[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY, HARVARD UNIVERSITY]

THE EFFECT OF A MAGNETIC FIELD ON THE POTENTIAL OF HYDROGEN OCCLUDED IN IRON

BY THEODORE W. RICHARDS AND WILLIAM T. RICHARDS

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Introduction

Although much has been written concerning the electromotive behavior of iron in solutions of its salts, as well as concerning the properties of occluded hydrogen and the chemical relations of magnetism, very little of the bulky literature appears to concern directly the joint effect under consideration in the present paper, namely, the effect of a magnetic field on the potential of hydrogen occluded by iron. Between 1867, when Graham[1] discovered the existence of occluded hydrogen in metals, and 1906, when one of us, with the assistance of Gustavus E. Behr, Jr.,[2] investigated its effect on the potential of iron, no important work bearing upon the problem seems to have appeared. This latter investigation merits a brief summary, since it was the progenitor of the present work. The authors obtained for the first time consistent values for the potential of iron, showing it to be partly dependent upon the method of preparation. They also recorded a number of observations proving that hydrogen occluded in iron temporarily raises the metal's potential (in a normal solution of ferrous sulfate) as much as a decivolt. They showed conclusively that this rise in potential was due neither to an allotropic form of iron, nor to the combination of iron with elements other than hydrogen. They pointed out that since hydrogen absorbed at low temperatures by finely divided iron does not affect the potential of the metal, and since the abnormal potential was above that of iron, which in turn was far above that of the hydrogen electrode in the same solution, the postulation of an especially active form of hydrogen became necessary. This active hydrogen was believed to be occluded in an atomic but un-ionized condition; its properties were not however, definitely stated. Three years after the last named investigation Förster[3] confirmed its outcome and E. P. Schoch[4] obtained similar results for nickel.

None of these investigators has considered the effect of a magnetic field on the occluded hydrogen. Turning now to this aspect of the problem, we find that, although electrolytic iron has been considerably studied as

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[1] Graham, *J. Chem. Soc.*, **20**, 235 (1867).

[2] Richards and Behr, Carnegie Inst. Pub., No. 61, **1906**; *Z. physik. Chem.*, **58**, 301 (1907).

[3] Förster, summarized in *Abh. d. deut. Bunsen-Gesellsch.*, No. 2, **1909**, p. 2. Förster and Herold, *Z. Elektrochem.*, **16**, 461 (1910)

[4] Schoch, *Am. Chem. J.*, **41**, 208 (1909).

regards its magnetic properties,[5] the results of these investigations likewise furnish no clue to its solution, except in so far as they indicate that iron containing hydrogen is of a different nature physically, and has different magnetic properties from ordinary iron. Smith,[6] on the other hand, has pointed out that hydrogen alloys are to be clearly distinguished from ordinary binary hydrogen *compounds*. His conclusion that metals occluding hydrogen have almost universally a specific magnetic susceptibility greater than $+ 0.9 \times 10^{-6}$ suggests a possible connection between occlusion and magnetic effect. The observed decrease in paramagnetism of palladium due to occluded hydrogen[7] and the interesting results of Pascal[8] seem also to indicate that a connection exists between the two effects. The expansion in the space lattice of palladium when large volumes of hydrogen are occluded[9] likewise led to the expectation of a positive result from the experiments to be described below.

Other work with significant bearing on the present problem is mentioned in the discussion at the end of this paper. Recent papers concerning the nature of "active" hydrogen (which has, of late, been the subject of much controversy) throw little light upon the matter, since triatomic hydrogen in the gaseous state is evidently very different from occluded hydrogen as regards its essential conditions of existence.

Preliminary Experiments

Since the magnitude of the expected potential effect could not be prophesied, and since the technique of experimentation best adapted for its determination had not been previously devised, several preliminary experiments were carried out before definitive measurement was attempted. These experiments indicated that probably a slight fall of the potential of the active hydrogen occluded in iron occurs at the moment of magnetization. They served chiefly to direct attention to the technical difficulties in the manipulation of the solution and of the iron, both charged and uncharged with hydrogen, when subjected to a strong magnetic field. Especially, irregularities in electromotive force were experienced with acidified solutions, because of the mechanical dislodging of bubbles of hydrogen, disturbed by the sudden change in the position of the electrode at the moment of magnetization. Moreover, the heating effect of the large actuating voltaic current had to be eliminated.

Preliminary tests were made also of the potential of the ordinary hydrogen electrode on platinum in a ferrous sulfate solution, when subjected to

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[5] Compare Terry, *Phys. Rev.*, **30,** 133 (1910), and Také Soné, *Sci. Repts. Tôhoku Imp. Univ.*, [1] **4,** 313 (1916).

[6] Smith, *J. Phys. Chem.*, **23,** 186 (1919).

[7] Biggs, *Phil. Mag.*, [6] **32,** 131 (1916).

[8] Pascal, *Compt. rend.*, **173,** 712 (1921); **174,** 457, 1698 (1922).

[9] Yamada, *Phil. Mag.*, [6] **45,** 241 (1923).

a magnetic field. No change as great as 0.0001 v. (the sensitivity of the earlier form of apparatus) was observed when the magnet was energized. This negative outcome indicates that magnetism does not affect (at least to any considerable extent) the degree of dissociation of ferrous sulfate in solution, for any such change would have affected the hydrogen-ion concentration. This is in accord with the investigation of Berndt[10] who found the conductivity of solutions unaltered by magnetism.

