calculated pressure in atmospheres for nickel oxide at $227°$, is $1.859 \times 10^{-45}$ and for zinc oxide, $1.333 \times 10^{-67}$.

Now the weight of a single molecule of oxygen is supposed to be not far from $7.36 \times 10^{-23}$ grams so that the gram molecular weight would contain $4.3 \times 10^{23}$ molecules. If the gas were under normal conditions, $0°$ C. and $1$ atmosphere pressure, the pressure exerted by a single molecule would be $\dfrac{1}{4.3 \times 10^{23}} = 2.3 \times 10^{-24}$ atmospheres in a volume of $22.4$ liters, or $4.1 \times 10^{-24}$ atmospheres at $227°$. An equal volume of oxygen in equilibrium with nickel oxide at this temperature would exert a pressure, according to Stahl, of $1.849 \times 10^{-45}$ atmospheres, so that a single molecule should exert a pressure approximately $2 \times 10^{21}$ times as great as the oxygen in equilibrium with nickel oxide, a result which would appear impossible.

*Summary.*—(1) The dissociation pressures of certain oxides of copper, cobalt, nickel, and antimony, have been determined at different temperatures, and when possible, the temperature has been determined at which the dissociation pressure equals the pressure of the oxygen in the air.

Results on the dissociation pressures of cupric oxide and nickelous oxide have heen compared with results calculated by Stahl from the formula of Nernst. In both cases, the observed pressures are very much higher than those calculated.

SHEFFIELD LABORATORY, NEW HAVEN, CONN.,
May, 1908.

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# ON THE DISSOCIATION PRESSURES OF FERRIC OXIDE.

BY P. T. WALDEN.

As early as 1848 H. Rose[1] noticed that if ferric oxide were heated in a porcelain furnace there resulted a black residue which ground to a black powder and gave the well-known blue precipitate when its solution was treated with potassium ferricyanide.

By means of his optical pyrometer Le Chatelier[2] determined the temperature of the hard porcelain furnace to be $1370°$. Evidently we may expect ferric oxide to begin to dissociate into oxygen and magnetic oxide at some temperature below $1370°$ and the pressure of the oxygen at that point should be at least equal to the pressure of the oxygen of the air ($160$ mm.). Assuming that the above dissociation is reversible, the pressure due to the oxygen evolved should be a function of the temperature and independent of the amount of solid.

[1] P. A., **74,** 440.
[2] High-temperature Measurements, Le Chatelier and Boudouard, p. 220.

The present investigation was undertaken in connection with work of a similar character by Foote and Smith on the oxides of copper, cobalt, nickel and antimony, in order to give more completeness to the subject and in the hope that the experimental determination of the pressures for ferric oxide would prove to be of some practical as well as theoretical value.

On account of the high temperature at which experiments had to be conducted a number of special difficulties were encountered but it is my belief that these have been sufficiently overcome to give the results a fair degree of accuracy.

At the outset it was found to be impractical to employ the form of Heraeus's foil furnace in use in this laboratory, so a simple electric platinum wire resistance furnace was constructed especially for this work. It consisted of a porcelain or quartz tube about 60 cm. in length and 15 mm. inside diameter. This was wound for about 30 cm. of its middle portion with platinum wire 0.02 of an inch in diameter, making approximately three turns to the centimeter in length. The tube and wire were then heavily painted with a cream, made by wetting finely powdered talc with sodium silicate solution. When this had dried over night in a warm place the paste hardened so as to hold the platinum wire securely and prevent the possibility of its being displaced and short-circuited. The tube was then enclosed in a sheet-iron box about seven inches in diameter and the box was filled with powdered magnesium oxide. A current of 5.5 amperes at 70 volts (385 watts) served with this apparatus to give a temperature of 1365°. It was found to be impractical to heat a porcelain tube much above 1300°, as the porcelain softened enough at 1350° to permit the tube to collapse under the pressure of the air. By using tubes made by the Wilson Maeulen Co. of the so-called "Electroquartz" it was possible to carry the temperature about 50° higher before the tube collapsed. These tubes however had disadvantages of their own which rendered them far from ideal for the purpose for which they were employed. In the first place every one of these quartz tubes which I used leaked air, even at room temperature. This difficulty was overcome by smearing with asphaltum varnish where the tube was to be cold and with the talc-water glass cement over the portions to be heated. A more serious difficulty even than the porosity was found in the tendency of these tubes to crack on reheating after they had been once heated to 1300° and cooled. I had more than one "Electroquartz" tube crack on a second heating when the temperature was being raised very slowly and had not reached 900°. This difficulty could be overcome by keeping the heat on the furnace night and day until the experiment was completed but this was often very inconvenient.

