, 1913.
[8] A preliminary report on the ferrous iron content and magnetic properties of the natural oxides of iron was presented at the December, 1915, meeting of the Geological Society of America.

Summary.

This investigation of the chemical relationships of the iron oxides has been undertaken as a basis for the study of the iron-bearing silicates at high temperatures. Measurements of the dissociation pressure of the iron oxides were made in a vacuum furnace with a heating tube of platinum-rhodium.

A study of the conditions of equilibrium shows that reproducible oxygen pressures can be obtained at a given temperature. Equilibrium is attained in a few minutes at high temperatures, although certain disturbing reactions go on slowly. One of these by-reactions is the reduction of the oxide by platinum, yielding oxygen and an iron-platinum alloy. This reaction accounts for the common occurrence of iron as an impurity in platinum.

Ferric oxides from various sources yield practically identical pressures (excluding certain minor exceptions which cannot as yet be explained). The same pressures are also attained on both rising and falling temperatures. The oxidation of magnetite gives pressures which are identical with those produced by dissociation of pure Fe_2O_3.

The pressure-composition isotherm for the system Fe_2O_3–Fe_3O_4 at $1200°$ indicates a continuous solid solution series from Fe_2O_3 over to a point very near Fe_3O_4, if not over the entire range to Fe_3O_4. The opacity of the products prevents an optical demonstration of the existence of solid solution in products with more than 18% FeO, but its existence can be shown optically in products which are more ferric than this. The pressure-composition isotherm at $1100°$ confirms that at $1200°$.

The major portion of the oxygen pressure curve of the system at $1200°$ lies between the limits 4 mm. and 1 mm. The pressure drops rapidly near Fe_3O_4, and raises rapidly near Fe_2O_3. Table VII contains a series of representative values.

TABLE VII.

Representative values of oxygen pressure in equilibrium with solid solutions between Fe_2O_3 and Fe_3O_4.

Percentage of FeO.	Percentage of iron which is ferrous.	Pressure at 1100°.	Pressure at 1200°.
0.90	1.0	0.37	5.0
1.80	2.0	0.22	3.6
2.71	3.0	0.17	3.0
4.52	5.0	0.13	2.6
9.09	10.0	0.10	2.15
13.70	15.0	0.092	1.80
18.37	20.0	0.085	1.55
23.07	25.0	0.069	1.27
27.83	30.0	0.052	0.85
31 03	33.33	<0.005	<0.04

Since the dissociation of Fe_2O_3 results in the formation of a solid solution, the pressure of oxygen and the composition of the solid phase depend upon the relation of the weight of the charge to the volume of the space into which the oxygen dissociates. This fact accounts for the variety and uncertainty of results heretofore obtained in experiments on the dissociation pressure of Fe_2O_3.

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THE VISCOSITY OF CERTAIN ALCOHOLIC SOLUTIONS.

BY O. F. TOWER.

About a year ago the author, in collaboration with Dr. Germann,[1] published the results of a series of determinations of the vapor pressures of solutions of three typical solutes in methyl and ethyl alcohols. It has seemed worth while to investigate in addition some of the other physical properties of such solutions. The electrical conductivity of those that are conductors have already been measured, so in this paper the results of viscosity determinations are given, together with a general discussion of the relations existing between the viscosity and other physical properties of such solutions.

The solutes were the same as those employed in the vapor-pressure determinations, viz., lithium chloride, potassium iodide and benzil; and in addition urea, since vapor pressures of solutions of this substance in ethyl alcohol have recently been published.[2] The urea used was a pure preparation and was further purified by two crystallizations from hot absolute alcohol; the other solutes were from samples which had been purified for the vapor tension work. They were all preserved after purification in a vacuum desiccator. The alcohols were purified by allowing "C. P." preparations to stand in contact with quick-lime for a year, after which they were distilled on to anhydrous copper sulfate and remained in contact with it for somewhat over a week. After this they were fractioned in vacuo in an apparatus like that described in the previous paper, and were then distilled, still in vacuo, on to weighed quantities of the solute. The solutions thus obtained were transferred to the viscosimeter by means of an apparatus essentially the same as that employed by Thorpe and Roger[3] for the same purpose, and were therefore in contact with ordinary air only for the moment they were being transferred from the distilling apparatus. In the viscosimeter they were in contact only with air which had been dried over phosphorus pentoxide.

[1] THIS JOURNAL, 36, 2449 (1914).

[2] Price, J. Chem. Soc., 107, 188 (1915).

[3] Phil. Trans., (A) 185, 415 (1894).