THE DISSOCIATION OF FERRIC OXIDE IN AIR.[1]

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

Received May 1, 1916.

In a paper which appeared in the April number of THIS JOURNAL,[2] the authors showed by measurements of dissociation pressure that ferric oxide (Fe_2O_3) and magnetite (Fe_3O_4) form a continuous series of solid solutions from Fe_2O_3 to Fe_3O_4, or at least to a point very near Fe_3O_4.

The form of the dissociation-pressure curves at $1100°$ and $1200°$ near the composition of pure Fe_2O_3 offers special interest. These curves rise rapidly as the percentage of FeO approaches zero, as if to become asymptotic to the axis of ordinates (see Fig. 1). The form of the curves led us to suggest[3] an explanation of an observation made by Baxter and Hoover during their work on the atomic weight of iron.[4] These investigators found that there was a constant difference in weight, amounting to about 0.2 mg. in 5 g., or 0.004%, between Fe_2O_3 heated in a current of air and the same oxide heated in a current of oxygen; the temperature was not measured but was estimated to be in the neighborhood of $1100°$. The oxygen value was the higher, and the atomic weight of iron derived therefrom agreed closely with that obtained from $FeBr_2$. Baxter and Hoover, however, very naturally hesitated to believe that there could be any dissociation of Fe_2O_3 at $1100°$ under a pressure of 152 mm. of oxygen, since Walden's results[5] had shown that Fe_3O_4 is formed in air only above $1350°$; they, therefore, ascribed the higher weight in pure oxygen to occlusion of a small quantity of this gas.

Minerals:
M = Magnetite
H = Hematites
Martites (pseudomorphs)
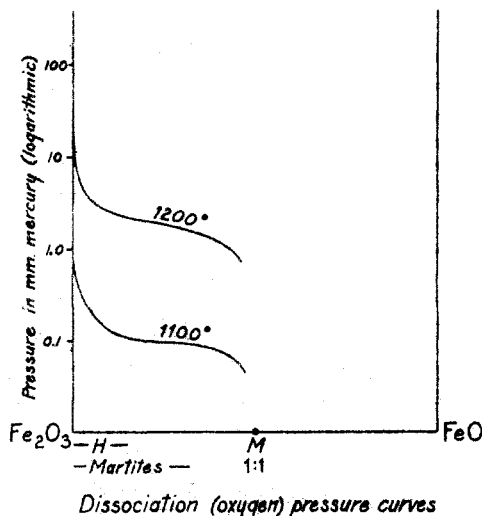
Fig. 1.—Pressure-composition isotherms of the system Fe_2O_3–Fe_3O_4.

Dissociation (oxygen) pressure curves

[1] Presented at the Urbana meeting of the Society. April 18, 1916.

[2] THIS JOURNAL, 38, 807–833 (1916).

[3] Loc. cit., p. 828.

[4] THIS JOURNAL, 34, 1657–1669 (1912).

[5] Ibid., 30, 1350–1355 (1908).

If the difference in weight between ignitions in air and in oxygen is due to occlusion of oxygen, then as the temperature is raised the difference should either be constant or should decrease, since it is very unlikely that the amount of occluded oxygen would be greater at high temperatures than at low temperatures. If, on the other hand, the difference is due to true dissociation, it is to be expected that the slope of the curves of dissociation pressure against composition (at constant temperature) between 152 and 760 mm. of oxygen will increase with the temperature, and that the difference in weight between oxygen and air ignitions will, therefore, also increase with the temperature.[1] This point seemed more easily susceptible of proof than it turned out to be, but the results which follow show clearly that a small but appreciable amount of dissociation of Fe_2O_3 does occur in air at temperatures above 1000°.

Materials.—Ferric oxide from pure electrolytic iron through the nitrate, and Kahlbaum's purest ferric oxide, were used in the experiments described below.[2] The oxygen was the commercial product supplied in cylinders.[3] It was purified by passing through a train containing, in the order named, soda-lime, calcium chloride, sulfuric and chromic acid, soda-lime, calcium chloride, copper oxide at 650–700°, potassium hydroxide which had been fused with permanganate, and phosphorus pentoxide. The air was also taken from a tank, and was purified through the same train. The line contained no stopcocks, and all joints were either sealed glass or Wood's metal joints, so that there was no chance of contamination of the gas current by reducing vapors from lubricated joints or stopcocks.

