



The Electromotive Force of Iron Under Varying Conditions, and the Effect of Occluded Hydrogen

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THE ELECTROMOTIVE FORCE OF IRON UNDER VARYING CONDITIONS, AND THE EFFECT OF OCCLUDED HYDROGEN.

The topics named in the title of this paper are of great practical importance, as well as of great interest from the theoretical point of view. The rate of rusting and the change of properties caused by the occlusion of hydrogen are essential factors in determining the permanence and strength of most modern buildings, bridges, and underground pipes. For this reason the literature which has already accumulated upon the subject has grown almost to the dimensions of a library in itself. The theoretical side of the matter also is of great interest. The cause of the sudden diminution of activity produced in iron under certain well-known circumstances has not yet found its definitive explanation, and the mechanism of the occlusion of hydrogen by a solid so tenacious and compact as iron is a theoretical question of no small interest.

Phenomena relating to these topics are considered together in this paper, because the method of investigation furnished evidence with regard to both. The matter was considered rather from the theoretical than the practical standpoint. The method was the determination of the electromotive force of iron, after subjection to a great variety of changing conditions, on immersion in a solution of one of its salts, in order by comparison of these different values of electromotive force to draw inference concerning the state of the metal and its occluded gas.

The object of the research, as originally planned, was to add to the experimental evidence concerning the significance of changing atomic volume, and it was proposed to discover whether or not changes in free energy were associated with changes of density and of other properties of the solid. During the progress of the work it was found that this matter could not be satisfactorily studied without studying the properties of occluded hydrogen, because, in spite of the great volume of literature upon the subject, certain important questions seemed to have remained hitherto almost untouched. Lack of time has as yet prevented the completion of the program; but the

present results, although only a part of the whole plan, are reasonably complete in themselves, and therefore worthy of separate publication. The subject will be taken up again in the near future.

For the sake of clearness and convenience, the present paper will be divided into two parts, entitled: Part I. "The Electromotive Force of Pure Iron under Varying Conditions;" Part II. "The Electromotive Force of Iron Containing Occluded Hydrogen."

PART I. THE ELECTROMOTIVE FORCE OF PURE IRON UNDER VARYING CONDITIONS.

When in a definite state of internal equilibrium, the electromotive force of a metal immersed as a reversible electrode in a definite solution of one of its salts must have a perfectly definite value under given conditions. A change in the internal state must of necessity change this electromotive force, unless the temperature happens to be exactly at the transition point. For this reason it seemed not improbable that the measurement of the electromotive force of iron which had been subjected to great stress would afford the most convenient method of determining whether or not this stress had affected a permanent alteration in the internal equilibrium of the metal, a "permanent set," as it is sometimes called, or an extraordinary condition of metastable equilibrium.

A solid may be subjected to a variety of stresses. The first which it seemed desirable to study was direct pressure, in order to determine if this pressure, by causing closer internal structure, diminishes the outward or dissolving tendency as measured by electromotive force, or if, on the other hand, the substance, when released from the pressure, returns at once to essentially the state in which it was before the pressure was applied. Experiment alone could decide between these alternatives.

It was desirable also to test the possibly opposite effect of a negative pressure, a distending tendency, such as the effect of stretching a wire to the breaking-point. This effect was also made the subject of experiments recorded below.

During these tests it was found that the temperature used in the reduction of the iron from its oxide caused a very important effect on the dissolving tendency, and therefore this matter also had to be considered in a special series of experiments.

PREPARATION OF MATERIAL.

In any research with iron it is of primary importance that the substance experimented upon should be pure—free from carbon, silicon, sulphur, phosphorus, manganese, and, as the following work testifies, from hydrogen also.

Most of the iron used in this research was prepared by a method which had been found in an exhaustive investigation of the atomic weight of the metal to yield good results.¹ It is true that not quite all the steps were used in the present work, but the more essential ones were retained, and a very pure sample of the metal was prepared. "Piano" wire of good quality served as the original substance; it was carefully sandpapered and wiped, and dissolved in dilute nitric acid. Concentrated acid was first used, but this oxidized the silicon to silicic acid, and filtration from the silicon itself (or silicide of iron, SiFe_2),² which the dilute acid leaves unchanged, was considered more safe, besides being more convenient. All iron carbide or graphite is either completely oxidized or else is unchanged and filtered out. The dilute acid also lessens the chances of any sulphur being oxidized to sulphate.

