

## THE INFLUENCE OF THE MAGNETIC FIELD ON THE PASSIVE STATE OF IRON.

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In an article<sup>1</sup> by one of us it was shown that the passive state of iron may be produced in an anode in numerous electrolytes by a definite current density, and reference was made to the work of Fredenhagen<sup>2</sup> showing the same fact though incorrectly ascribed to the electromotive force employed. In an article by Nichols and Franklin<sup>3</sup> it was shown that the passive state of iron in nitric acid may be destroyed by placing the iron in a magnetic field of great intensity. It seemed of interest, therefore, to determine whether the passive state of iron as an anode might likewise be influenced by the magnetic field. To determine this question a number of experiments were carried out, but it was found impossible to destroy the passive state, when once established, by any magnetic field which we were able to produce with the apparatus available. Nevertheless, a distinct influence of the magnetic field upon the transition from the active

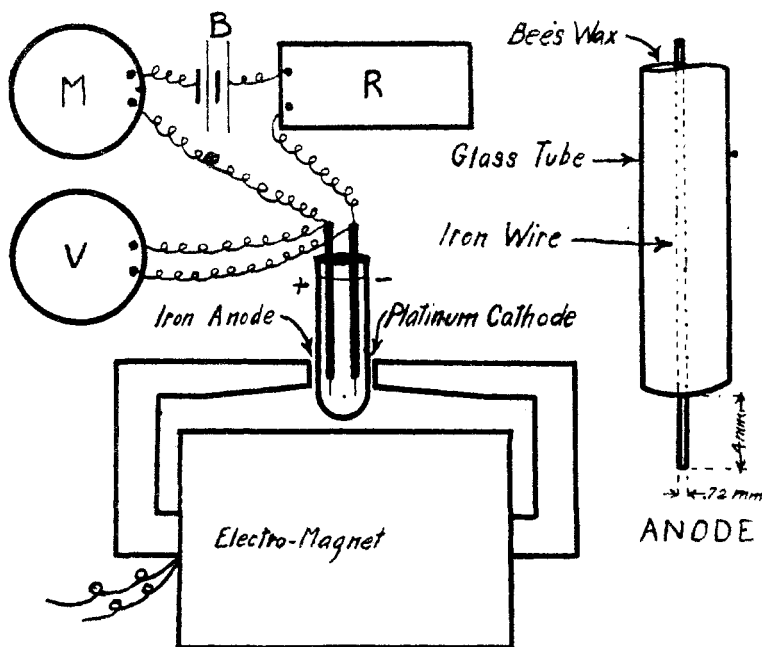


Fig. 1.

APR 1910 MARC DARRIN

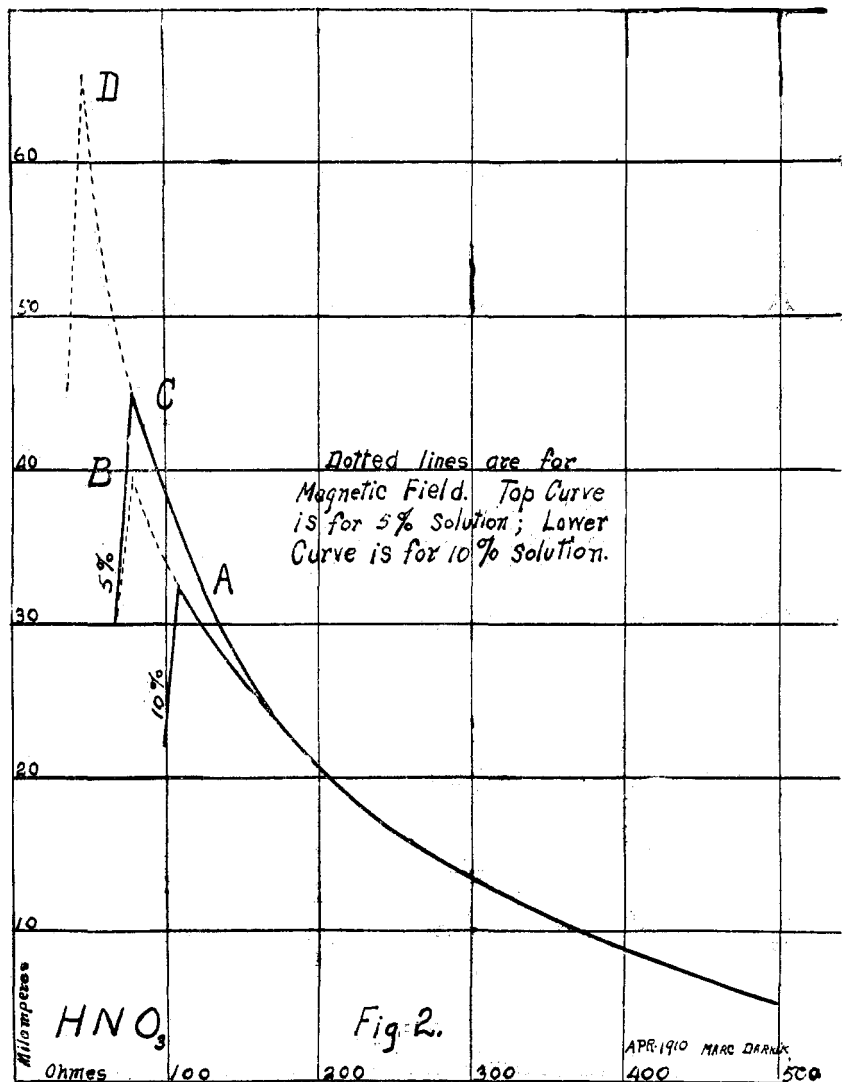
<sup>1</sup> THIS JOURNAL, 30, 1718 (1908).