Apparatus.—A horizontal tube furnace was used, made of platinum wire wound on an alundum furnace core. The arrangement of the ignition tube is shown in section in Fig. 2. The central tube was at first of fused silica, later of Haldenwanger porcelain, 20 mm. inside and 25 mm. outside diameter. This was connected at one end to a fused silica tube by means of a water-cooled brass sleeve and Wood's metal fillings. The brass sleeve had a side tube for the admission of oxygen or air. The end of the silica tube was closed by a brass sleeve with a screw cap, in which was a smaller brass bushing large enough for a 1 mm. platinum wire.

[1] It is assumed that the oxide is cooled rapidly enough to avoid reoxidation as the temperature falls. This was accomplished in our experiments by withdrawing the boat quickly into a water-cooled silica tube. The rate of reoxidation is, however, so slow that cooling the boat in the furnace itself by merely shutting off the current will produce differences of weight between air and oxygen ignitions.

[2] These oxides have been described in our previous paper (p. 811). The oxide from electrolytic iron used here was not, as there described, made directly from the first nitrate, but from a recrystallized nitrate.

[3] Manufactured by the Linde Air Products Company. Baxter and Hoover also used Linde oxygen.
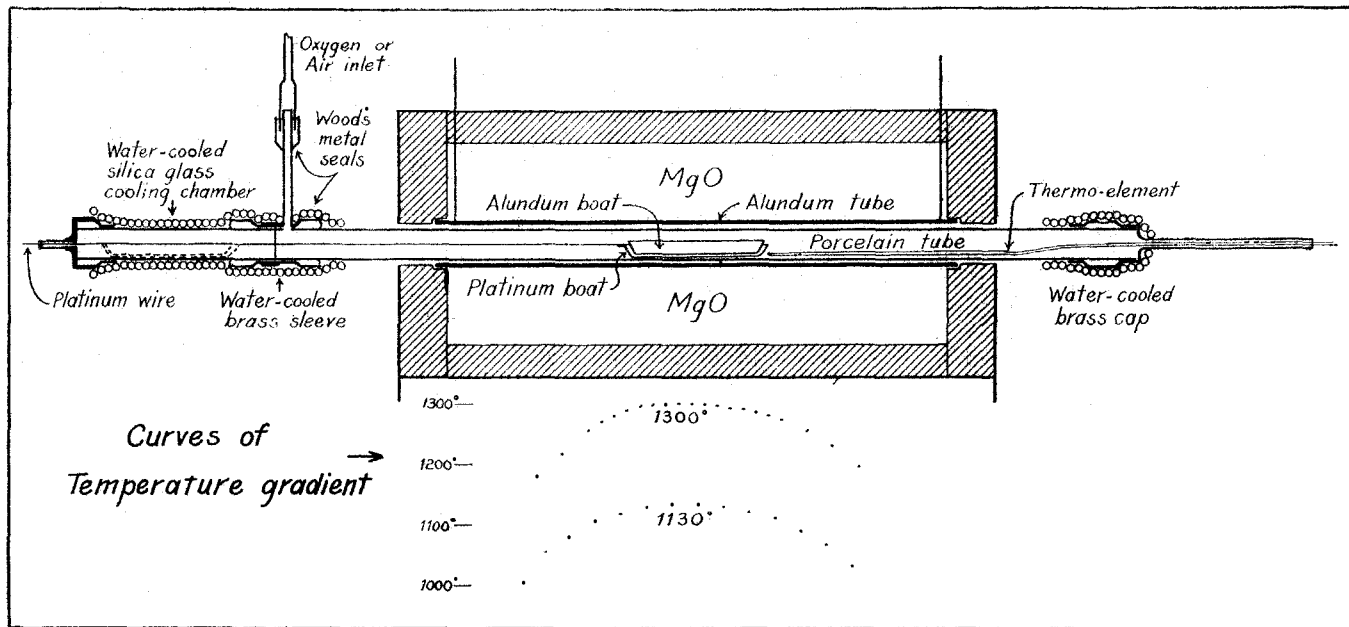
Fig. 2.—**Apparatus for experimental ignition of ferric oxide in air and in oxygen.**

At the opposite end of the furnace the porcelain tube was closed by a water-cooled brass cap through which entered the platinum-platinrhodium thermoelement.