With these facts in mind a more accurate determination was undertaken. The experimental work falls naturally under two main divisions.

I. The measurement of the e.m.f. of iron in ferrous sulfate solutions of various concentrations, containing various proportions of (a) ferrous, (b) ferric and (c) hydrogen ions, in order to ascertain the effect of impurities and the best solution for measurement of the magnetic effect.

II. The determination of the effect of magnetism on the potential of pure iron, and of hydrogen occluded in pure iron.

I. Measurement of the Potential of Pure Iron in Various Concentrations of Ferrous Sulfate, Ferric Sulfate and Sulfuric Acid

Solutions.—The stock solution of ferrous sulfate was made from an especially prepared pure specimen of C. P. crystallized salt (no further purification being necessary), and was kept over iron wire in an atmosphere of hydrogen. That of ferric sulfate was prepared by adding to pure ferrous sulfate an excess of pure sulfuric and nitric acids, evaporating to drive off the excess of acid, dissolving in boiling distilled water, filtering off the amount of ferric hydroxide formed, and diluting as needed.

Since it was soon evident that a trace of ferric salt affects greatly the potential of iron in a ferrous sulfate solution, all such solutions (except those to which known quantities of ferric sulfate had been added) were prepared and kept in an atmosphere of hydrogen.

The solutions were prepared (in bottles previously filled with hydrogen) from boiled, distilled water through which hydrogen had been freely bubbled during and after boiling. They were driven out of the bottles when needed by the pressure of hydrogen from a suitable generator. The primary ferrous sulfate solution was approximately normal, and the stock sulfuric acid solution was 3 *N*. Their concentrations were accurately determined by titration with standardized potassium permanganate and sodium hydroxide solutions, respectively, which, in turn, were compared with an oxalic acid solution of known concentration. All rubber connections not absolutely necessary were replaced throughout the apparatus by sealed glass joints. Such few rubber connections as could not be avoided were made from heavy-walled pressure tubing coated inside with a semi-solid mixture of paraffin and vaseline, and (in the final experiments) outside with collodion, and were firmly wired to the glass tubing. These precautions produced a system which retained the necessary pressure of hydrogen gas indefinitely.

From the stock solutions described above, solutions varying in concentration with respect to sulfuric acid and ferrous sulfate were prepared in hydrogen as desired. All the solutions save the most dilute, unacidified ferrous sulfate solution (which hydrolyzed

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[10] Berndt, *Ann. phys.*, **23**, 932 (1907).

slightly, precipitating a small amount of brown basic salt) remained practically unchanged during the month over which measurements extended. Solutions intended to contain ferric sulfate were made up with less precaution against oxidation, since it was obvious that exactness was not significant in these cases.

The normal potassium chloride solution used in the calomel electrode was prepared from a guaranteed specimen of potassium chloride subsequently twice recrystallized. The mercurous chloride used was also very pure; it was shaken with N potassium chloride solution and mercury. The mercury used was thrice redistilled from the best mercury obtainable.

Preparation of Iron.—The metallic iron used throughout (unless otherwise specified) was prepared by the reduction of ferric oxide, which had been obtained by igniting ferric nitrate (thrice recrystallized) made from pure iron wire and pure nitric acid. The hydrogen used in the reduction process was electrolytically prepared, and was passed through a purification train free from rubber, containing glass wool, potassium hydroxide, and phosphoric anhydride. Finally, the gas was passed over a mass of previously reduced iron, raised to perhaps 800°, in order to remove any traces of impurity capable of combining with hot iron. The reduction was carried out in a quartz boat within a quartz combustion tube, at a bright orange heat. Before reduction, a platinum wire was imbedded in the powdered oxide with a long protruding end, which subsequently served to connect it to the electrometric system. The sintered lump of iron was transferred in the air to the electrode vessel, a procedure justified both by our experience and by the results of Richards and Behr.[2] Iron thus prepared gives promptly a satisfactory potential, being free from the film of oxide ordinarily encountered, as well as from any occluded hydrogen[11] capable of affecting its electromotive force.

Cell-Chain Apparatus.—Fig. 1 illustrates the cell-chain arrangement which was found most convenient for the type of measurements necessary for the work.

A is the vessel for containing the iron electrode, with a hydrogen-bubbling inlet I (to which, at D, the flask containing the solution in which potentials are to be measured is shown temporarily attached), a hydrogen outlet E and a ground stopper N containing a tube in which is sealed a platinum hook from which the iron H hangs during measurement. The calomel electrode vessel B is of a familiar type except for the funnel G with its stopcock which allows the electrode to be flushed at will. The two 3-way stopcocks K and K′ permit flushing of the liquid junction by suction through it before each measurement to insure reproducibility of potentials. The apparatus, during measurement, was immersed to the level L L′ in an electrically heated thermostat kept at 25° ± 0.05° by a large toluene-mercury regulator. The ferrous sulfate solutions were introduced into the electrode vessel only after it had been filled with hydrogen. Study of the diagram will suggest the necessary technique. The ferrous solutions were stirred by hydrogen, often bubbled through them.

The potential of the calomel electrode was checked against the normal zinc electrode and a standard cell, with satisfactory results.

