it may well be noted that up to the present all attempts to apply this or any similar procedure to the estimation of larger amounts of potassium have proved futil.

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THE INFLUENCE OF THE MAGNETIC FIELD ON PASSIVE NICKEL AND IRON.

BY HORACE G. BYERS AND AGNES FAY MORGAN. Received August 10, 1911.

In a previous article¹ it was shown that when using iron as an anode in various electrolytes the density of the current required to produce the passive condition is very materially increased when the anode is placed in a magnetic field. The amount of current required varied not only with the intensity of the field but also with different electrolytes and with the length of time of exposure of the iron to the electrolyte and perhaps with other factors; but in every case the required current density per square centimeter was greater in the magnetic field than out of it. A natural development of this work was an investigation of similar nature with nickel and steel as anodes.

In view of the rather rare instances of magnetic effects upon chemical action a brief summary of the literature of the subject may be in place. So far as we are aware the first contribution was by Professor Remsen² who showed that iron in a solution of copper sulfate is protected at the ends when in a magnetic field. Rowland and Bell³ explain the action on the supposition that more energy is required to remove the iron from points nearest the magnetic poles induced by the magnetic field. They also present experimental evidence in support of their conclusion. Wolff⁴ explains the protection on the basis of an accumulation of iron salts at the magnetic poles.

The articles cited all deal with a *protection* of iron from chemical action by magnetization. On the other hand Nichols and Franklin in a series of articles⁵ call attention to the destruction of the passive condition of iron, when in concentrated nitric acid, by means of a magnetic field and take issue with the explanations offered by Rowland and Bell.⁶ Andrews⁷ showed that magnetized steel and unmagnetized steel show differences of potential in nitric acid (sp. gr. 1.42) of approximately 0.03 volt, at low temperatures the magnet being positive, while at 90° the voltage

- ² Am. Chem. J., 3, 157 and 6 (1881 and 1885).
- ³ Am. J. Sci., [3] **36,** 39 (1888).
- ⁴ Am. Chem. J., 17, 122 (1895).
- ⁵ Am. J. Sci., [3] 31, 272 (1886); [3] 34, 419 (1887); [3] 35, 290 (1888).

¹ Byers and Darrin, This Journal, 32, 750 (1910).

⁶ Loc. cit.

⁷ Proc. Roy. Soc. London, 48, 116 (1891).

GENERAL, PHYSICAL AND INORGANIC.

rizes to 0.3 volt and the direction of the current is reversed. He also showed¹ that magnetized steel dissolves more rapidly in copper chloride solutions than unmagnetized bars of the same steel. Brendt² investigated the heat of solution of iron within and without the magnetic field and discovered no measurable differences. Duhem³ deduces the theoretical conclusion that the heat of solution should be very slightly smaller in the field.

Experimental.

Nickel.—The nickel used in the following experiments was Merck's "100 per cent. thin wire" and a plate of "Rein nickel" rolled into a thin sheet. The apparatus used is as shown in the cut. The magnet was

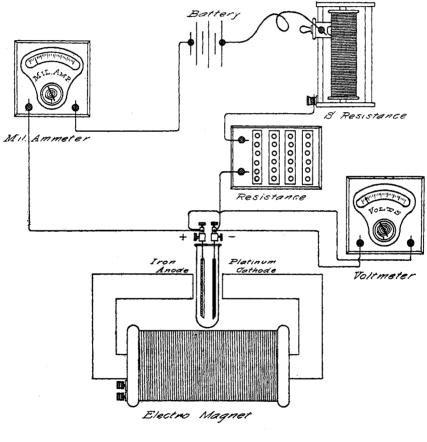


FIG. 1.

¹ Proc. Roy. Soc. London, 52, 114 (1893).

² Z. physik. Chem., 9, 512 (1906).

⁸ Ziel und Struktur der physikalischen Theorien.

1758

the same as that used by Byers and Darrin.¹ The electrodes were made by sealing the wires into glass tubes by means of paraffin. The current source was three U. S. storage cells. The current passing was read by means of Weston milliammeter with a scale of 150 and graduated to $1/_2$ milliamperes. A key, not shown in cut, was used in circuit with the voltmeter and was only used to define the transition point from active to passive condition.

Several undetermined factors combine to render the results less accurate than could be desired, viz., the rise of temperature due to the heating of the magnet when in action, the variation in the method of changing resistance, which seems to cause variation in transition points, the variation in the size of the electrodes by gradual solution while active and in the use of plates of different quality from the wire. The effect of stirring the electrolytes was also undetermined. The work shows that these, and perhaps other variables prevent exact duplication of results but the uniform character of the effect observed is unmistakable and represents. at least qualitatively, the effect of the magnetic field on the current density required to render nickel passive. The operation was as follows: the platinum nickel couple was inserted in a test tube containing the electrolyte and connected with the storage cells and ammeter, using a resistance sufficiently great so that the amount of current passing is less than sufficient to render the nickel passive. Without undue delay the resistance in the circuit was then diminished by means of the resistance box until the passivifying density was nearly reached, the final adjustment being made by the slide-wire resistance. When, after several trials. the exact current density required to produce passivity of the nickel anode was determined (a result indicated by a sudden drop of the reading on the ammeter, a rise in the voltmeter reading and the appearance of bubbles on the nickel) the anode was measured and the result recorded. The nickel was then rendered active by breaking the circuit and removal of the anode. (Note.-If a sufficient time is not allowed for the nickel to become thoroughly active, the density of the current required to again produce the passive state is greatly lessened. It will be observed that this fact increases the certainty of the results detailed.)

