as soon as the solution became concentrated, it crystallized readily upon cooling. The solid was powdered; washed with alcohol and dried at room temperature. This pyromucate was easily soluble in water.

*Europium Meta-nitro-benzenesulfonate*, $[C_6H_4(NO_2)SO_3]_6Eu_2.6H_2O$.—An aqueous solution of meta-nitrobenzenesulfonic acid was treated with a slight excess of europium hydroxide. The excess of hydroxide was filtered off and the solution evaporated. The crystals were washed with alcohol and dried at 80° for some time. The salt was slightly yellowish and very soluble in water. By a simple ignition it was found to contain 21.63% $Eu_2O_3$, while the calculated amount comes to 21.65 $Eu_2O_3$.

DURHAM, N. H.

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# RELATION BETWEEN THE MAGNETIC FIELD AND THE PASSIVE STATE OF IRON. III.

BY HORACE G. BYERS AND SETH C. LANGDON.

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Since the discovery of the passivity of iron by James Keir in 1790, a very great number of investigations have been devoted to it and allied phenomena. These investigations have been summarized by one of us in an article published in 1908.[1]

It was there pointed out that none of the numerous suggestions as to the cause of passivity were satisfactory, and an attempt was made to define the term which by reason of extension to similar phenomena has become confused. The term was defined as properly used when applied to an element when it "shows abnormal electrochemical relations and a chemical inactivity not corresponding to its ordinary behavior and not in accord with its position in the electromotive series of the elements."

Using this definition we find that up to the publication of the article mentioned it was recognized that certain metals become "passive," *i. e.*, behave abnormally, when used as an anode provided the electrolyte is of a given type, chiefly oxygen compounds, and provided excessive temperatures are avoided. It was also there shown that in addition to the character of the electrolyte and the temperature another determining factor in the establishment of the passive condition in a given metal as an anode is the density of the current employed. A fourth factor is the time during which the current passes. It is the purpose of the present paper to show that still another factor enters into the establishment of the passive state upon a metal.

In 1910 and 1911 it was shown by one of us, together with Marc Darrin and A. F. Morgan[2] that the establishment of the passive state of iron and

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[1] THIS JOURNAL, 30, 1718.

[2] *Ibid.*, 32, 750; 33, 1757.

nickel anodes was much retarded, *i. e.*, a higher current density was required in a given electrolyte at a given temperature, if the apparatus were placed in a magnetic field. These investigations were not exhaustive, partly because of the character of the magnet used and the impracticability of maintaining constant conditions. Since 1911 we have been put in possession, partly by the assistance of the C. M. Warren Fund of the American Academy of Arts and Sciences, of a large Weiss magnet capable of furnishing a field of 36000 gauss and provided with cooling devices and other adjustments for control.

With this assistance the investigation was continued because of the interest attaching to an apparent connection between a chemical reaction and the influence of a magnetic field. We say "apparent connection" for reasons detailed below, and we deem the subject interesting because, while on theoretical grounds chemical reactions should be influenced by the magnetic field, yet not a *single authentic case has yet been reported* where any direct effect has been demonstrated.[1]

*Experimental.*—The arrangement of the apparatus used in the first series of experiments is shown in Fig. 1, and consisted of a short test tube, containing the electrolyte, and 0.5 *N* solution of sulfuric acid, supported between the poles of a Weiss magnet. The anode was a piece of piano wire, diameter 0.72 mm., sealed in a glass tube with paraffin so that exactly 4 mm. was exposed. The cathode was a platinum wire exposing an equal area. The electrodes were connected in series with five U. S. storage batteries, a resistance box with a range from 0.1 to 1000 ohms and a Weston milliammeter (Model 1). A voltmeter, as a shunt, with a key connected the electrodes.