Both platinum and alundum boats were used. Further details concerning these will be contained in the experimental results.

Weighings were made on an Ainsworth type QA analytical balance adjusted to a sensibility of 0.01 mg. By controlling the atmosphere within the balance by means of caustic potash, and taking weighings at measured intervals after removal from the desiccator, it was found possible to obtain results reproducible to 0.02 mg. in 10–15 g., including all the variations possible in igniting and handling the boat.

The temperature gradient of the furnace tube was explored by means of a thermoelement. At 1300° the temperature was uniform within 15° over the length of the boat, which was 100 mm. long.

Procedure.—The furnace was first heated to a definite constant temperature, with the boat and charge standing in the silica cooling chamber and oxygen or air passing. When constant conditions were attained, the boat was pushed into place in the center of the furnace by means of a platinum wire. At the end of the heating, the boat was rapidly withdrawn by means of the wire to the water-cooled silica cooling chamber, from which it was transferred when completely cooled to a desiccator containing phosphorus pentoxide.

Constancy of Weight of Platinum.—For the first experiments a boat of pure platinum was used, as in the work of Baxter and Hoover. When heated alone in oxygen and in air, the boat lost very little weight, much less than was to be expected from the results of the experiments of Burgess and Sale.[1]

In the presence of iron oxide, however, a decidedly different result was obtained. Two different effects are distinguishable: (1) At a temperature of 1200° or higher, the platinum reacts with the ferric oxide, absorbing iron and giving off oxygen;[2] the net result is a loss in total weight, but a gain in the weight of the boat as determined after removing the oxide and cleaning the boat in hydrochloric acid. (2) Below 1200° there is still a continuous loss in total weight, though less than at higher temperatures; but the weight of the boat alone shows an equivalent loss. In other words, the ferric oxide, while remaining constant in weight, seems to have acted as a catalyzer for the oxidation of the platinum by gaseous oxygen.

The summarized records of the heatings and the changes in weight of the boat are presented in Table I. In nearly all cases the loss of the boat when containing Fe_2O_3 is very much greater than its loss alone. The only

[1] *J. Ind. Eng. Chem.*, **7**, 561–564 (1915); *Bull. Bur. Standards.* **12**, 289–316 (1915).
[2] Sosman and Hostetter, *J. Wash. Acad. Sci.*, **5**, 293–303 (1915).

exception is the set of two heatings covering 34 hours which gave a loss of only 0.04 mg.; in this case, however, over half of the heating was at 1000°, and the heatings were made in a current of air, both conditions being unfavorable for oxidation of platinum. A part of the losses after heating with Fe_2O_3 must undoubtedly be ascribed to solution of platinum by hot dilute HCl, in which the boat was allowed to stand for about one minute in order to remove adhering powder of Fe_2O_3. The loss so caused must have been very small, however, because standing half an hour in concentrated HCl, which in the presence of air is known to dissolve platinum, removed only 0.10 mg.

TABLE I.

Changes of Weight of Platinum Boat when Heated Alone and in Presence of Fe_2O_3.

Number of heatings.	Time. hours.	Gas.	Temperature.	Boat contained.	Wt., mg.	Change of wt., mg.
0	0	......	....	......	13158.60	....
6	30.9	Air and oxygen	1050–1100°	Fe_2O_3	13156.88	—1.72
1	5.0	Air	1150°	Fe_2O_3	13154.41	....[1]
4	17.5	Air	1140–1230°	Fe_2O_3	13155.25	+1.11
7	33.6	Air and oxygen	1075–1105°	Fe_2O_3	13154.45	—0.80
1	5.0	Oxygen	1100°	No charge	13154.40	—0.05
1	5.0	Air	1100°	No charge	13154.30	—0.10
1	16.25	Oxygen	1100°	No charge	13154.49	....[2]
					13154.43	—0.06
3	36.5	Oxygen	1100°	Fe_2O_3	13150.14	—4.29
					13150.04	—0.10[3]
2	34.0	Air	1100–1000°	Fe_2O_3	13150.00	—0.04
4	42.0	Oxygen	1050–1100°	Fe_2O_3	13149.18	—0.82

It is conceivable that heating for a long time in oxygen might put the surface of the platinum in a condition to be more easily attacked by dilute HCl. To test this, the platinum boat in which the various alundum series were heated (see following section), which had been exposed to oxygen and air at temperatures of 1100–1300° for a total of 573 hours, was treated with hot dilute HCl in the usual manner. It lost 0.30 mg., and on a second treatment 0.11 mg. Even after this long heating, therefore, the loss caused by the HCl treatment is considerably less than the losses produced in a few hours by heating in contact with Fe_2O_3.