A. The Electromotive Force of Iron in Ferrous Sulfate Solutions

With this arrangement, measurements were made as follows. In the first place, the potential of the pure iron electrode in N ferrous sulfate solutions was found to agree satisfactorily with the values of previous investigators,[2,3] as the following results make clear.

[11] Baxter, *Am. Chem. J.*, **22**, 363 (1899).

Table I

Potential of Iron Electrode in Ferrous Sulfate Solutions

Normality of ferrous sulfate	1.02	0.366	0.039
Potential of iron-calomel chain	0.741	.753	.778
Cor. av. of Richards and Behr's results[12]	.742	...	...

Corresponding to the concentration effect, as expressed by the Nernst equation, the values of the potential are seen to increase as the solution becomes more dilute. If the conductivities of the three solutions are taken as, respectively, 260, 129 and 16.5 (found by graphic interpolation from the data of Klein)[13] and the ionic concentrations are taken as proportional to these quantities, the second solution should have shown a potential about 0.009 greater than the first, and the third about 0.026 greater than the second. The actual differences are respectively 0.012 and 0.025, respectively, showing agreement as close as could be expected, considering the existence of slightly differing junction potentials and hydrolytic effects.

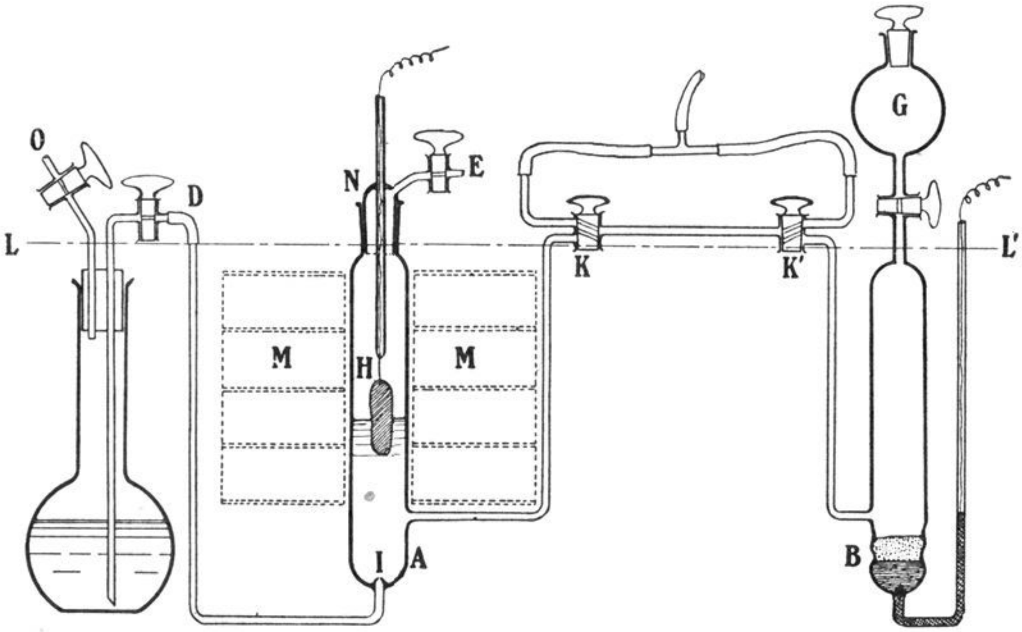

Fig. 1.—Electrometric apparatus. H represents the iron electrode surrounded, when desired, with the magnet MM. B is the calomel electrode. The glass tube between $K' K''$ was in fact bent through 180° in order to economize space in the thermostat. The details are sufficiently explained in the letter-press

The temperature coefficient of the potential of the complete cell (Fe, N $FeSO_4$, N KCl, HgCl, Hg) was found by repeated experiments to be not more than 0.00001 volt. Thus, no great constancy of temperature is needed if both electrodes are at the same temperature. Variation in temperature of one only of the electrodes is more serious, since each has

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[12] The average of these results was 0.795 with the *decinormal* calomel electrode.

[13] Klein, *Wied. Ann.*, **27**, 151 (1886).

separately a temperature coefficient of about 0.6 millivolt per degree.[14] In order to avoid error from this source the whole cell, including the electromagnet used later, was immersed in a thermostat constant to within 0.05°.

B. The Electromotive Force of Iron in Ferrous Sulfate Containing Various Concentrations of Ferric Sulfate

No data are at hand showing the effect on the potential of iron in ferrous sulfate caused by the presence of small amounts of the more highly oxidized ferric ion in the solution. Therefore, after preliminary experiments, the following measurements were made to discover the effect of this impurity.

TABLE II

EFFECT OF FERRIC ION

Solution	Potential of iron	Total normality of iron by $KMnO_4$	Normality of ferrous sulfate	Conc. of ferric iron in same terms
1	0.759	0.327	0.327	0.000
2	.719	.332	.329	.003
3	.687	.346	.329	.017
4	.630	.415	.327	.088

The potentials, in solutions more concentrated in ferric sulfate than No. 2 are not very definite, because (except in No. 1) the electrode and solution are not in equilibrium. The ferric ion is constantly being reduced by the metallic iron in contact with the solution. Bubbling hydrogen gas from the base of the electrode vessel served as the stirring agent, and in Solutions 3 and 4 caused great alterations in the value of the potential. On the other hand, in Solutions 2 and 1 (containing little or no ferric sulfate) stirring was without effect on the results. In another trial a portion of Solution 4, stirred for three hours in the presence of the iron electrode, became completely reduced, the potential rising with decreasing rapidity until it attained the true equilibrium potential of iron in a solution of 0.415 *N* in ferrous salt. The values given in Table II were obtained as follows: for five minutes after the introduction of the iron, the solutions were left tranquil; then they were stirred by hydrogen gas, and the potential was recorded as soon as it had become constant (about one minute afterwards).