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[1] NOTE: To reach the conclusion stated above the authors have examined all the available literature bearing upon this question and append the following bibliography for the assistance of anyone seeking information upon the subject: Armin, *Gilb. Ann.*, **3**, 59 (1800); **5**, 394 (1800); **8**, 279 (1801); Ritter, *Beitr.*, **2**, 238 (1805); Cavallo, *Phil. Trans.*, **1787**, 16; Maschmann and Hausteen, *Gilb. Ann.*, **70**, 234 (1822); Schweizger and Dobereiner, *Schweigg. J.*, **44**, 85 (1825); Ludicke, *Gilb. Ann.*, **68**, 76 (1821); Kastner, *Kastner's Arch.*, **6**, 448 (1825); Hunt, *Phil. Mag.*, **28**, 1 (1846); **32**, 252 (1848); Rendu, *Ann. chim. phys.*, **38**, 196 (1828); Erman; *Gilb. Ann.*, **26**, 139 (1807); Dulk, *Kastner's Arch.*, **6**, 457 (1825); Erdman, *Schweigg J.*, **56**, 24 (1825); Remsen, *Am. Chem. J.*, **3**, 157 (1881); **6**, (1885); Cheneveau and Bohn, *Compt. rend.*, **136**, 1579 (1903); Jahr, *Z. Elektrochem.*, **4**, 177 (1898); **5**, 197 (1899); Schweitzer, *Phys. Z.*, **4**, 852 (1903); Gutton, *Compt. rend.*, **138**, 268, 568 (1904); de Hemptinne, *Compt. rend.*, **138**, 754 (1904); Thompson, *Proc. Roy. Soc.* (*B*), **82**, 557; 396; Dunlap, *Science N. S.*, **33**, 68 (1911); Magnusson and Stevens, *Am. J. Phys.*, **29**, 124 (1911); Janet, *J. Phys.*, [2] **6**, 286; M. Löb, *Am. Chem. J.*, **13**, 145 (1891); Bucherer, *Weid. Ann.*, **58**, 564; de Hemptinne, *Z. physik. Chem.*, **34**, 669 (1900); Byers and Morgan, THIS JOURNAL, **33**, 1757 (1911); Rowland and Bell, *Am. J. Sci.*, [3] **36**, 39 (1888); Wolff, *Am. Chem. J.*, **17**, 122 (1895); Nichols and Franklin, *Am. J. Sci.*, [3] **31**, 227 (1886); [3] **34**, 419 (1887); [3] **35**, 290 (1888); Andrews, *Proc. Roy. Soc.*, **48**, 116 (1891); **52**, 114 (1893); Brendt, *Z. physik. Chem.*, **9**, 512 (1906); Squire, *Am. J. Sci.*, **145**, 443 (1898).

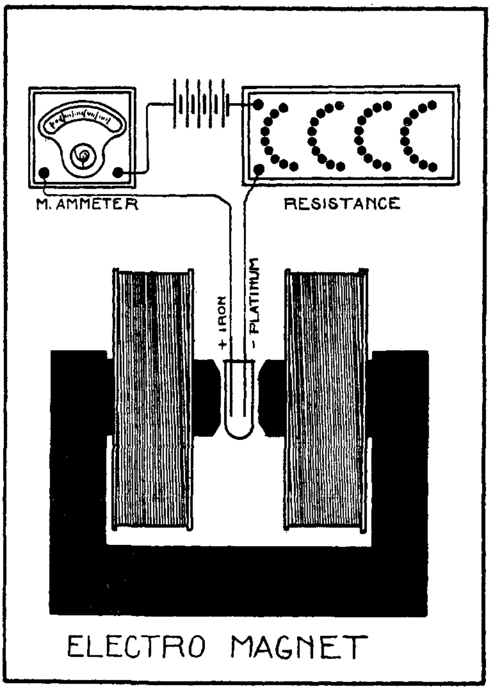

Fig. 1.