The nitrate formed was then concentrated and recrystallized three or four times. Recrystallization is here a peculiarly good method of purification, because the ferric nitrate has an unusual crystal form; therefore most impurities can only be held mechanically.³ The recrystallized salt was then heated in a platinum dish at a moderate temperature in an electric oven. The nitric acid was partly driven off and the dry, dark-red basic nitrate was then powdered in a Hempel steel mortar⁴ and heated to full redness to complete the denitration. It is important that this operation be carried out in steps as described, because in this way a fine, spongy powder is obtained which allows of perfect reduction. If denitrated too quickly by too high a temperature the oxide obtained is exceedingly hard and the powder consists of very compact particles, in which the complete reduction of the core is more or less uncertain and decidedly less rapid.

The oxide so produced was reduced in a stream of electrolytic hydrogen⁵ in an unglazed porcelain boat⁶ set in a hard glass combustion-tube when a low-temperature reduction was desired, or in a large glazed porcelain tube⁷ in a gas-furnace when a higher temperature was used.

¹ Richards and Baxter, *Z. f. anorg. ch.*, **23**, 245 (1900); *Proc. Amer. Acad.*, **35**, 253 (1900).

² Lebeau, *Bull. Soc. Chim., Paris*, (3) **27**, 39-42 (1902); *Ann. Chim. Phys.* (7), **26**, 5-31 (1902).

³ T. W. Richards, *Zeitschr. f. phys. Chem.*, **46**, 189 (1903).

⁴ W. Hempel, *Z. f. ang. Chem.* **14**, 843 (1901).

⁵ The generators used were zinc amalgam, dilute hydrochloric acid, platinum cells, and were of the convenient form used by Cooke and Richards, *Proc. Amer. Acad.* **23**, 168 (1887). The hydrogen was twice washed in strong caustic solution and dried by passing through two caustic potash towers.

⁶ Unglazed, because at the high temperature used the glaze frequently fused with the iron.

⁷ Hempel water-cooled stoppers were used in the porcelain tube.

The iron from these reductions was of a gray color and of a porous structure. A piece of it could usually be broken with ease between the fingers and rubbed to powder. This consistency was of course due to its mode of preparation, the powdered oxide having been simply pressed into the boats and the temperature having been only high enough to cause slight cohesion between the particles, not to fuse the mass.

The cohesion of the particles varied considerably with the temperature at which the reduction was carried on, a product reduced at 600° having no cohesion at all, while one heated to about $1,100^{\circ}$ for some time could be broken only with some difficulty. The color also varied, owing to the difference in degree of subdivision, from almost black to a clear, silvery gray.

A convenient index of complete reduction was the absence of any trace of black oxide in the cooler portions of the boat; for water formed in the hotter places is decomposed in the somewhat cooler ones, and if the reduction is not complete water is of course present. Ordinarily, the reduction was carried out by heating the substance in a rapid stream of hydrogen for three or four hours with a Bunsen burner, and then for about half an hour at the highest temperature of the blast lamp. Such iron showed not the slightest trace of black oxide, even when finely powdered in a mortar. After heating the iron remained in a continuous stream of dry hydrogen until quite cold, and was then transferred for preservation to a good desiccator containing finely divided fused caustic potash. No trace of oxidation was ever visible on iron thus preserved; but, as will be explained later, the electromotive force measurements gave clear evidence that an exceedingly thin coating of oxide or adsorbed oxygen had been formed, and therefore, for the more accurate experiments, small boat-loads of pieces about the size of peas were reduced a second time and sealed in hydrogen until just before using, thus avoiding the possibility of oxidation. Whenever this specially sealed iron is used in the experiments below the fact is mentioned. The sealing was done as follows: A hard glass tube was drawn out in several places, having between each contracted place a boat containing porous iron. Three or four such boats in series were laid in a combustion furnace, and after reduction the boats were sealed off by drawing out the contracted places.

All this iron undoubtedly contained hydrogen in greater or less amounts. Although, as Baxter^{*} has shown, the *weight* of hydrogen retained by pure iron ignited at a high temperature is inconsiderable, some of the other properties of the occluded gas are more important, as will be seen. Most of the hydrogen can be expelled by heating for a long time in vacuum, or by standing for a long time in dry air; but in order to drive out the last traces fusion in vacuum is necessary.

^{*}Baxter, Am. Chem. Journ., 22, 363 (1899).

METHOD OF MEASUREMENT.

