

ART. XXIV.—*The Electromotive Force of Magnetization*;* by
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AT the Ann Arbor meeting of the American Association for the Advancement of Science, we described some singular modifications in the relation of iron to acids which occur when the reaction takes place within the magnetic field. The present paper deals with the behavior of iron when that metal acts as one electrode in a voltaic circuit, and is at the same time subjected to magnetization.

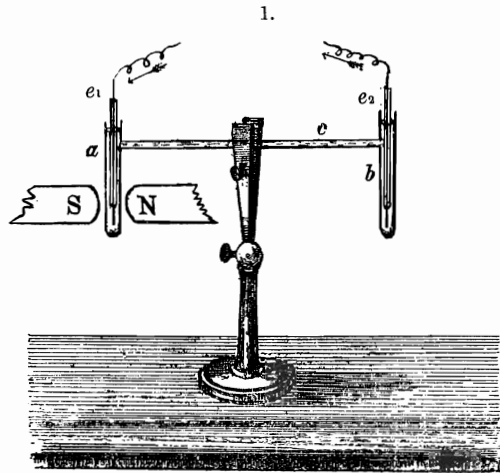
A galvanometer placed in a circuit consisting of two electrodes of iron, metallically connected on the one hand, and dipping, on the other, into a cell containing any liquid capable of dissolving them, will indicate the existence of a current whenever the reaction between the metal and the liquid differs in character or rapidity at the two terminals. There are always at work a number of causes of such inequality of action, and the electro-motive force between iron poles in any liquid which attacks them freely is not inconsiderable. It amounts as a rule to several thousandths of a volt and even when special precautions have been taken to secure homogeneity in the elements of the circuit, a sensitive galvanometer will not fail to show the existence of a current. If one of the terminals be placed within a magnetic field, new differences of potential will be developed, both from the magnetization of the iron and from the change in the chemical relations between the metal within the field and the liquid. This electro-motive force we have proposed to call *the electro-motive force of magnetization*.

With the exception of two papers by Dr. Theodor Gross† of Berlin, which came to our notice too late to enable us to take advantage of their valuable contents in our investigation, we know of no observations of the effect of magnetization upon the voltaic behavior of iron. Dr. Gross's research deals chiefly with the electro-motive force due to the magnetization of the iron, and touches only incidentally upon the nature of the currents produced when one of a pair of iron electrodes has its electro-chemical relations to the solution modified by being placed within the magnetic field. It is with the latter phase of the subject, principally, that our experiments have to do.

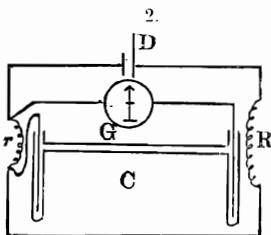
* Paper read at the New York meeting of the American Association for the Advancement of Science, August 11, 1887.

† Th. Gross; Ueber eine neue Entstehungsweise galvanischer Ströme durch Magnetismus: Sitzungsberichte der Wiener Academie, vol. xcii, 1885.

The first form of cell, which we used, consisted of two glass tubes, *a* and *b* (figure 1), about 1^{cm} in diameter and 10^{cm} long. These were closed at the lower end and were connected by a



narrower glass tube (*c*), about 50^{cm} in length. The electrodes, *e*₁ and *e*₂, consisting of soft-iron wire, were inserted through the open ends of *a* and *b*. They were exposed to the liquid for about 1^{cm} at their lower ends. When this apparatus was filled with a liquid capable of dissolving iron, it formed a single cell, one terminal of which could be placed between the poles of an electro-magnet, while the other was well outside of the field. When the free ends of the wires, *e*₁ and *e*₂, were connected through a sensitive galvanometer, it was found that, although the terminals were taken from the same piece of wire, and were immersed in the same liquid, a measurable current was always flowing in the circuit. The electro-motive force was constant neither in amount nor in direction. In many liquids it changed but slowly, however, and could be balanced by means of a variable counter-



electro-motive force introduced into the circuit. For this purpose a Daniell's cell was placed in circuit with two variable resistances, *R* and *r* (figure 2). The cell with iron electrodes was shunted around *r*, and the ratio *R/r* was so adjusted that the current in the shunt circuit, due to the Daniell cell, was just sufficient to reduce the galvanometer deflection to zero. The

galvanometer could then be sensitized to any desired extent, but the fluctuations in the electro-motive force of the iron cell were such that the balance was never more than momentarily maintained, and the galvanometer drifted continually.