The average loss of weight per hour of the boat heated alone, as calculated from the figures of Table I, is 0.006 mg.; the average loss per hour when heated in contact with Fe_2O_3 is 0.043, or seven times as great. There is certainly a decided difference in the effect of the two sets of conditions, which seems best explained by assuming a catalytic action of Fe_2O_3 on the reaction between platinum and oxygen. This catalytic effect of ferric oxide on certain oxidation reactions has long been known. Its effect

[1] Boat accidentally amalgamated. Cleaned in HNO_3 and HCl.
[2] New set weights.
[3] Stood 30 min. in conc. HCl.

on the oxidation of sulfur dioxide by oxygen is, perhaps, the most familiar.

In the hope of getting a boat that would be more constant in weight, we obtained from the American Platinum Works a boat made of an alloy containing 4% of rhodium. This lost weight, when heated alone, even more rapidly than the old boat. The figures are given in Table II.

TABLE II.

Loss of Weight of Boat Containing 4% Rhodium.

Treatment.	Wt., mg.	Loss, mg.	Loss per hour, mg.
Original weight...........................	16774.45	..	..
Heated 17.0 hours, in oxygen, at 1100° with basic ferric nitrate in boat................	16768.89	5.56	0.33
Heated alone 3.0 hours, in oxygen, at 1100°..	16768.49	0.40	0.13
Heated alone 3.0 hours, in oxygen, at 1100°..	16768.24	0.25	0.08

The result must not be taken as an indication that the presence of rhodium increased the rate of loss. This particular boat was made after the European war had cut off the supply of pure platinum and rhodium, and probably contained a little iridium, indications of which were seen on the thermoelement tubes. Iridium is known to be considerably more volatile than platinum or rhodium, and its presence would cause a greater rate of loss from the platinum-rhodium boat.

Constancy of Weight of Alundum Boats.—Alundum gave much more satisfactory results at all temperatures than did platinum. It is almost absolutely constant in weight at 1200° and lower. This is not surprising, when it is considered that alumina is a fully saturated oxide, while platinum is an oxidizable metal.

The so-called "alundum" boats are made of fused pure alumina, bonded together by a vitrified silicious bond. The boats which we used were of the composition designated as "RA 84." Above 1200° they lost weight at a uniform rate, probably because of volatilization of alkali or silica from the bonding material. The changes in weight of an alundum boat are shown in Fig. 3. To prevent the loss of small particles, which we found were scraped off when the unprotected boat was dragged through the furnace tube, the boat was placed inside of a platinum boat, from which it was removed for weighing. At 1300°, the highest temperature used, the alundum showed no sign of sticking to the platinum, and it seemed to lose no weight through abrasion in handling.

To test the effect of the binding material on the loss of weight, we made several ignitions on a boat made of the mixture "RA 98," which is more porous and contains less binder than "RA 84." The loss was decidedly less at 1300°, but was still measurable at 1200°. The results on alundum are contained in Table III.

The question of a possible reaction between ferric oxide and the material of the boat must also be considered. At 1200° no evidence of reaction

could be found. At 1300°, the highest temperature used, microscopic examination showed that a trace of Fe_2O_3 had been taken up by the
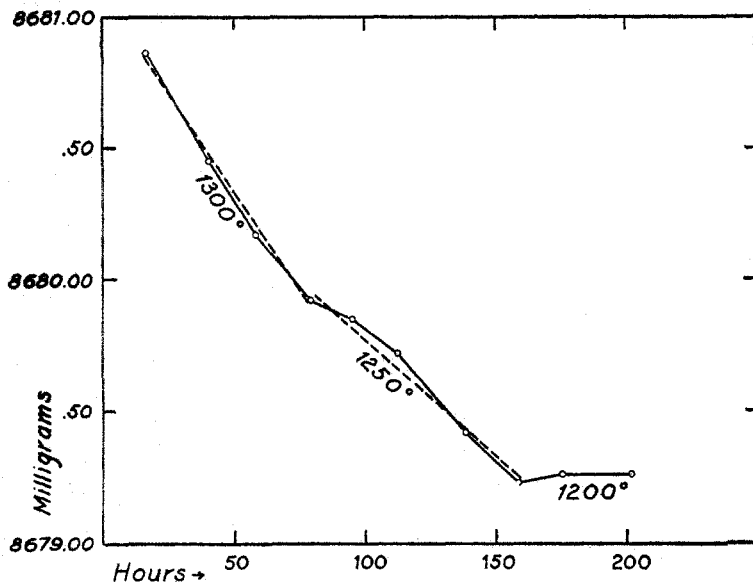