The solution-tension of the iron was measured as its electromotive force in a normal solution of ferrous salt, in this case ferrous sulphate. The sulphate ion is desirable here, since it is neutral as regards passivity phenomena, having neither passivizing nor activizing effect.⁹ The voltage of the cell Fe, $n\text{FeSO}_4$, $n/10\text{KCl}$, HgCl , Hg, was measured by the well-known compensation method of Poggendorff.¹⁰

A d'Arsonval galvanometer served as zero instrument, being sensitive to 0.001 volt with the resistance used. A Helmholtz cell was used as a standard of comparison. Its exact value was 0.993 international volt, as determined by a comparison with carefully prepared cadmium normal elements. These agreed accurately among themselves, and were assumed to possess at 21.50° C. the value 1.0185 volts. They agreed also with the standards of the Jefferson Physical Laboratory.

As a standard electrode the mercury-calomel-potassium chloride electrode first suggested by Ostwald¹¹ was considered the best for the reasons he so convincingly puts forward in his argument with Wilsmore.¹² In the present research tenth normal instead of normal potassium chloride was usually used as the electrolyte. All values of electromotive force are given for the whole cell, Fe, FeSO_4 , KCl, HgCl , Hg, a definite measurable quantity, instead of for the single potential difference Fe, FeSO_4 , because of the uncertainty as to the absolute value of the decinormal electrode. If 0.56 volt is supposed to be the value of the normal calomel electrode, the value 0.612 volt for the tenth-normal electrode should be used, as recently determined by Sauer¹³ and verified by us. Subtracting this from the values given, a value comparable to the commonly accepted values of single potential differences will be obtained.

A special arrangement of the decinormal electrode was adopted, in order to prevent its contamination with iron. To the connecting-tube, used for immersion in the ferrous sulphate cell, was attached above a siphon-inlet from a large bottle of decinormal potassium chloride on the shelf above. The fact that it was possible to wash out the tube of the decinormal electrode by means of this fresh solution removed the possibility of variation through the backward diffusion of normal ferrous sulphate or other electro-

⁹ Sackur, Z. f. Electrochem., 10, 843 (1904).

¹⁰ Ostwald-Luther, Physico-Chemische Messungen, p. 367.

¹¹ Lehrbuch, 2, 945 (1893).

¹² Z. f. Physik., ch. 35, 333 (1900); *ibid.*, 36, 91 (1901).

¹³ Z. f. Physik., ch. 47, 184 (1904). That is, $N/10$ electrode = 0.612 volt if the $N/1$ electrode is called 0.560 volt.

lyte. By means of this arrangement one such electrode lasted through a whole season and at the end of that time gave no test for iron in the cell itself. Thus the uncertainty of this possible error is removed and the nuisance of repeated renewal of the electrode done away with. The arrangement is shown on the left-hand side of figure 1.

The usual arrangement of the iron and of the cell was as shown in figure 1, and on a larger scale in figure 2. The sample, about half the size of a pea,

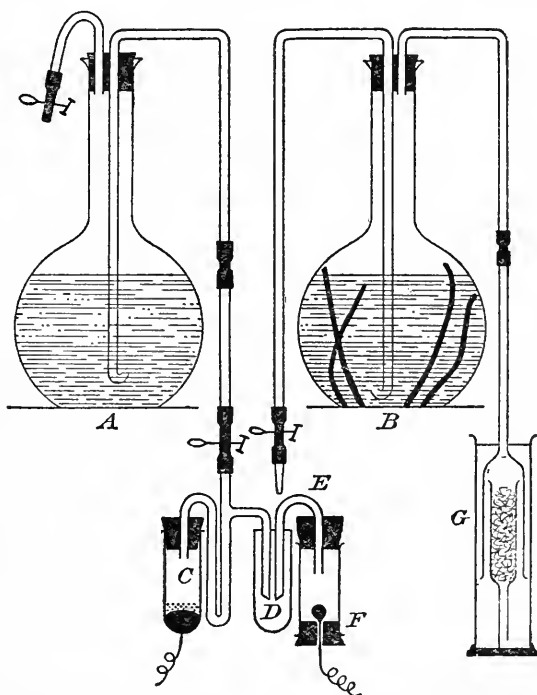


FIG. 1.—THE CELL AND ITS APPURTENANCES.