In carrying out the experiments the material to be heated was reduced

to a fine powder, placed in a platinum boat and ignited over an ordinary gas blast lamp. The boat with its contents was then placed in the middle of the furnace tube and the junction of the wires of a platinum and platinum-rhodium thermo-couple was brought directly over the middle of the boat. The wires were carefully insulated from each other and also as far as possible from the hot walls of the furnace tube. The ends of the pyrometer wires were cooled with ice water and then connected with a galvanometer. The whole apparatus was carefully standardized with another whose error was known. I believe that the errors due to the method of experimentation are greater than those due to the instrument. The furnace tube was connected with a mercury manometer and with an evacuating pump and the pressure reduced to about 1 mm. The apparatus was allowed to stand for twenty-four hours before heating in order to ascertain whether all joints were tight. The current was then thrown in and the temperature gradually raised to the desired point and as gradually lowered, pressures being read at the same time on the manometer. For each reading the temperature was held as nearly stationary as might be for ten minutes.

*Ferric Oxide.*—Several independent experiments were made and the results showed excellent agreement. Pressures read on falling temperatures were about 20 to 30 mm. higher than the pressures for the corresponding temperatures when rising. This discrepancy seemed to be caused by the sintering of the material which probably so glazes the surface of the particles as to prevent the ready reabsorption of the oxygen. In spite of these differences the extent to which the oxygen was taken up left no doubt that the reaction is reversible. I have selected the lower values read with rising temperature as more nearly representing the correct pressures. The following table represents the average of several closely agreeing results:

| Temperature. | Pressure (mm. of mercury). |
|---|---|
| 1100° C. | 5.0 |
| 1150° C. | 7.0 |
| 1200° C. | 9.0 |
| 1250° C. | 20.0 |
| 1300° C. | 59.5 |
| 1320° C. | 90.5 |
| 1340° C. | 138.5 |
| 1350° C. | 166.0 |
| 1360° C. | 202.0 |
| 1380° C. | 297.0 |
| 1390° C. | 352.5 |
| 1400° C. | 454.0 |

These results are plotted in Fig. 1.

A period of about eight hours was devoted to completing an entire series of observations with both rising and falling temperature. Very possibly

this time was not long enough to allow the pressure to reach its maximum before each reading was taken.   In that case the true pressures would be somewhat higher than those which I have recorded and the curves should
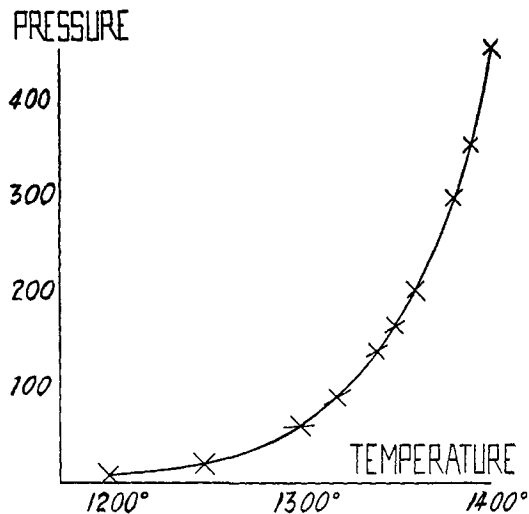
PRESSURE



Fig. 1.

be steeper.   At 1350° the pressure is very nearly 160 mm. which corresponds to about one-fifth of an atmosphere or the pressure due to the oxygen in the air.   These results then indicate that ferric oxide is stable in the air up to 1350° (approximately).   von Jüptner[1] calculates that 1030° is the temperature at which ferric oxide begins to give off oxygen in the air.   It is perhaps worth noting that von Jüptner quotes Tholander's statement that ferric oxide loses oxygen in the air at a white heat and also the determinations of White and Taylor who found about 1200° to be the temperature of a white heat.   Le Chatelier[2] accepts the value 1300° for a white heat, which Pouillet determined by comparison with a gas thermometer.

*Ferro-ferric Oxide.*—Carefully selected crystals of the mineral magnetite were chosen for this experiment.   The material was reduced to a fine powder in an agate mortar and introduced into the furnace in a platinum boat without previous heating.   The pressure was reduced to 1 mm. and the temperature raised to 1300° and maintained at this point for two hours while the pump was run at frequent intervals to remove any oxygen formed from a trace of ferric oxide that might be present.   The apparatus was then sealed and heated to 1350° where the temperature was held for one hour.   No change could be observed on the manometer.

[1] Theorie der Eisenhüttenprozesse, page 12.
[2] High-Temperature Measurements, Le Chatelier and Boudouard, page 246.