Fig. 3.—Changes in weight of alundum boat of composition "RA 84" heated in oxygen.

vitreous binder of the boat, but that no reaction had occurred with the fused alumina.

TABLE III.

Loss of Weight of Alundum Boats Heated in Oxygen.

Temperature.	Time. hours.	Wt.. mg.	Change. mg.	Change per hour. mg.
		RA 84		
1300°	16.5	8680.86		
1300°	23.0	8680.45	—0.41	
1300°	19.1	8680.17	—0.28	—0.015
1300°	20.9	8679.92	—0.25	
1250°	16.0	8679.85	—0.07	
1250°	17.4	8679.72	—0.13	
1250°	26.0	8679.42	—0.30	—0.009
1250°	20.5	8679.23	—0.19	
1200°	16.9	8679.26	+0.03	
1200°	26.8	8679.26	0.00	+0.001
		RA 98		
1200°	17.5	6690.12	..	
1200°	52.7	6689.90	—0.22	—0.004
1300°	18.2	6689.80	—0.10	
1300°	19.8	6689.56	—0.24	—0.009

Dissociation of Fe_2O_3.—On account of the changes in weight of platinum in contact with Fe_2O_3, the results obtained with the platinum boat

were not entirely satisfactory. A difference in weight between air and oxygen ignitions was clearly shown, however, as will appear from Fig. 4. The curve represents the changes in weight at 1100° of ferric oxide made from nitrate (electrolytic iron) after correction for the change in weight
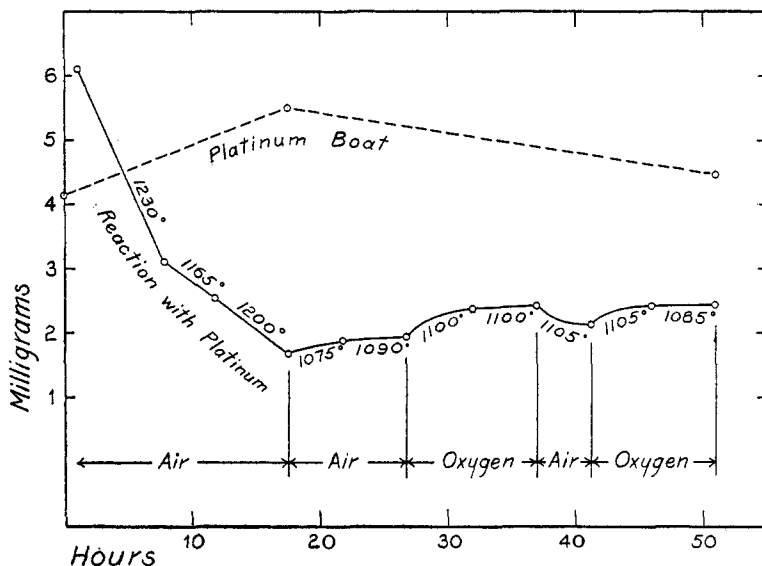

Fig. 4.—Changes in weight of ferric oxide heated in a platinum boat in air and in oxygen.

of the platinum boat. To eliminate the small losses caused by removal of the oxide from the boat, which was done twice during the series, the weights are all referred to a common basis. The original weight of oxide was 12.196 g., and the weight of the boat 13.154 g.

The series made in the alundum boat is plotted in Fig. 5. The boat weights were corrected according to the rates of loss shown in Fig. 3, and were then deducted from the total weights as determined, to give the data plotted in Fig. 5. Kahlbaum's oxide was used.