In very weak acids and in solutions of FeSO_4 , FeCl_2 , NH_4Cl , and similar salts, these fluctuations were not such as to preclude the possibility of making measurements, but in concentrated acids they were for the most part so rapid and irregular as to put galvanometer readings out of the question. In nitric acid, of considerable strength, these fluctuations were so remarkable as to deserve special mention. The electro-motive force, amounting to a considerable fraction of a volt, changed sign continually, carrying the spot of light across the galvanometer scale, to and fro, with great rapidity. The frequent and irregular oscillations continued with undiminished violence until the electrodes were entirely dissolved or the acid nearly neutralized. Upon first closing the circuit one of the iron terminals would be slightly more active than its fellow. The tendency of the less active electrode would then be to protect the other from the attack of the acid, rendering it temporarily passive, as a piece of platinum would do under the same circumstances. The passive terminal would then react in like manner upon the first and electro-motive force would be reversed again and again until the electrodes were consumed.

In those cases in which the fluctuations were not such as to make the attempt at compensation ineffectual, we were able to make measurements of the initial electro-motive force of the cell and of the changes in electro-motive force caused by the action of the magnet.

One of the iron terminals was placed between the poles of a large electro-magnet. To obviate any direct effect of the magnet upon the galvanometer needle, the galvanometer was set up in a room several hundred feet distant from that in which the former instrument was located. The "iron" cell having been connected with the wires leading to the galvanometer room, the initial electro-motive force was balanced by the method already described, and the galvanometer was brought to the desired degree of sensitiveness by means of a governing magnet. One observer then proceeded to make galvanometer readings at intervals of fifteen seconds, while another magnetized and demagnetized the electro-magnet every two or three minutes, reversing the magnetizing current each time. The electro-magnet in question has been described in a previous paper.*

Like most large instruments of the kind, it required several seconds after the circuit had been closed to attain its full

* This Journal, vol. xxxi. p. 272.

strength; and it retained considerable residual magnetism when the circuit was broken. By the following very simple device, however, the residual magnetism was almost entirely destroyed. A reversing switch of Poggendorff's pattern and an ordinary telegraph key were placed in series in the magnetizing circuit. While the magnet was in function, a piece of soft iron wire about 1^m long was suspended by magnetic attraction from the underside of one of the pole pieces. The wire served as an indicator of the magnetic condition of the poles. Upon breaking circuit with the key the residual magnetism was sufficient to hold it in position. When, however, the current was first reversed by means of the Poggendorff switch, and then broken at the instant when the magnet was passing through the condition of neutrality, the proper moment being indicated by the dropping of the suspended wire, the magnet was left thoroughly demagnetized. The interval of time between reversal of the current and neutrality was about two seconds.

After each series of readings, the galvanometer was calibrated, the resistance of the iron cell was measured and the strength of the magnetic field was estimated by a modification of Rowland's method. The instrument used in most of these measurements was Edelmann's form of the Wiedemann galvanometer, read with telescope and scale. For some experiments in which a high degree of sensitiveness was necessary a Thomson reflecting galvanometer of 2500 ohms resistance was used.

It was found possible by this method, excepting when the fluctuations in the initial electro-motive force of the cell were very marked, to detect changes amounting to much less than .00001 volts.

We experimented with a variety of reagents, including nitric, hydrochloric and sulphuric acids; ferrous sulphate, ferrous chloride, and ammonium chloride, in aqueous solutions, and finally, sulphuric acid, to which potassium bichromate had been added, and hydrochloric acid containing potassium chlorate. In every case there was unmistakable evidence of the development of a permanent electro-motive force due to the influence of the magnet. The smallest effect, .000008 volts, was observed with terminals in concentrated nitric acid, the iron being passive—the largest effect in those solutions in which rapid oxidization took place. In a solution consisting of dilute sulphuric acid containing potassium bichromate, the electro-motive force of magnetization amounted to .039 volts. In the same acid, the concentrated sulphuric acid of commerce diluted with ten parts of water, without the addition of the potassium bichromate, it was only .0005 volts. Concentrated hydrochloric acid (sp. gr. 1.1768), gave .003 volts, the same acid, diluted with four parts

of water, only .00002. When potassium chlorate was added to the dilute acid, the effect due to the magnet became very marked, amounting certainly to several hundredths of a volt; but the fluctuations in the initial electro-motive force were such as to make readings impossible. In nitric acid diluted with nine parts of water the effect was also very large, but it was so masked by the initial fluctuations described in a previous paragraph, that no quantitative determinations were secured. The strength of field during these experiments was about 10,000 H.