<sup>2</sup> Z. physik. Chem., 63, 1 (1908).

<sup>3</sup> Am. J. Sci., [3] 31, 272 (1886); [3] 34, 419 (1887).

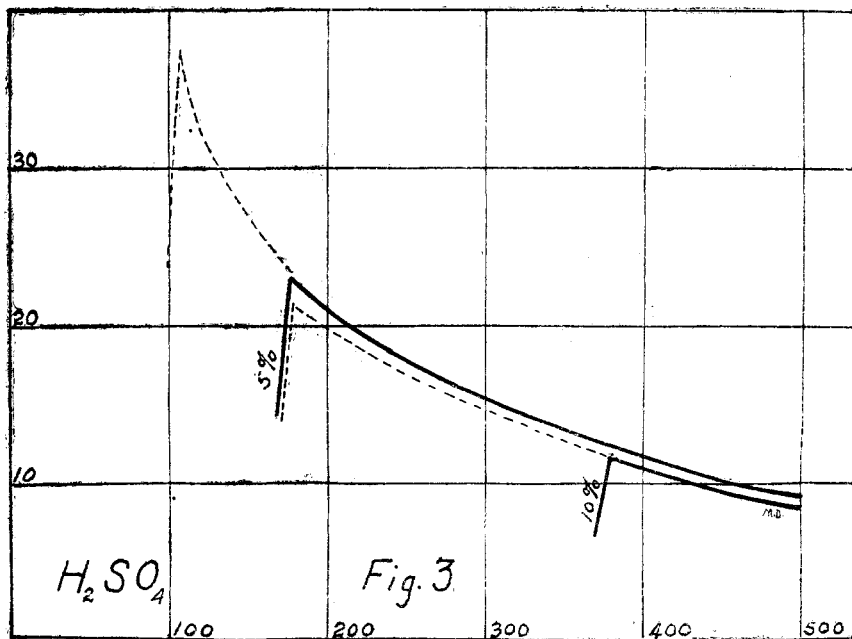
to the passive state was demonstrated in several solutions, the details of the work being given below. It should be noted that not only is the transition from the active to the passive state of iron when used as an anode produced by a given current density, but that this transition point is extremely sharp and well defined.