At the beginning of each experiment, the current flowing was small, with a large resistance in the box, and the iron anode was active. As rapidly as possible the resistance was diminished and the current required for the change to the passive condition determined. This change is characterized by a sharp rise in potential difference, as shown by the voltmeter, a change in the appearance of the iron, an evolution of oxygen, and a drop in the current shown on the milliammeter. The "critical" current noted in the accompanying Table I is that which produces these changes within ten seconds after the imposition of a given current. These results are given for various samples of wire, numbered separately, and with various strengths of magnetic field. The results as tabulated show clearly the rise of "critical" current with field strength and the general character of the curve is shown in Fig. 2.

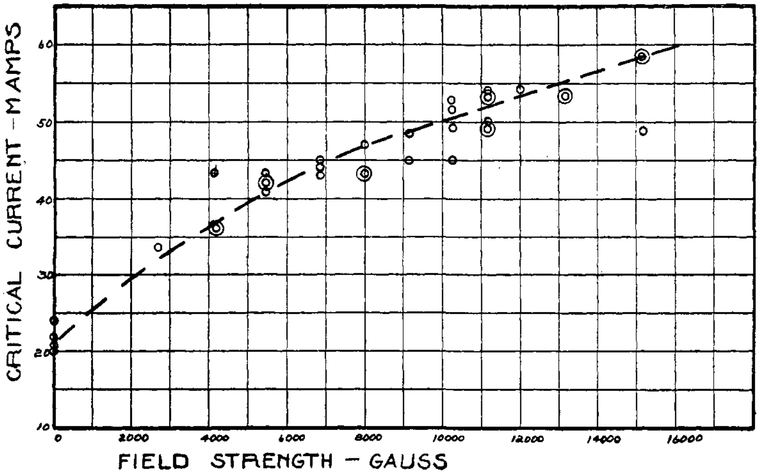

Fig. 2.

TABLE I.

| No. | Critical current. M. amps. | Field strength. Gauss. |
|---|---|---|
| 1a | 20 | 0 |
| 1b | 24 | 0 |
| 3a | 21 | 0 |
| 8a | 22 | 0 |
| 3b | 33 | 2700 |
| 1c | 43 | 4100 |
| 3c | 36 | 4100 |
| 5e | 36 | 4100 |
| 7e | 43 | 5500 |
| 9d | 41 | 5500 |
| 10a | 42 | 5500 |
| 10c | 42 | 5500 |
| 3e | 43 | 6800 |
| 6d | 45 | 6800 |
| 6e | 44 | 6800 |
| 4c | 43 | 8000 |
| 4d | 43 | 8000 |
| 10d | 47 | 8000 |
| 2d | 45 | 9200 |
| 4e | 48 | 9200 |
| 2e | 49 | 10300 |
| 5a | 45 | 10300 |
| 6a | 49 | 10300 |
| 6b | 52 | 10300 |
| 6c | 53 | 10300 |
| 9a | 49 | 11200 |
| 9b | 53 | 11200 |
| 9c | 54 | 11200 |
| 11a | 53 | 11200 |
| 11b | 49 | 11200 |
| 11c | 50 | 11200 |
| 5b | 54 | 12000 |
| 7d | 53 | 13200 |
| 8d | 53 | 13200 |
| 7a | 48 | 15200 |
| 7b | 58 | 15200 |
| 7c | 58 | 15200 |

During the progress of these experiments it was noted that violent stirring of the electrolyte was produced when in the magnetic field and without carrying the field strengths to a greater intensity the effort was made to determin if this agitation of the electrolyte by the field had any bearing on the delay in the establishment of the passive condition. This is important also because of the extreme views of Fredenhagen[1] and of Grave.[2] The former, supported by many other investigators,

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[1] *Z. physik. Chem.*, 43, 1; 63, 1.

[2] *Ibid.*, 77, 513.

viewing the establishment of passivity as coincident with saturation of iron with occluded oxygen, the latter as simultaneous with complete removal of occluded hydrogen. It was thought that perhaps stirring the electrolyte with various gases would throw light upon both of these questions.

The results were of a character which led us to the tentative conclusion that the effects shown by the magnetic field were wholly due to the stirring set up thereby and consequently the stirring experiments were extended to the use of a water motor, giving a slow mechanical stirring, and an electric motor giving a rapid motion. The stirring with gases was produced by delivering the gas into the electrolyte, from below and on both sides of the anode through a double nozzle jet.