It will be evident from the curves of Fig. 5 that a prompt change of weight follows each change from air to oxygen or back again, the weights in air being lower than those in oxygen. Furthermore, the difference between air and oxygen is greater at the higher temperatures than at the lower. This indicates that the differences in weight are due not to adsorption of oxygen at the higher oxygen pressure, but to a small amount of dissociation of Fe_2O_3 in air.

Coincident with the series of weight changes there occurs a gradual increase in the total weight of the oxide. This must come from the sublimation of some substance on to the oxide charge, possibly platinum, or alkali or silica from the porcelain tube. This steady gain in weight,

independent of the dissociation and re-oxidation, was confirmed by another series made at 1100–1200° in oxygen in an alundum boat, with a new charge of Kahlbaum's oxide.   As shown in Table IV there was a steady, though very small, gain in weight.   The total gain, after an initial loss
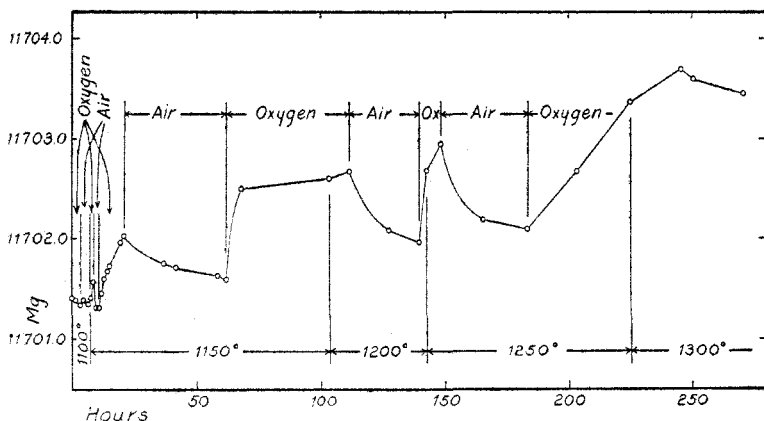

Fig. 5.—Changes in weight of ferric oxide heated in an alundum boat in air and in oxygen.

due to moisture, was 2.00 mg. on 10.605 g. Fe_2O_3, or 0.019%; a gain of 0.010%, part of which may have occurred during the initial heating, could have resulted from the oxidation of 0.09% FeO which is present in the original oxide.

This slow gain undoubtedly masks at 1100–1200° the small decrease of weight of the oxide in oxygen which should occur with rising temperature in the series of Fig. 5, if the dissociation curve really has the form of an asymptote to the pressure axis.   At 1300°, however, at the end of the curve of Fig. 5, a loss of weight in oxygen is observed which may represent the beginning of an appreciable dissociation even at 760 mm. oxygen pressure.

TABLE IV.

Kahlbaum's Ferric Oxide Heated in Oxygen in Alundum Boat.

Temperature.	Total time. hours.	Wt. boat and Fe_2O_3. mg.	Temperature.	Total time. hours.	Wt. boat and Fe_2O_3. mg.
...	0	19283.03	1200°	66.1	19283.65
1150°	16.9	19282.47	1200°	85.9	19283.83
1150°	22.2	19282.66	1200°	109.3	19284.36
1150°	41.7	19282.88	1200°	127.8	19284.47

Not many cases have been studied of this type of dissociation, in which only one of the two components is volatile, and in which a solid solution is left behind by the escape of the volatile component.   One which was mentioned in our previous article is the system $CoCl_2.6NH_3-CoCl_2.2NH_3$.[1]   The

[1] Biltz and Fetkenheuer, Z. anorg. Chem., **89,** 106 (1914).

dissociation-pressure isotherm of this system may be interpreted in exactly the same manner as our Fe_2O_3–Fe_3O_4 system, and it is quite possible that additional measurements nearer the composition of pure $CoCl_2.6NH_3$ than those made by the authors referred to would show a similar "asymptotic" curve.