Table II shows clearly the great effect of ferric salt, and proves that in order to obtain accurate results in our magnetic determinations, ferric sulfate must be excluded. Incidentally, the "titration curves" of the hydrogen-ion potentials of mixed iron solutions were determined by means of the usual platinized-platinum hydrogen electrode. The hydrogen-electrode

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[14] Richards, *Proc. Am. Acad.*, **33**, 3 (1897). This paper refers to the calomel electrode. Since the total iron-calomel cell has almost no temperature coefficient, that of the iron alone must be nearly equal to the value for the calomel electrode, with the opposite sign.

potential changed on gradually adding ferric to ferrous sulfate, in a typical S-shaped curve, from the usual value to the oxidation-reduction potential when the added ferric iron reached about 0.3% of the total iron present (the ferrous salt was 0.364 *N*).

C. The Electromotive Force of Iron in Ferrous Sulfate Containing Various Concentrations of Sulfuric Acid

Recently one of us, in collaboration with Theodore Dunham,[15] showed that the addition of acid to zinc sulfate solution raises the potential difference of amalgamated zinc immersed in it to a greater extent than is to be expected from the decrease of dissociation of the sulfate—an effect which was traced to junction potential. Similar phenomena might be expected here. The behavior of iron in acid solutions was important for the present purpose, for reasons to be stated later.

Accordingly, in order to determine the optimal solution for the obtainment of a constant iron potential the following series of typical measurements was made.

TABLE III

EFFECT OF ADDED SULFURIC ACID

Solution	Potential of cell chain system	Normality of ferrous sulfate	Normality of sulfuric acid added	Hydrogen electrode-calomel potential	Hydrogen-ion concn.
1	0.753	0.366	0	0.579	9.1×10^{-6}
2	.753	.365	.001	.483	4.0×10^{-4}
3	.724	.393	.100	.432	3.0×10^{-3}
4	.669	.366	.25	.370	3.4×10^{-2}
5	.634	.390	.50	.353	6.4×10^{-2}

With concentrations of sulfuric acid above 0.1 *N* the values are not exactly reproducible. The irregularity is chiefly due to two causes: in the first place, the concentrations of both acid and ferrous iron vary as the acid attacks the iron, and in the second place, the bubbles of resulting hydrogen, clinging to the iron, have a tendency to reduce it to the hydrogen potential, which is much lower than that of iron. Stirring tends to correct both causes of irregularity by mixing the solution and by displacing the adhering gas; but the correction is obviously incomplete. The two disturbing effects together mask entirely, indeed overtop, the opposite effect of the hydrogen ion at the liquid junction. Of course, since the situation could not involve equilibrium, no great consistency was to be expected. The experiments served their purpose in showing that ferrous sulfate solutions must not be over 0.01 *N* as to free acid if they are to be used for the exact measurement of the electromotive force of iron immersed in them.

Iron Amalgam.—The above outcome, while opposite to that observed with amalgamated zinc, parallels the behavior of unamalgamated zinc.[16]

[15] Richards and Dunham, THIS JOURNAL, **44**, 681 (1922).

[16] Ref. 15, p. 680.

The former, of course, gives no trouble either by dissolving or by becoming coated with a film of hydrogen. Accordingly, attempts were made to use iron amalgam, of which the potential has never been satisfactorily measured. The saturated liquid amalgam (containing only about 0.0013% of iron[17]) was found to be too dilute to give constant results, either in stationary or slowly dropping electrodes. A strip of pure iron, coated with mercury electrolytically, yielded no better results. Freshly reduced porous iron easily and satisfactorily amalgamated by contact with a mercury cathode under dil. sulfuric acid, then gave a more constant but still slightly variable potential of about 0.73 with the calomel electrode (instead of 0.74 given by spongy reduced iron). The reason for the irregularity is doubtless the extremely limited solubility of iron in mercury, because of which a surface equilibrium of iron with the ferrous sulfate solution cannot be maintained. In any case, iron amalgam would have been unsuitable for our experiments upon occluded hydrogen, now to be described.

It follows from the foregoing experimental work that the most trustworthy iron potential is to be obtained in a solution of ferrous sulfate of concentration at least 0.4 *N*, containing no ferric salt and not more than 0.01 *N* in sulfuric acid. A small amount of sulfuric acid is, however, advisable to prevent the gradual alteration of the concentration of the solution, due to hydrolysis, oxidation and consequent precipitation of the basic salt. The solutions described in Part II were made in accordance with this evidence.

II. Measurement of the Effect of Magnetism on the Potential of Iron and Occluded Hydrogen

Materials.—The ferrous sulfate stock solution, prepared and kept essentially as described in Part I, was approximately normal; it was slightly acidified (0.01 *N*) with sulfuric acid. The other substances were prepared as before.

Apparatus.—The cell chain also was unchanged.