The couple is then replaced in the electrolyte and the experiment repeated exactly as before with the exception that the test tube is placed between the poles of the magnet and the new density of current determined and the area of anode remeasured. It should be mentioned that any diminution of area would tend to diminish the apparent density required, which fact renders the increased current more striking.

The results obtained will be given in detail for nitric acid and the results summarized thereafter, only the summaries being given.

¹ Loc. cit.

A. Results with nitric acid.

TABLE I.

Diameter of anode.	Current required	Surface.		In magnetic field.						
	to cause passivity in milliamp.		Current per sq. cm.	Diameter.	Current for passivity in milliamp.	Sur- face.	Current per sq. cm.			
0.049	122	0.154	792	0.048	141	0 151	933			
0.046	125	0.1445	868	0.045	148	0.140	1057			
0.042	126	0.134	940	0.0445	125	0.139	900			
0.040	104	0.1256	832	0.043	143	0.135	1051			
0.038	115	0.119	966	0.0425	128	0.1346	955			
0.0355	103	0.115	927	0.040	121	0.1256	968			
0.033	95	0.1036	922	0.035	136	0.110	1236			
••				0.033	III	0.1036	1077			
• •	• • • •	• •		0.031	115	0.097	1185			

Electrolyte 10 per cent. HNO_3 . Anode nickel wire 1 cm. exposed. Without magnetic field.

SUMMARY.

Without m	agnetic field.	In mag	netic field.		
Number of experiments.	Average cur- rent per sq. cm. in milliamp.	Number of experiments	Average of rent per sq. cm. in milliamp.	Increase due to field.	
7	892	9	1051	159	

TABLE II.

	v	Vithout n	agnetic field.	In magn		
Electrolyte.	Anode.	No. of experi- ments.	Current per sq. cm. in milliamp.	No. of experi- ments.	Current per sq. cm.	due to field
5 per cent. HNO ₈	Nickel wire	4	465	3	726	261
1 per cent. HNO ₃	Nickel wire	5	247	2	324	77
5 per cent. HNO ₃	Nickel plate	2	297	2	385	88

TABLE III.

		Wi magne				
民lectrolyte.	Anode.	No. of experi- ments.	per	No. of experi- ments.	Current per sq. cm.	Increase due to field.
5 per cent. H ₂ SO ₄	Nickel wire	7	450	5	550	100
10 per cent. H_2SO_4	Nickel wire	8	471	6	627	156
10 per cent. H_3PO_4	Nickel plate	I	46	I	51	5
5 per cent. H_3PO_4	Nickel plate	2	39.7	2	42.I	2.4
N NaNO ₃	Nickel plate	2	3.7I	2	4.46	0.75
$o.t N NaNO_3$	Nickel plate	2	2.81	2	3.13	0.32
$0.5 N \text{ K}_2 \text{SO}_4 \dots \dots$	Nickel plate	8	2.38	IO	3.00	0.62

Steel.—In the following experiments the anodes used were of steel and were made from large knitting needles, broken into convenient lengths, or of watch-springs straightened and cut into suitable pieces. The amount of carbon was not determined with exactness, but the needles were of much the softer steel. The anodes were covered as before with paraffin NOTES.

with the exception of a measured portion at one end. The current density required to render a piece of steel passive was first determined and then the anode was placed across the poles of the electromagnet and after about five minutes was removed and the passive point again determined. The polarity of the end used was determined by means of a compass needle. The individual results varied somewhat, as was to be expected, but on the whole were remarkably uniform and always of the same character.

Table IV shows the mean results obtained.

TABLE IV.									
Anode. Soft steel	Electrolyte. 5 per cent. HNO ₃	4 No. of expts.	 Current for un magnetized steel per sq. cm. 	A No. of expts.	b Curreutfor N.pole.	u No. of expts.	Current for S. pole.	du mag	rease e to gnet- tion. S. 92
Hard steel	5 per cent. HNO ₃	12	382	6	426	6	454	44	72

Discussion.

The results presented are preliminary and are published because of the very interesting character of the phenomenon. It is our hope, by using a very much more powerful magnet and by taking pains to govern temperature and other conditions, to obtain quantitative results of greater value. In the meantime we feel that the following points are established:

1. The current density required to render nickel passive is materially increased when in the magnetic field, as was shown to be the case with iron.

2. Steel when magnetized is more difficult to render passive than is the same steel unmagnetized and soft steel is affected to a greater extent than hard steel. This accords with the observations of Andrews.¹

3. The positive pole of the magnets is more easily rendered passive than is the negative pole.

The cause of these magnetic effects in no way appears to be indicated by the experiments and we shall have no hypothesis to offer until many more facts have been determined.

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NOTES.

Photosensitiv Antimonite Cells.—The fact that natural sulfide of antimony shows a very strong alteration of its electrical conductivity under the influence of light-radiation was discovered in 1907 by F. M. Jaeger.²

¹ Proc. Roy. Soc., London, 49, 489 (1893).

² Proc. Royal. Acad. Sci. Amsterdam, 9, 808 (1907). Z. kryst. Min., 44, 45 (1908).