Recently von Jüptner[1] has calculated by the use of Nernst's formula (log. $p = \dfrac{Q'}{4.57\ T} + 1.75\ T + 2.8$) the oxygen pressures for the dissociation of several oxides of iron. The following table shows a comparison between these calculated values and those which I obtained experimentally for the dissociation $3Fe_2O_3 = 2Fe_3O_4 + O$.

| Temperature. | Pressure (mm. of mercury). | |
|---|---|---|
| | Calculated (v. Jüptner). | Determined (Walden). |
| 927° C. | 32.7 | .... |
| 1100° C. | .... | 5.0 |
| 1127° C. | 1059.4 | .... |
| 1300° C. | .... | 59.5 |
| 1327° C. | 13231.6 | .... |
| 1330° C. | .... | 113.0 |

Stahl[2] has calculated by the same method the pressure of oxygen due to the dissociation $2CuO = Cu_2O + O$ to be 0.02 mm. at 927° C. In order to give an experimental confirmation to his results, Stahl had Koch make the following experiment under his direction:[3] Five g. of cuprous oxide were mixed with 16.7 g. of ferric oxide in a covered porcelain crucible and the whole heated in a muffle for fifteen minutes to 750° C. A strongly magnetic product was obtained. Stahl draws the conclusion that the ferric oxide is reduced by cuprous oxide at this temperature according to the following equation:

$$Cu_2O + 3Fe_2O_3 = 2CuO + 2Fe_3O_4.$$
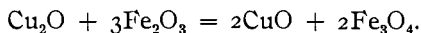
This interpretation of the experiment is in accord with the calculated results of von Jüptner and Stahl but contradicts my results and those of Foote and Smith[4] on the dissociation pressures of cupric oxide. I could obtain no readable pressure for ferric oxide lower than 1050°, whereas Foote and Smith got 15.8 mm. for cupric oxide at 900°.

I repeated Koch's experiment, using an electric furnace for heating with the tube open to the air to avoid the question of possible reducing gases, and obtained his strongly magnetic product. To show that the result was in no way connected with the reduction of the ferric oxide by the cuprous oxide I substituted cupric oxide for cuprous and obtained a product that was even more strongly magnetic than the first. A test of this material with potassium ferricyanide gave no trace of blue precipitate. The formation of a magnetic product in Koch's experiment may be accounted for upon the supposition that ferric and cupric oxides unite to form a double magnetic oxide according to the following equation:

$$Fe_2O_3 + CuO = CuFe_2O_4 \text{ (magnetic).}$$
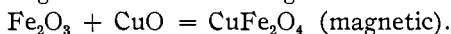
[1] Theorie der Eisenhüttenprozesse, page 9.
[2] *Metallurgie*, **4**, 682 (1907).
[3] *Ibid.*, **4**, 688 (1907).
[4] THIS JOURNAL, **30**, 1345.

This compound ($CuFe_2O_4$) was prepared by List[1] and its strongly magnetic properties described in 1878.   I prepared it by heating mixtures of cupric and ferric oxides in several different proportions and separating the product from the excess of uncombined simple oxide by gravity and magnetism.   Analyses for copper gave 25.60 and 25.83 per cent. of copper Calculated for $CuFe_2O_4$, 26.57.

My work on this magnetic material led me to believe that there is at least one other magnetic double oxide of iron and copper not yet described. Work on this and other similar substances is now in progress in this laboratory.

The fact that Koch obtained the same substance although he used cuprous oxide in a covered crucible is easily understood when it is recalled that cuprous oxide is not stable in the air at temperatures below $1025^{o2}$ and that the change to cupric oxide is probably rapid enough at $750°$ to give an appreciable quantity of that compound in fifteen minutes.   Even though the crucible cover was perfectly tight, which is not probable, the oxygen inside the crucible must have been completely absorbed with the formation of cupric oxide.

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June, 1908.

## THE DETERMINATION OF IONIC HYDRATION FROM ELECTROMOTIVE FORCE.

BY GILBERT N. LEWIS.

In the theory of concentration cells an important point seems to have been hitherto overlooked.   It has been supposed that the electromotive force is a true measure of the change of free energy in the transfer of salt from the higher to the lower concentration.   This is only true if the transfer of salt is the only process that takes place when a current passes through the cell.   This is not always the case.   If the ions present in solution are *hydrated*, water will be carried in both directions when the current passes, and if the cation carries more or less water than the anion, a definite transfer of water in one direction or the other will result from the passage of the current.   Since the activity[3] of the water is not the same in the concentrated and the dilute solution, this transfer will be accompanied by a change in free energy.

The electrical work which can be obtained from such a cell, when one

[1] *Ber.*, **11**, 1512.
[2] Foote and Smith, THIS JOURNAL, **30**, 1345.
[3] For the definition of the term activity see Lewis, *Z. physik Chem.*, **61**, 129 (1907).