The electromagnets (which were slipped from below over the iron electrode cell in such a way that the iron occupied about the center of the helix) were wound for the purpose, and fully coated with hard paraffin when hot. The stronger of the two electromagnets (No. 1, used in the definitive experiments) was wound with about 3000 turns of insulated 0.4mm. copper wire on a copper frame, which consisted of a copper tube (20 mm. in diameter and 50mm. long) as a core, with wide copper flanges or vanes at intervals to conduct away the heat developed by resistance. This was actuated by about a 2 ampere current from a 110-volt battery. The less powerful magnet (No. 2) was wound with larger wire and took a greater current, but it had only about 0.4 times the lifting power of the first. They were connected with a suitable ammeter, switches and rheostats. Induced currents on making or breaking the circuit were avoided by allowing neither of the electrode wires to run parallel to the d. c. leads; and stray currents were excluded by careful insulation of the wires. The thermostat in which the measure-

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[17] Richards and Garrod-Thomas, *Carnegie Inst. Pub.*, **118**, 54 (1909).

ments were made was placed two meters from the potentiometer system, of which the sensitivity was 0.00001 volt.

The Effect of the Magnetic Field on the Potential of Pure Iron.—Since many investigations[18] have shown that in general a magnetic field is without effect on chemical change, a negative result was anticipated from this measurement. This conclusion was verified by many preliminary experiments. More careful trial showed that there is in fact a very slight progressive decrease in the potential after exposure to a strong magnetic field. The procedure in each case was the same. When the electrometric apparatus and the cell system had been completely prepared for measurement and the potential of the iron had been observed and noted, the magnetic circuit (Magnet No. 1) was made. As successive divisions on the galvanometer scale were passed by the beam of light, the seconds elapsed after making the circuit were recorded. The small decrease of potential was fairly regular. On breaking the circuit after 20 seconds there was no change for 1.5 seconds, followed by irregular changes for a few seconds, and after five minutes more the potential had returned to within 0.3 millivolt of the original value.

The following four trials, which were the last and the most carefully made, are typical and exhibit sufficiently the behavior of the iron under these conditions. The cell measured was, Fe, $FeSO_4$ (1.02 *N*), KCl (*N*), HgCl, Hg; its initial potential was always very nearly 0.741 v. at 25°.

Table IV

Fall of Potential (in Millivolts) on the Magnetization of Pure Iron Electrodes in Ferrous Sulfate

Magnet No. 1

Time of Magnetization Seconds	Expt. 1	2	3	4
1	0	0	0	0
2	0.1	0.1	0	0
3	.1	.1	0	0.1
4	.2	.2	0.1	.1
5	.3	.2	.1	.2
10	.4	.4	.3	.4
20	1.0	.8	.7	.8
		[Circuit broken]		
300	0.3	.3	...	...

Although the fairly regular slight fall of potential during the incidence of the magnetic field was much smaller than those (to be noted) which occurred when occluded hydrogen is present, and does not seriously complicate the conclusions to be drawn, nevertheless explanation is desirable. It could not have been due to a change in the "solution pressure" of the iron, for that would have been instantaneous, not gradual. The strong magnetic field might, however, tend to concentrate the ferrous salt in the

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[18] See, for example, Loeb, *Am. Chem. J.*, **13**, 145 (1891).

immediate vicinity of the iron electrode.[19] This gain in concentration would be progressive, and would lower the potential. Whether the gain in concentration around the iron could equal the 3% necessary to cause the change observed in 10 seconds is, however, doubtful. After the magnetic field had been removed, the agitation of the solution by bubbles of hydrogen would slowly restore the original condition as, in fact, it did. The irregularities immediately after the break may be ascribed to irregular mixing of the solution. In view of the uncertainty as to the cause of this after-effect, no conclusions will be drawn from the behavior of the iron after breaking the circuit. The experiments were sufficient to show that the apparatus functioned as well as could be expected, and also served as a satisfactory basis for comparison with those carried out with hydrogenized iron.

The Effect of the Magnetic Field on the Potential of Occluded Hydrogen.—For each experiment a piece of pure spongy reduced iron, with imbedded platinum wire, was made a cathode in the slightly acid solution of ferrous sulfate. When coated with electrolytic iron rich in occluded hydrogen, it was quickly transferred to the electrode vessel, and its potential was at once measured. Thus, potentials for the chain-cells as high as 0.810 v. (0.07 v. above the normal value) were obtained. Even higher potentials could have been attained if more acid had been added to the solution in which the iron was charged with hydrogen. This was not done because such a procedure would have caused variability during the potential measurement, due to the mixing of the acid solution with the electrolyte in the measuring cell. Hence, the same concentration as that in the electrode vessel was used for the charging electrolyte. The iron was frequently recoated electrolytically—the escape of the occluded hydrogen soon making its potential too low to be significant for the purpose in hand. Hydrogen occluded during electrolytic deposition does not raise the potential as much as that occluded by quenching the iron, as was proved by Richards and Behr.[2] Being only superficially deposited, the hydrogen soon escapes. It does, however, give an effect quite sufficient for our purpose, making the more elaborate apparatus for quenching unnecessary.