- | | |
|---|---|
| A. Reservoir of decinormal potassic chloride. | D. Connecting receptacle containing ferrous sulphate. |
| B. Reservoir of normal ferrous sulphate containing pure iron wires. | E. Inverted U tube. |
| C. Calomel electrode (decinormal). | F. Iron electrode (enlarged in fig. 2). |
| | G. Automatic hydrogen generator, protecting Reservoir B from air. |

was inserted in a running noose of platinum wire, the end of which projected through a fine hole in a cork stopper. The noose was then pulled tight, drawing the sample against the cork, and the wire was fastened by winding around the shank of an iron tack on the other side of the cork. The cork was fitted into one end of a glass tube and carefully sealed with molten paraffin. The tube was filled with normal ferrous sulphate solution by



means of a siphon from the reservoir, and an inverted U-tube and stopper were inserted in the top to make connection with an open test-tube containing ferrous sulphate fastened alongside by means of a rubber band. In this way the iron was kept for some time safe from oxidation, yet always open to measurement. The arrangement is illustrated in figure 2. When the end of the tube of the decinormal electrode (*C* in figure 2) was dipped into this test-tube full of ferrous sulphate, the cell was complete and ready for measurement. A large number of "iron electrodes" could be placed around

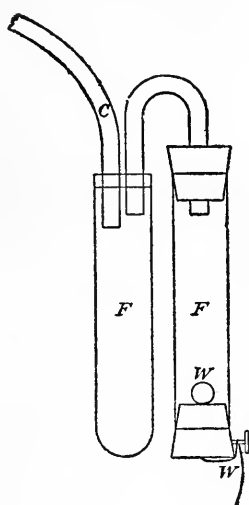


FIG. 2.

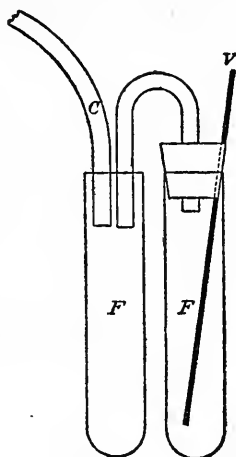


FIG. 3.

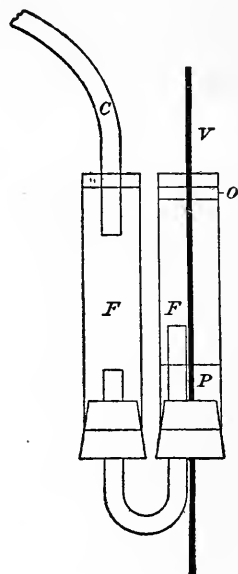


FIG. 4.

RECEPTACLES FOR IRON ELECTRODES.

- C.* Tube leading to decinormal electrode.
- F.* Contains normal ferrous sulphate solution.
- O.* Protecting layer of paraffin oil.

- P.* Hard paraffin.
- V.* Iron wire.
- W.* Platinum wire and loop for holding porous iron.

the sides of the thermostat, all attached to one wire, and the change of connection from one cell to another was made by simply lifting the iron stand to which the decinormal electrode was attached and dipping the end of the standard electrode's tube into the next test-tube. Thus a large number of measurements could be taken with a minimum expenditure of time and trouble, a very necessary matter in an investigation involving thousands of measurements. The thermostat, electrically regulated and heated, in which the electrode was immersed, was kept at 20.0° C. The normal ferrous

sulphate used was prepared by dissolving almost the necessary amount of pure crystals in a quantity of water, adding a small measured amount of sulphuric acid, and making up to a liter. Then pieces of piano wire, carefully cleaned, were added. The acid acting on the iron thoroughly reduced the solution, the amount of the acid having been so chosen that just the necessary amount of iron dissolved to make the solution normal. Several months were needed to remove the last traces of acid—an essential condition. The flask was connected with an automatic hydrogen generator whose cock was always open, and when liquid was withdrawn through the siphon hydrogen took its place. This also is represented in figure 1. Thus after having once prepared the solution, it could be kept indefinitely, perfectly constant and always at hand.

THE EFFECT OF PRESSURE.

In the following work the term "porous iron" will be used for the sake of brevity to designate the iron which had been reduced from oxide in the manner described on pages 6 and 7.

The results of a series of preliminary experiments with this porous iron are given in table 1.

The first two were made with samples which had merely suffered exposure to air. The next four had received further treatment, having been put into a small iron mortar such as is used in powdering rocks, and beaten with a heavy hammer. Under this treatment the friable, porous iron became compact and gained a shining metallic surface. The electromotive forces of these samples were then measured after immersion in normal ferrous sulphate. The cracked and powdered edges of numbers 2 and 3 were covered with shellac, so that only the smooth metallic surface was exposed to the solution.