*Experimental Method.*—The apparatus was connected as shown in Fig. 1. A 20 cc. test tube, containing the electrolyte, was placed between the poles of a powerful electromagnet (5825 turns of No. 18 wire; run by 110 volts



d. c. ; amperage, 3 amp. ; distance between poles 2 cm. ; area of poles 7 sq. cm. ; diameter of coil 16 cm. ; length of coil 17 cm.). The anode was made by sealing into a glass tube, with beeswax, a piece of soft piano wire (diameter 0.72 mm.) such that only 4 mm. was exposed at the immersed end; the cathode consisted of a small strip of platinum foil at the end of a similar glass rod. The electrodes were put in series with two U. S. storage cells *B* (giving a constant current of about 5 v.), a rheostat *R* and a delicate Weston milliammeter *M* reading directly to half milliamperes. A voltmeter *V*, with a telegraph key, was connected across the circuit between the two electrodes. When the iron anode was active, the voltmeter would indicate but slight differences in potential between the two electrodes, and the milliammeter would show between 10 and 70 milliamperes passing through the circuit; when the iron changed to the passive state, there was a sharp rise in the voltmeter (to about 4 v.) and a corresponding drop in the milliammeter of about 10 milliamperes.

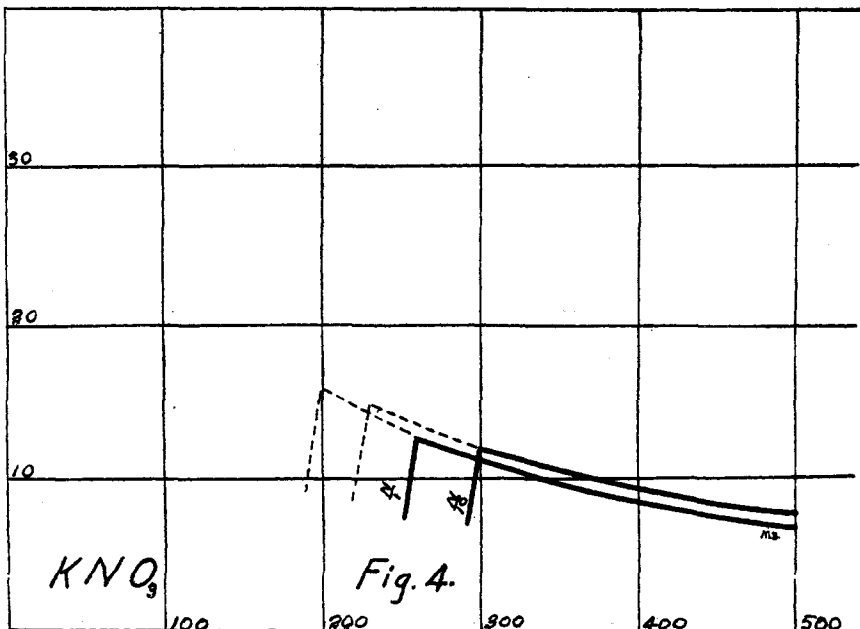
*Experimental Results: Nitric Acid Electrolyte without Magnetic Field.*—The test tube was filled with a 10 per cent. solution of  $\text{HNO}_3$ . The rheostat was set at 500 ohms, and electrodes immersed in solution, as in Fig. 1. The result of this experiment is best understood by following the curve in Fig. 2; the resistance introduced at the rheostat is represented by abscissa, the amperage passing through the circuit by ordinates. As the resistance was lessened from 500 ohms to 400, 300, and 200, the



amperage steadily increased till a point was reached at "A" when on removing 10 more ohms, the current dropped suddenly from 32.5 milliamperes to 20 milliamperes, marking the transition point from active to passive state, which is also shown by liberation of oxygen at the anode and a bright metallic surface of the iron.