The potentials of successive pieces of iron thus charged with electrolytic hydrogen were carefully measured until their rates of decrease were precisely known. Then the magnetic circuit (using Magnet No. 1) was in each case closed. Within four seconds a greatly accelerated fall of potential was always observed corresponding to an effect often 20 times as great as that produced on pure iron. In a few seconds more the rate of fall returned to the normal. The striking acceleration of the fall of potential was roughly proportional to the excess of potential shown by the occluded hydrogen, as will be seen.

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[19] Nichols and Franklin, *Am. J. Sci.*, [3] **31**, 272 (1886); **34**, 419 (1887); **35**, 290 (1888).

Table V records the four final and most carefully conducted experiments, which are typical of all. The first column gives the times during which the iron was under magnetic influence, the next four columns give the corresponding falls of potential below their initial values (which latter are given in millivolts in the third line from the bottom) and the sixth column records the average behavior of pure iron (free from hydrogen) taken from the previous table. The next to the last line gives the rate of fall of potential before the incidence of the magnetic field, and the last line gives the steady fall after ten seconds of magnetization with the field still energized.

TABLE V

FALL OF POTENTIAL (IN MILLIVOLTS) ON MAGNETIZATION OF HYDROGENIZED IRON ELECTRODES IN FERROUS SULFATE

Time of magnetization Seconds	Hydrogenized iron				
	Expt. 1 (Curve B....Q)	2	3	4	Pure iron (Curve D)
1	1.0	1.0	0.7	0.5	0.0
2	3.0	2.0	2.0	1.1	.05
3	4.0	3.5	2.3	1.1	.08
4	3.5	3.0	2.3	1.1	.15
5	3.6	3.1	...	1.3	.20
10	4.1	3.7	2.6	1.4	.38
20	5.1	4.5	3.0	1.6	.8
Initial e.m.f. in millivolts......	810	796	785	775	741
Initial rate of fall (mv./sec.)...	0.125	0.125	0.050	0.025	0.000
Final rate of fall (mv./sec.)....	.10	.08	.04	.020	.040

The figures in the second and sixth columns are plotted in the accompanying graph (Fig. 2), which depicts the behavior of iron containing the maximum amount of occluded hydrogen (Curve A...Q) and that of pure iron (Curve D). From these figures a corrected value for the effect of magnetism on the potential of occluded hydrogen may readily be derived. The sharp cusp is perhaps due to the sudden excessive swing of the galvanometer; the dotted line (NP) in the diagram may indicate more nearly the true effect on the potential.

There can be no doubt, however, that in four seconds after the incidence of magnetization, the potential of the most highly hydrogenized iron had fallen 3.5 millivolts, whereas its normal rate of decrease (due to the slow escape of the occluded hydrogen) would have lowered it in that time only 0.5 millivolts. A net effect of 3.0 mv. is therefore to be ascribed to the magnetization. The potential of pure iron (Curve D), in the same time under the same field, would have lost only 0.15 mv. Subtracting this latter value from 3.0 we have 2.85 mv. as the most conservative estimate of the effect of the magnetic field on the potential of hydrogen, when the potential is 0.069 v. above that of pure iron. There is, to be sure, some doubt about the subtraction of the quantity 0.15, because the effect observed with pure iron may not influence the potential of occluded hydrogen, but in any case this effect is of minor importance.

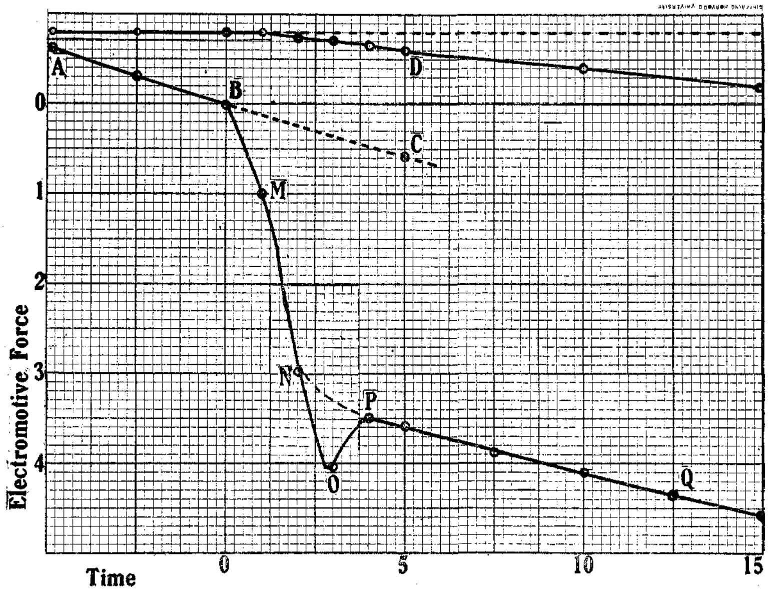

Fig. 2.—Fall of potential of occluded hydrogen on magnetization. Potentials in millivolts are plotted as ordinates; times in seconds as abscissas. The curve A B C indicates the fall of potential when hydrogenized iron is not magnetized. The curve B M N O P Q indicates the behavior of the potential after magnetization, which begins at zero time B, when the original potential of the cell was 0.81 v. Line D indicates the behavior of the potential of pure iron under magnetic influence, also applied at zero time

Table VI records similar calculations for the other experiments. Evidently the effect is roughly proportional to "overvoltage," which is dependent upon the amount of occluded hydrogen present.