A theoretical extension of our interpretation of the dissociation pressure curve seems to fit in with Langmuir's work[1] on the adsorption of gases by solid surfaces. It appears probable that the atoms of an adsorbed gas are really in direct chemical combination with the atoms in the surface of the adsorbing solid; these surface atoms, by reason of their position, are in a chemical state which is somewhat different from that of the atoms within the body of the solid. The oxygen atoms adsorbed on the surface of a small crystal of ferric oxide may, therefore, be considered as chemically combined, and their chemical environment is not essentially different from that of the oxygen atoms just within the bounding "surface" of the crystal, for this surface itself, as the X-ray analysis of crystal structure shows, is only a layer of iron and oxygen atoms spaced according to some uniform plan. If Maxwell's demon were sitting in the midst of a group of small ferric oxide crystals which held some oxygen adsorbed, and if he were counting the oxygen atoms which escaped as the temperature was raised, it might be difficult or impossible for him to say when the adsorbed oxygen had all been given off, and true dis-sociation had begun. The essential continuity of the two kinds of combination of oxygen may be
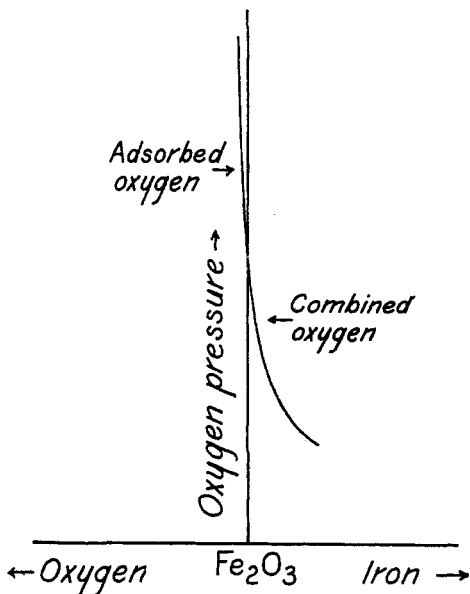

Fig. 6.—A theoretical interpretation of the form of the curve of dissociation-pressure against composition for compositions near ferric oxide.

expressed by drawing our dissociation-pressure curve as in Fig. 6.

The great ease of dissociation of the first small fraction of a per cent. of the oxygen of Fe_2O_3 serves to account for the fact that out of 75 or more iron oxides, natural and artificial, which we have analyzed in this laboratory, only one failed to show a determinable amount of ferrous iron.

[1] THIS JOURNAL, **37**, 1139–1167 (1915); Phys. Rev., **6**, 79–80 (1915).

Summary.

Previous work by the authors has shown that Fe_2O_3 dissociates to form a solid solution of Fe_3O_4 in Fe_2O_3, and that the curve of dissociation pressure against composition at a given temperature rises rapidly as the composition approaches pure Fe_2O_3. The present experiments show that there is a measurable dissociation of Fe_2O_3 in air at all temperatures between 1100° and 1300°, and that the amount of dissociation increases with the temperature. This is shown by the increasing difference in weight between ignitions in air and in oxygen as the temperature is increased. The dissociation-pressure-composition curve thus takes the form of a curve asymptotic to the axis of ordinates, when the ordinates are pressures.

The best container for the Fe_2O_3 at 1100° and 1200° is alundum (bonded fused alumina) which is almost absolutely constant in weight at these temperatures, although it loses weight steadily at higher temperatures. The loss in weight of pure platinum at 1000–1200° is very small, but is considerably increased if the platinum is in contact with ferric oxide.

WASHINGTON, D. C.

THE SEPARATION OF ERBIUM FROM YTTRIUM.

[PART I.]

BY P. S. WILLAND AND C. JAMES.

The element erbium, or neoerbium as it is sometimes termed, is very much rarer than was formerly supposed. Very small amounts, when mixed with yttrium, cause the precipitates and solutions to show a pink or rose color. Also, concentrated solutions of yttrium nitrate, containing very small quantities of erbium, show a strong absorption spectrum due to the latter element. During the last few years, practically no work has been done upon this substance apart from the researches of Hoffmann and Burger.[1] These investigators obtained erbium salts which, if not absolutely pure, are the purest yet known. They also claim that erbium is a simple definite element and not complex, as stated by Auer von Welsbach. This is entirely in agreement with the later work of one of the authors who has submitted erbium bromate to a very long series of fractionation without causing any change in the absorption spectrum. All differences observed were proved to be due to varying conditions of concentration, acids or acidity.

Fractional crystallization, so far, has failed to separate erbium from yttrium rapidly. This type of operation, when bromates or ethylsulfates are employed, quickly removes terbium, dysprosium and holmium in the

[1] Ber., 41, 308 (1908).