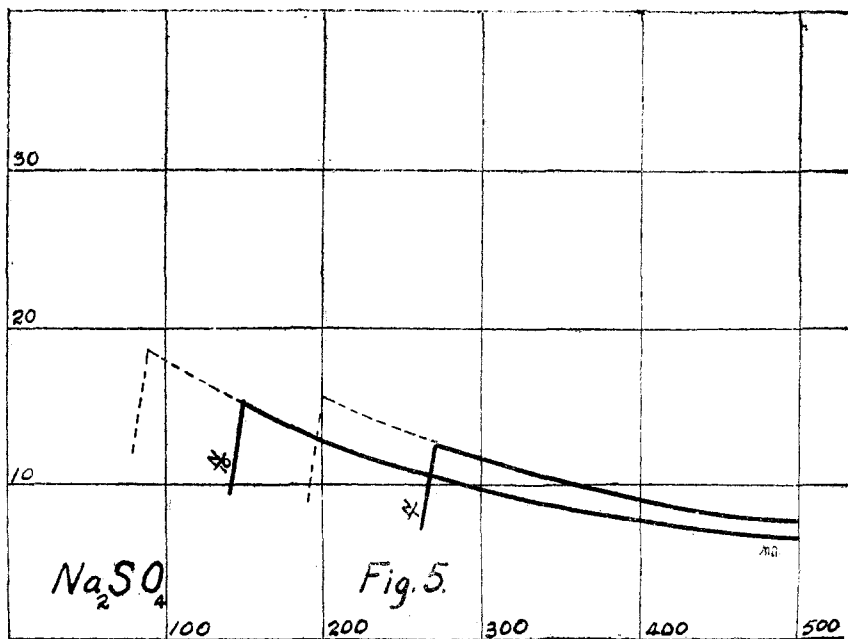
*In a Magnetic Field.*—The above experiment was repeated in a magnetic field. Looking at the same curve (Fig. 2), the effect is readily seen; the transition point has been moved from A at 110 ohms resistance in rheostat, to B at 80 ohms. In other words, without the field, the sufficient and necessary strength of current to render the iron anode passive was 32.5 milliamperes; within a magnetic field, it would not become passive until the current had been raised to 40 milliamperes. This experiment with nitric acid was repeated many times, all results checking satisfactorily.

The above experiments were again repeated with a 5 per cent. solution of nitric acid. Here the effect of the magnet is even more marked (2), the transition point coming at C (45 milliamperes) without the field, and at D (65 milliamperes) within the field, a difference of 20 milliamperes. When the current through the electromagnet was stopped at any point between D and C (or in the former case between B and A) the iron *immediately* changed to the passive state, but once in this state the magnet was unable to restore it to the active condition. The only ways in which this could be done were by reducing the current

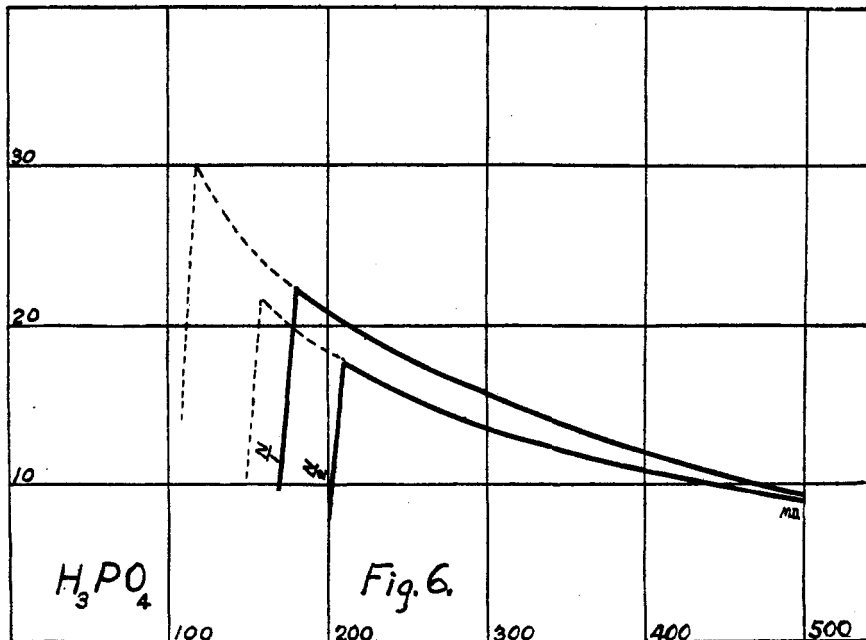


strength to a minimum with about 4000 ohms, by breaking the current, by bringing the electrodes into contact within the solution. This second transition point from *passive to active*, at about 4000 ohms was sharp, but difficult to measure accurately, and all efforts failed to show definitely whether it was affected by the magnetic field.