Table VI

Relation of Overvoltage to Effect of Magnetic Field (Volts)

	Expt. 1	2	3	4	Pure iron (corr.)
Overvoltage..................	0.069	0.055	0.044	0.034	0.0000
Corr. effect of magnetization....	.0029	.0024	.0020	.0009	.0000

The approximate proportionality shown by the first three pairs of figures in Table VI leaves no doubt in the mind as to the reality of the effect under observation. Many other similar experiments were made using different specimens of iron and less intense magnets. They all confirmed the results recorded above, and may be omitted. It is worthy of note that the main effect with hydrogenized iron was found to be roughly proportional to the intensity of the magnetic field, as would indeed be expected. On the other hand, the almost negligible effect observed with pure iron fell off very rapidly as the magnetic intensity diminished, and became entirely negligible with electromagnet No. 2.

In order to make sure that no accidental vitiating circumstance could have crept into the work, the most probable sources of error were especially studied. To prove that the effect was not due to change of temperature a sensitive thermometer was placed in the center of the electromagnet and the current allowed to flow precisely as in the electrometric experiments. No rise of temperature as great as 0.01° was observed during 20 seconds, the total time of the observations. Further, in order to make sure that the normal fall of potential of hydrogenized iron, when not magnetized, was a smooth curve, a number of trials were made in which this potential was followed over a longer time than that demanded by the experiment. In every case the fall of potential was found to yield a smooth curve of the exponential type. This fall in potential is doubtless due largely to the deposition of iron from the ferrous sulfate solution by the active hydrogen, which is thereby diminished in concentration at the surface of the iron while the corresponding change of concentration of the comparatively large bulk of solution is unimportant. The rate of fall in any given instance appeared to vary with the overvoltage, and somewhat with other conditions (such as the temperature of ignition of the iron), as would be expected.

Induction currents, if due precautions had not been taken, might of course have produced serious complications. That these were not present is shown by the fact that pure iron and iron containing but little hydrogen failed to show the striking drop in potential on the incidence of the magnetic field which was shown by iron rich in hydrogen under precisely the same conditions. Any possible (but unlikely) effect of the magnet on the junction potential would also be ruled out of consideration by Table VI.

From the results given above it appears indisputable that a magnetic field reduces the "solution pressure" of hydrogen occluded in iron. A similar effect might be expected with all ferromagnetic metals. This fact is of considerable interest in relation not only to the nature and manner of occlusion of hydrogen, but also to the characteristics of ferromagnetism.

Discussion of Results

Let us study first the initial process of occlusion. Unquestionably, the occluded hydrogen in the metal comes from ionized hydrogen in the electrolytic solution. Upon the passage of current from solution to iron cathode this hydrogen is deposited upon the metallic surface, each single ion taking on an electron. Since the metal is a good conductor negatively charged, one can hardly conceive that the atom of hydrogen should retain its positive charge. Indeed, as the negative current flows from the solution to the electrode, electrons must be surrendered (in accordance with present theory) in order that the transfer of electricity may be possible.

In thus giving up its positive charge (or taking on an electron), the hydrogen atom may behave in one of several ways.

1. It may combine with another hydrogen atom, forming a hydrogen molecule which may be occluded, adsorbed, or evolved as a gas. That this is the chief occurrence, there can be no doubt; but that this process is not the cause of the overvoltage is shown by the fact that hydrogen gas lowers rather than raises the potential of iron.

2. Hydrogen might be occluded in a triatomic condition, when it would doubtless show a high potential; but the size of the triatomic molecule alone would make its presence in the iron doubtful.[20] Moreover, it is extremely unstable. Therefore occluded triatomic hydrogen is not a plausible source of abiding "overvoltage." That hydrogen *desorbed* from a metal may be triatomic is not necessarily disproved. Anderson[21] has shown that hydrogen desorbed from platinum is extremely active as a reducing agent. Traces of triatomic hydrogen too small to be shown by volume changes or interferometer tests may be present, due to the occasional combination, of three hydrogen atoms simultaneously issuing from the metal.[21a] Indeed as some of the authors just quoted have suggested, it is an open question whether H_3 is not found in small quantities whenever H_2 is produced.

3. The hydrogen atom may form an unstable hydride with iron. This possibility has been considered by others in detail with regard to palladium.[22] The strongest arguments seem, perhaps, to lie with Harding and Smith and Yamada, who favor the existence of a solid solution rather than of a compound. Our own results seem to support this conclusion as regards iron, since we find that the incidence of the magnetic field causes a drop in the potential, which would be supposed to indicate increased affinity between iron and hydrogen if the latter were held in chemical combination. But Morris Loeb[18] has shown that under a much more powerful magnetic field than we employed, the rate of progress of two sensitive iron reactions is in fact unchanged within the limit of measurement. Although perhaps the evidence is not wholly conclusive, his results make it seem highly probable that a magnetic field does not influence the progress of chemical reaction, even when ferromagnetic substances are present. Since the

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[20] Usher, *J. Chem. Soc.*, **97**, 400 (1910). Lind, THIS JOURNAL, **41**, 545 (1919). Chattock and Tyndall, *Phil. Mag.*, [6] **16**, 24 (1908). Wendt and Landauer, THIS JOURNAL, **42**, 930 (1920). Grubb, *Nature*, **111**, 600 (1923). *Science*, **57**, 696–7 (1923). Wendt and Landauer, THIS JOURNAL, **44**, 510 (1922).