Hydrogen was supplied from a Kipp generator at a low pressure with consequent moderate stirring effect. The air and also nitrogen were furnished under small hydrostatic pressure, which was not the same in the two different gases, and the oxygen from a pressure cylinder. The violence of the stirring was, therefore, greatest with oxygen. The motor stirring was produced by using a rotating anode and to determin if the type of motion were important the motor was geared with an eccentric so as to produce a rapid perpendicular motion of the anode. The results of these various stirring effects are given in tabular form in Table II and for comparison the effect of a magnetic field of 12,000 gauss intensity without stirring and coincident with stirring, is given. Also in column 1 the critical density without the field is given. The right hand set of figures in each column shows the critical density in the field.

TABLE II.

| | 1. No stirring. | | 2. $H_2$. | | 3. $N_2$. | | 4. Air. | | 5. $O_2$. | | 6. Water. | | 7. Electric. | | 8. Eccentric. | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | No. field. | F. | | F. | | F. | | F. | | F. | Motor. | F. | Motor. | F. | | F. |
| | 20 | 42 | 43 | 57 | 48 | 60 | 50 | 67 | 63 | 67 | 55 | 70 | 93 | 95 | 112 | 117 |
| | 22 | 48 | 42 | 62 | 48 | 68 | 58 | 72 | 76 | 77 | 61 | 96 | 104 | 83 | 97 | 95 |
| | 21 | 47.5 | 41 | 58 | 56 | 70 | 67 | 70 | 77 | 68 | 53 | 92 | 85 | 97 | 97 | 88 |
| | 20 | 40 | 54 | 67 | 57 | 63 | 68 | 60 | 80 | 58 | 55 | 75 | 97 | 102 | 91 | 93 |
| Mean: | 21 | 44 | 45 | 61 | 53 | 65 | 61 | 70 | 74 | 74 | 56 | 83 | 95 | 94 | 99 | 98 |

It will be noted that the magnetic field retards the establishment of the passivity, as indicated by the larger critical densities shown under F in column 1. Agitation of the electrolyte also produces retardation as shown in the left hand columns in 2 to 8 inclusive, and the more violent the effective stirring the greater the retardation. It will be noted also that the field increased the effect of the agitations of lesser violence but with increased violence of stirring the "field stirring" produces a decreasingly additional effect until with the electric motor and eccentric no influence of the field is apparent.

It seems to be conclusive therefore that the magnetic field offers resistance to the establishment of passivity simply because of the stirring effect which it produces upon the electrolyte when undergoing electrolysis,

TABLE III.

| No. | Critical current. | Revolutions per minute. |
|---|---|---|
| 1a Table I | 20 | 0 |
| 1b Table I | 24 | 0 |
| 3a Table I | 21 | 0 |
| 8a Table I | 22 | 0 |
| 4d | 32 | 330 |
| 2a | 26 | 400 |
| 2b | 27 | 400 |
| 8b | 38 | 420 |
| 8a | 30 | 420 |
| 8c | 38 | 420 |
| 9a | 38 | 420 |
| 1d | 28 | 420 |
| 1c | 32 | 480 |
| 7c | 33 | 510 |
| 9b | 33 | 510 |
| 4c | 33 | 540 |
| 8d | 33 | 540 |
| 1a | 37 | 600 |
| 1b | 37 | 600 |
| 3b | 50 | 600 |
| 9c | 36 | 600 |
| 9d | 38 | 600 |
| 4b | 41 | 660 |
| 3c | 44 | 800 |
| 10d | 44 | 840 |
| 6a | 39 | 840 |
| 2c | 34 | 900 |
| 2d | 36 | 900 |
| 6b | 42 | 980 |
| 6c | 44 | 990 |
| 3a | 56 | 1000 |
| 10a | 50 | 1020 |
| 10b | 50 | 1020 |
| 11a | 55 | 1040 |
| 7a | 47 | 1080 |
| 7b | 47 | 1080 |
| 6d | 46 | 1200 |
| 5a | 46 | 1400 |
| 10c | 60 | 1500 |
| 2e | 50 | 1800 |
| 4a | 60 | 1800 |
| 5b | 61 | 2100 |
| 11b | 75 | 2400 |
| 11c | 89 | 3000 |
| 11d | 100 | 4000 |

which stirring is visible in a strong magnetic field through the violent agitation of the bubbles of liberated gases.