*Results with Other Substances.*—Using solutions of sulphuric acid instead of nitric acid, the four curves in Fig. 3 were plotted. They are of the same general nature as the nitric acid curves and illustrate well the effect of the magnet. Figs. 4 and 5 show the effect of the magnetic field on potassium nitrate and sodium sulphate solutions, respectively; in neither case is it nearly as great as for the active acids, but clearly of the same character. Fig. 6 is for phosphoric acid solutions. Here the effect of the magnet is greater than for the salts, but not as great as for the active acids. Similar experiments were made, using sodium hydroxide, potassium dichromate, dipotassium phosphate and monopotassium phosphate. Under all conditions solutions of the first three substances rendered the iron passive. In the case of a normal solution of monopotassium phosphate, however, by careful manipulation, the transition from active to passive iron could be found. However, this electrolyte did not behave as any one of the others, seeming to have properties akin to both the two opposite classes of electrolytes represented by sodium hydroxide and nitric acid, respectively. Although iron could be rendered active in this



solution, it would pass into the passive state within a considerable range of current density or by simply a short lapse of time. No effect of the magnetic field could be measured with this solution. With a 0.1 *N* solution, the passive properties were still more marked, so much so, that it could not be rendered active even temporarily. This is, of course, due to the hydrolysis of the salt. Two facts, which must be noted in



connection with each of these passivity phenomena are: in no case, were any of the results affected in any way by the direction of the current through the electromagnet or by the relative positions of poles and electrodes; in no case, did the magnet cause a change in the amount of current passing through the electrolyte, or in the relative potentials of the two electrodes.

*Conclusion.*—In solutions of nitric, sulphuric and phosphoric acids, also of nitrates and sulphates, the transition point of passive iron to active iron is a function of current density but the transition is retarded by the magnetic field. It is of course recognized that passivity is also a function of temperature and concentration, but in these experiments they are constants and the only variables are current density and magnetic flux.

In the article previously referred to,<sup>1</sup> the writer gave a résumé of the various views in regard to passivity and stated that "none of them are satisfactory but that when experimental development warrants it

<sup>1</sup> THIS JOURNAL, 30, 1718 (1908).

he confidently expects the cause of passivity to be found to be an altered state of the metal itself, being produced by any one of several agents." The above experiments coupled with those of Nichols and Franklin seem to show that this altered state may be analogous to that of a number of magnets, the negative poles of which are all presented to the electrolyte, this orientation being produced by the various agents which cause the passive state. This view is not presented as proved but is tentative, and may lead to better work in this direction.

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## THE INFLUENCE OF CHLORINE UPON THE DETERMINATION OF NITRIC NITROGEN.

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It is known that chlorine has an appreciable effect upon the determination of nitric nitrogen by the phenyldisulphonic acid method. Very little information, however, is available as to the amount of chlorine which may be present and not affect the reliability of the results. In connection with the study of the influence of irrigating water upon the movement and production of nitric nitrogen in the soil, this question was investigated quite thoroughly in this laboratory.<sup>1</sup> The results are of interest to others working along similar lines and also to chemists who are working with problems in sanitary water supply.

The chlorine in the soil under consideration was determined as follows: An aliquot portion of the extract of the soil, prepared as for the nitric nitrogen determination, was titrated against a one-hundredth normal silver nitrate solution. The results obtained are given in Table I. The results are expressed as parts of chlorine per million parts of soil.

TABLE I.—AMOUNT OF CHLORINE PRESENT IN THE SOIL EXTRACT.  
Depth of soil in feet.

No of plot:	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
41 G. . . . .	0.849	0.814	0.496	0.923	0.567	0.779	0.744	0.673	0.815	0.496
42 G. . . . .	0.886	0.779	0.697	0.838	0.795	0.602	0.567	0.602	0.673	0.496
43 G. . . . .	0.780	0.425	0.921	0.709	1.134	0.496	0.922	0.496	0.425	0.425

These results indicate quite clearly that the chlorine in the soil under consideration did not exceed 1.134 parts per million.

It was then necessary to determine whether this amount of chlorine would interfere with the determination of nitric nitrogen by the phenyldisulphonic acid method. With this object in view, varying amounts of sodium chloride were added to given quantities of the standard potassium nitrate solution. The nitric nitrogen was then determined in the usual way. The results are very interesting and will be found in Table II. The results are expressed as parts per million.

<sup>1</sup> Utah Experiment Station, *Bull.* 106, p. 80.