[21] Anderson, *J. Chem. Soc.*, **121**, 1153 (1922).

[21a] The paper of Mitchell and Marshall [*J. Chem. Soc.*, **123**, 2448 (1923)], which substantiates the statement above, arrived while our paper was in press.

[22] Smith and others, THIS JOURNAL, **38**, 2577 (1916); **40**, 1508 (1918). Newbery, *ibid.*, **41**, 1887 (1919). Ref. 6. Ref. 9. McKeehan, *Phys. Rev.*, **21**, 334 (1923).

behavior of the hydrogen is actually changed, whereas we should not expect its affinities to be changed by magnetism, we may infer that the effect under consideration is not primarily concerned with the existence of a compound. In this connection it is worthy of note that after the sudden magnetic effect has been accomplished, the overvoltage decreases at nearly its previous rate during the continuance of the magnetic influence.

4. The hydrogen atoms set free from the solution may at once individually enter interstices in the iron too small to admit molecular hydrogen or water, and thus be temporarily stored in monatomic condition. This seems to us to be the most reasonable explanation. Undoubtedly there is affinity between the hydrogen and the iron; this affinity may be designated as chemical or cohesive (adsorptive) according to one's definition of these words, but at any rate the combination is apparently not in definite atomic proportions. The monatomic hydrogen would naturally have a high potential, which would manifest itself as an overvoltage, slowly diminishing as the hydrogen escapes after the discontinuance of the charging current, in conformity with fact. In the light of the new results this conclusion, which was reached seventeen years ago by one of us in collaboration with Behr,[2] seems to be supported. Hydrogen gives an excessive potential in iron only when it has been previously brought into atomic condition in contact with the metal, either electrolytically, as in the present case, or by quenching, as in the investigation of 1906. The results of Baxter[11] showing that iron reduced at a high temperature contains but little free hydrogen and our experience that pure iron thus prepared gives a normal and not an excessive potential, are not discordant with this conclusion. Before cooling, any atomic hydrogen would have escaped through the hot metal, and only a very small amount of molecular hydrogen would be adsorbed.

The work of Sieverts[23] showing that hydrogen occluded in metals does not follow Henry's law (being proportional in amount not to the pressure, but to the square root of the pressure) contributes strong confirmation to the conclusion that occluded hydrogen is present in the atomic condition. In drawing an analogy between the behavior of iron and palladium, one must not forget that the temperature coefficient of the occlusion of hydrogen by iron is positive, whereas that of the occlusion of hydrogen by palladium is negative.

Conclusion

The weight of evidence thus seems to be in favor of the view that occluded hydrogen is in the atomic condition, but not ionized, and that magnetism affects its potential not because of any change in affinity between hydrogen and iron, but rather because of some change in the texture of the occluding metal due to magnetostriction. That the fine

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[23] Sieverts, *Z. Elektrochem.*, **16**, 707 (1910).

interstices or pores containing the atomic hydrogen should change in form would not be surprising since, of course, iron in bulk is altered in dimensions by magnetic influence. Perhaps the shock at the moment of magnetic impulse causes the hydrogen to sink more deeply into the metal. Any more definite attempt to picture the mechanism of the action would be premature. Whatever the final detailed explanation of the effect may be, one cannot help thinking that knowledge of the decrease of the potential of occluded hydrogen in a magnetic field will contribute toward an ultimate interpretation of the nature of magnetism in metals, as well as of the molecular condition and mode of occlusion of hydrogen, and of the "overvoltage" which occlusion produces.

We are indebted to the Carnegie Institution of Washington for some of the apparatus employed.

Summary

The potential of iron in ferrous sulfate is found to be altered only very slightly by the application of a magnetic field. This almost negligible alteration is probably to be traced in part to diffusion in the electrolyte under the magnetic influence. On the other hand, the potential of hydrogen occluded in iron is found to be distinctly lowered, in amount roughly proportional to the intensity of the magnetic field employed. With a given magnetic field the decrease of "overvoltage" is approximately proportional to the "overvoltage" itself, amounting (with the strongest magnet employed) to about 5% of the "overvoltage" value. Many minor details, such as the effect of changing ferrous ion and hydrogen-ion concentration, of the presence of ferric salts, and other pertinent phenomena, are considered.

CAMBRIDGE 38, MASSACHUSETTS

[CONTRIBUTION FROM THE EPPLEY LABORATORY]

THE EFFECT OF VARIOUS PREPARATIONS OF MERCUROUS SULFATE ON THE ELECTROMOTIVE FORCE AND HYSTERESIS OF WESTON STANDARD CELLS

BY WARREN C. VOSBURGH AND MARION EPPLEY

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Since the solubility of a finely divided substance is dependent on the size of the particles, standard cells set up with mercurous sulfate sufficiently finely divided should have abnormally high electromotive forces.

Steinwehr[1] attempted to show this experimentally, but his results were criticized by Hulett[2] who considered that the effect of the size of the particles was not to be feared

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[1] Steinwehr, *Z. Elektrochem.*, **12**, 578 (1906).

[2] Hulett, *Trans. Am. Electrochem. Soc.*, **14**, 88 (1908); *Phys. Rev.*, **27**, 337 (1908). See also van Ginneken, *Z. physik. Chem.*, **75**, 687 (1911).