The stirring of an electrolyte during electrolysis was first noted by Hurnuzescu[1] in 1895. Ashcroft in 1905 obtained a patent upon stirring fused electrolytes by a magnetic field and describes his experiments in 1906.[2] In 1907, Frary[3] made application of Ashcroft's method to the rapid deposition of metals by electrolysis, substituting the magnetic field for rotation.

As additional evidence bearing upon this conclusion the rate of rotation of the anode was measured and the corresponding critical current determined. The results are given in Table III.

Here again as in Table I the numbers refer to a given anode and the letters to the different experiments with each. These data are graphically represented in Fig. 3. The variable results obtained are not important as bearing upon the conclusion because of the factors which are not under exact control. It will be evident that the stirring effect of a magnetic field will vary with the position of the anode in the field and with any deviation from the perpendicular position, which interferes with symmetrical stirring. The experiments were all at room temperature, which, of course, is variable to some extent. The wire anodes used, when partially dissolved were flattened on the sides, so that the resulting sharp edges were

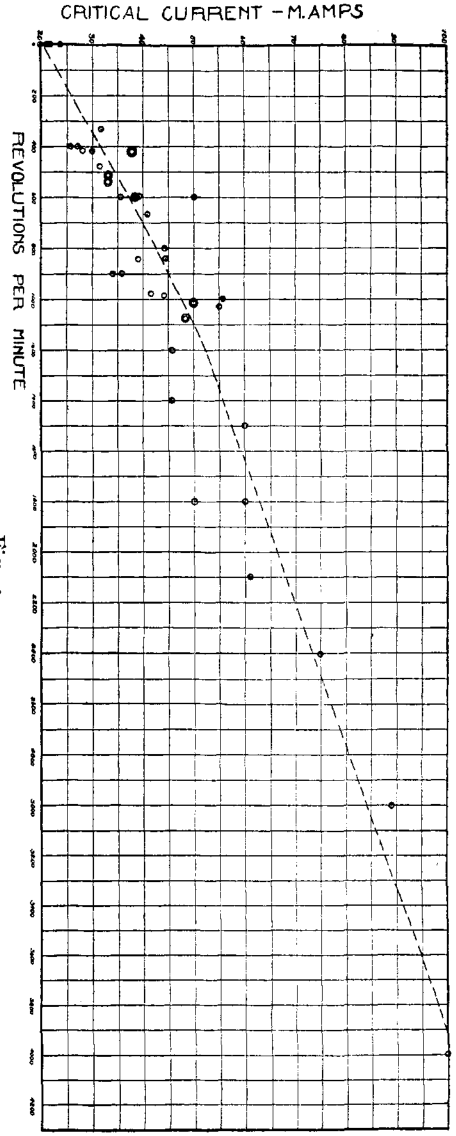

Fig. 3.

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[1] *Elec. Rev.*, 42, 322.

[2] *Electrochem. Met. Rev.*, 4, 145.

[3] THIS JOURNAL, 29, 1592.

in the direction of the lines of force of the field. In the stirring by motor the results vary also within limits and these variations are to be ascribed not only to changes in rate during a given experiment but the stirring by a given rate of rotation also depends upon variation from exact axial rotation.

A comparison of Figures 2 and 3 shows the approximate ratio between the effect produced by the field in gauss and the rotation of the anode. This relation, if exact, is then a means of calculating approximately the strength of the field to be used to secure stirring effects of a given value in an apparatus such as that of Frary.[1]

Explanations of the cause of the stirring of an electrolyte by the field are offered by Drude[2] and by Urbasch,[3] but which, if either, is satisfactory seems impossible to determin from data as yet available.