In the hope of eliminating these fluctuations in the initial electro motive force, two modifications of our apparatus were made. In the first, it was so arranged that a current of the fresh solution passed through both arms of the cell and the products of the reaction were carried away from the neighborhood of the terminals almost as soon as formed. In the second modification, terminals were prepared the surface of which consisted of pure iron, electrolytically deposited. When these prepared terminals were used, the fluctuations were somewhat less marked than when the original surface of the iron wire was exposed, but the adoption of these two modifications led to no new results. A more important modification consisted in the substitution of platinum or copper for the iron terminal outside of the field. These metals, being unaffected by the magnet, could be placed in close proximity to the magnetized terminal: the internal resistance of the cell was thereby greatly diminished and its form simplified. The iron-copper and iron-platinum cells were placed between the poles of the electro-magnet, and the investigation consisted in determining the electro-motive force before and after the magnet had been made active. The most satisfactory results were obtained with a cell patterned after the Daniell battery—a two-fluid cell in which copper immersed in sulphate of copper was separated from the iron pole by a porous diaphragm, the iron being submerged in a solution of ferrous sulphate or of ferrous chloride. A cell of this description, in which a neutral solution of ferrous sulphate surrounded the iron, and which possessed an initial electro-motive force of .6072 volts, increased to .6361 volts when placed within the field. Similar results were obtained with other solutions.

In the various forms of apparatus already described the currents due to magnetic action did not always flow in the same direction. The iron terminal within the field would sometimes act as zinc toward the unmagnetized electrode, sometimes as platinum. To determine the law governing the direction of the currents due to the electromotive force of magnetization we tried the following experiments. The terminals of iron wire used in our original apparatus were supplanted by cylin-

ders of soft Norway iron 1^{cm} long and 4^{mm} in diameter. These were placed horizontally in the solution and were attached to the end of copper wires. The wire was in each case thoroughly insulated from the liquid, and the iron bar itself was protected by a coating of wax with the exception of a single portion of its surface, which to the extent of a few square millimeters was exposed to the action of the liquid. Under these conditions, the direction of the electro-motive force developed between the terminal within the field and a similar one outside was found to depend upon the portion of the bar exposed and the position of the latter with reference to the lines of force. Whenever the exposed surface was in the neighborhood of an induced pole within the soft iron electrode it became in its relations to iron outside of the field, as zinc to platinum. Whenever on the contrary the exposed surface was situated in a neutral portion of the bar, it became as platinum in its relations to unmagnetized iron. When platinum, carbon or copper was substituted for the unmagnetized electrode the electro-motive force of the cell thus formed was increased by magnetization, in the case in which a pole of the iron terminal was exposed to the liquid and diminished by magnetization when the surface acted upon lay in the middle of the bar. A reversal of direction in the current flowing between such a bar of iron in the field, one end of the bar being exposed to action, and an unmagnetized iron terminal, could be produced by turning the former in the field. When the axis of the bar was parallel to the lines of force and it was accordingly magnetized longitudinally, it acted as a zinc pole, the current flowing from its surface through the cell to the unmagnetized electrode. When turned through 90° upon an axis perpendicular to the line joining the poles of the electro-magnet, the bar became magnetized transversely and the direction of the current was reversed.

Between bars lying with their axes parallel to the lines of force, the end of one and the middle of the other of which was exposed, the effect was more marked than between either of them and a piece of unmagnetized iron; the bar with exposed pole acting as zinc, that exposed in the middle as platinum.

After having determined the conditions which govern the direction of the current, we turned our attention to the relation between the strength of the magnetic field and the electro-motive force which it is capable of producing. The cell selected for this work was an iron-platinum element, containing a solution of potassium bichromate in dilute sulphuric acid. In this liquid the electro-motive force of magnetization was so marked that when the cell was placed between the pole pieces of the electro-magnet the influence of the residual magnetism of the latter upon its electro-motive force could easily be de-

tested. Measurements were made in fields varying in intensity between 2000 H., and 20,000 H. The results are given in the following table. They show the manner in which the effect in question increases with the strength of the field.