The retardation of the passive state by the field appears to be independent of the position of the anode with respect to the lines of force. This is shown by the results obtained in a field of 12,000 gauss, given in Table IV.

TABLE IV.

| | Anode perpendicular to lines of force. Critical current. | Anode parallel to lines of force. Critical current. |
|---|---|---|
| 1 | 42 m. amp. | 44 m. amp. |
| 2 | 48 m. amp. | 40 m. amp. |
| 3 | 47 m. amp. | 46 m. amp. |
| 4 | 40 m. amp. | 46 m. amp. |
| Mean | 44.3 | 43.5 |

This result seems striking in view of Remsen's observation that a difference of electromotive force is established between two iron rods in a magentic field when parallel but not when perpendicular to the lines of force.

The previous observations[4] that the passivity once established is maintained by a minimal current and that the passivity is not destroyed by a magnetic field[5] are confirmed. For example iron passive in an 0.5 *N* sulfuric acid solution and kept in that condition by a current of 4.5 milliamperes remains passive when placed in a field of upwards of 20,000 gauss. This is unexpected in view of the results recorded by Nichols and Franklin.[5]

## Summary.

The magnetic field retards the establishment of the passive state upon iron and nickel anodes because of the stirring produced by the field in electrolytes undergoing electrolysis. This variety of stirring can be dupli-

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[1] *Loc. cit.*

[2] *Z. Elektrochem.*, 8, 65, 229; 9, 666.

[3] *Ibid.*, 7, 114, 527.

[4] Byers, *Loc. cit.*

[5] Byers and Darrin, *Ibid.*

cated by mechanical stirring through gases or by rotation or other movement of the anode. The change of chemical behavior of the metals is, therefore, due only indirectly to the magnetic field and the conclusion cited previously in this article is still valid.

Further, the examination of the phenomena of passivity shows it to be influenced by the following factors: *a*, character and condition of the metal; *b*, temperature; *c*, electrolyte employed; *d*, density of current; *e*, time of passage of current; *f*, character and extent of movements of the electrolyte.

In view of these variables and the examination of the literature t no longer is surprising that no satisfactory explanation is at hand; since, so far as we know, during any investigation, no adequate attempt has been made to control more than two factors. If, therefore, a correct conclusion has been reached it is perhaps more accidental than otherwise.

Why stirring an electrolyte should delay the establishment of passivity does not seem clear to us. If passivity is due to an adhering layer of oxygen or to the formation of an oxide it may be argued either that rotation of an anode should spread evenly, and, therefore, complete the film more readily; or that friction would delay the same result. Again stirring with oxygen would apparently facilitate the formation of such a film and with hydrogen would hinder the same. Both gases produce like effects. Again, such ought not to be the case if passivity is the natural state of iron and activity is due to the catalytic action of occluded hydrogen, as suggested by Graves.[1]

In short we are only prepared to repeat a previous statement, "no explanation of the phenomena of passivity even approximately satisfactory has yet been produced—we have none to offer. When the experimental development warrants it, we confidently expect the cause of passivity to be found in an altered state of the metal itself, this alteration, whatever its character, being produced," or prevented, "by any one of a number of different agencies."

UNIVERSITY OF WASHINGTON.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

# AN ATTEMPT TO PREPARE NITRO-NITROGEN TRICHLORIDE, AN ELECTROMER OF AMMONO-NITROGEN TRICHLORIDE.[2]

BY WILLIAM A. NOYES.

Received April 24, 1913.

The idea, first proposed in its modern form by Arrhenius,[3] that electrolytes are more or less completely separated in aqueous solutions into

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[1] *Loc. cit.*

[2] Presented in abstract at the Milwaukee Meeting of the American Chemical Society, March, 1913.

[3] *Z. physik. Chem.*, 16, 4116 (1895).