TABLE.
Influence of the Strength of Field upon the Electro-motive Force of Magnetization.

Strength of field.	E. M. F. in volts.
2000 H.	·0008 volts.
3600 	:0045
5040 	·0208
7770 	·0386
8400 	·0424
12750 	·0487
16300 	·0510
19700 	·0680

We had noticed in the course of our experiments that a layer of the more or less magnetic solution of the salts of iron, produced by the reaction, always gathered around the induced poles of the electrode within the field. In this way a two-fluid battery was formed between the iron within the field and that outside, whenever the surface nearest the poles of the magnetized electrode was exposed. The terminal within the field was thus surrounded by a concentrated solution of its own salts, and was in a measure protected against the direct attack of the acid. In the case however in which a neutral portion of the electrode within the field was exposed, the products of the reaction were continually withdrawn by magnetic attraction towards the pole-pieces, and the surface was left more open to attack than the opposing electrode outside of the field.

For the purpose of ascertaining whether this arrangement of the solution in the field would tend to produce the effects which have been described, measurements were made of a variety of batteries in which iron formed one electrode. The results were such as to make it evident that the influence of the magnet could, in part at least, be thus explained. An iron-carbon cell, the liquid being nitric acid diluted with one part of water, was found to have an E. M. F. of ·88 volts. When the acid was placed in a porous cup, containing the carbon pole, and the iron was submerged in weak sulphuric acid (1:10), the E. M. F. rose to 1·33 volts. The same metals in dilute sulphuric acid containing potassium bichromate gave 1·05 volts which was increased to 1·32 by placing the carbon and bichromate solution in a porous cup and the iron in dilute sulphuric acid. A cell with iron and platinum, in a solution consisting of 200^{cc} of strong hydrochloric acid, 200^{cc} of water and 20^{grms} of potassium chlorate, gave 1·17 volts. When converted into

a two-fluid battery, the iron submerged in weak sulphuric acid, the platinum in the above solution, the E. M. F. became 1.39 volts. When the iron in the last case was submerged in dilute hydrochloric acid the result was nearly the same, the E. M. F. being 1.41 volts. In sulphuric acid containing potassium permanganate the same metals gave 1.44 volts, which rose to 1.60 volts when the platinum and solution were placed in a porous cup and the iron was dipped in sulphuric acid containing no oxidizing agent. Iron and platinum in ferrous chloride showed only .74 volts, but a two-fluid battery with iron—dilute hydrochloric acid—ferrous chloride—platinum gave 1.07.

In all these cells the electro-motive force obtained by the solution of iron with ferric reaction was smaller than when a ferrous reaction occurred. The application of this fact in the explanation of the electro-motive force of magnetization is very manifest. When the *poles* of an electrode within the magnetic field are exposed to action, the gathering of the salts of iron around the exposed surface tends to bring about a change from *ferric* to *ferrous* reaction and to *increase* the electro-motive force. A corresponding *decrease* follows when a neutral surface is exposed within the field. The extent to which the electro-motive force of a cell in which a ferric reaction is taking place may be reduced by briskly stirring the solution and exposing the surface of the iron to the fresh acid, thus doing mechanically what is done magnetically when the reaction occurs, at a neutral surface, within the field, was shown by the following experiment. A one-fluid cell, consisting of iron and platinum in nitric acid diluted with four parts of water, had an electro-motive force of 1.07 volts. Stirring reduced it to .95 volts. When left undisturbed it immediately regained its former intensity.

The electro-motive force developed between the poles of one iron electrode placed within the magnetic field and the neutral parts of a similar electrode in the same cell, will also exist between the poles and intermediate portions of a single piece of iron. Consequently there will always be local action between different portions of the surface of iron exposed to chemical action within the field, the currents passing through the liquid from the regions nearest the induced poles.

It is doubtless to this local voltaic action, which has its source in the electro-motive force of magnetization, that the various phenomena, described in our papers on *the chemical behavior of iron in the magnetic field*,* and on *the destruction of the passivity of iron by magnetization*,† are to be ascribed.

* This Journal, vol. xxxi, p. 272.

† Ibid., vol. xxxiv, p. 419, Dec., 1887.