TABLE 1.—*Preliminary experiments—Electromotive force of iron against decinormal electrode.*

Time elapsed after immersion.	Sample 1, porous iron.	Sample 2, porous iron.	Sample 3, beaten iron.	Sample 4, beaten iron.	Sample 5, beaten iron.	Sample 6, beaten iron.
Minute.	Volt.	Volt.	Volt.	Volt.	Volt.	Volt.
1	0.704	0.655	0.655
2	0.674	0.685
4	0.754	0.755
20	0.780	0.774	0.724	0.720	0.674	0.722
55	0.737	0.728	0.674	0.736
240	0.801	0.799

A glance at the table shows that the beating had made considerable difference in the electromotive force of the iron in every sample which had been beaten. It will be shown later, however, that this difference was due not to the compression, but to another effect of the treatment.

This effect was soon found to be closely connected with another relation to be observed in the above figures; namely, the fact that after immersion the electromotive force of each piece of iron begins at a low point and rises, attaining constancy at a maximum only after some time. In order to study this phenomenon more closely, six other small pieces were immersed in the solution and readings of the electromotive forces taken at short intervals. The numerical results are given in table 2.

Because it was evident that the electromotive force continued to rise slowly for a very long time, four of these pieces were carefully sealed up with paraffin immediately after immersion in order to prevent oxidation. This was done in order to determine the electromotive force of the final equilibrium. After three days No. 9 and No. 10 were opened and measured; and after five days No. 11 and No. 12.

TABLE 2.—*The increase of electromotive force with time—Iron electrode against decinormal electrode.*

Time elapsed after immersion.	Sample 7.	Sample 8.	Sample 9.	Sample 10.	Sample 11.	Sample 12.
	Volt.	Volt.	Volt.	Volt.	Volt.	Volt.
0 ^h 2 ^m	0.590	0.690
0 2.75	0.645	0.745
0 6	0.685	0.764
0 13	0.714	0.774
0 50	0.749	0.785
73 0	0.789	0.793
78 0	0.791	0.794
119 0	0.782	0.784
120 0	0.784	0.786

This was later repeated with other samples, which gave similar results. It should be noted that after several days a pale-green precipitate of ferrous hydroxide was always found in the tube, but this seemed to exercise no considerable effect on the potential until seven or eight days had passed and the amount had become large. Even then by shaking the constant value of the potential was usually regained.

Thus it was obvious that spongy iron which has been exposed to the air always gives at first an abnormally low electromotive effect, which slowly rises. The only reasonable hypothesis capable of explaining the phe-

nomenon seems to be the conclusion that the exposure to the air results in the formation of an exceedingly thin coating of oxide or at least of adsorbed oxygen, and that when this coating is removed, by solution or reduction, the true electromotive force is obtained.¹⁴

Accordingly, the iron to be used in the succeeding experiments was sealed in hydrogen. The tubes were broken open just before the samples were to be used, and their electromotive forces were measured as soon as possible afterwards. In this way the exposure to air was as short as possible and the theory was confirmed, for they were found to attain their maximum values very promptly.

With these samples a more careful study of the effect of pressure was begun. A number of preliminary experiments were made with pressures produced by 30,000 and 60,000 pounds. These pressures were quite sufficient to cause cold-welding of the particles of the porous iron, giving firm, hard plates with bright metallic surfaces. The area of these surfaces was seldom more than the half of a square centimeter, hence the pressures were approximately 30,000 to 60,000 kilograms per square centimeter. The compression was done between two smooth plates of steel in a large testing-machine in the Engineering Department of Harvard University. The pressure was great enough to press the soft iron into the steel plates, leaving distinct indentations. The iron was handled only with iron pincers. Everything with which it came in contact was kept scrupulously clean. The edges of the compressed pieces being cracked and split, they were embedded in soft paraffin before immersion in the ferrous sulphate solution, leaving exposed for measurement only the center, which had certainly borne the full effect of the pressure.

It appeared that iron thus treated gave results in no way different from the spongy pieces before compression, except that the compact specimens were slower in reaching their maxima. When reached, these maxima were essentially identical with those of the porous specimens.

Nevertheless, it seemed worth while to carry the matter further. Through the kindness of Lieutenant-Colonel J. G. Butler in charge, it was possible to subject other portions of pure spongy iron to still greater pressure on the magnificent testing machine at the United States Arsenal at Watertown, Massachusetts. This machine is capable of not only exerting a weight-effect of 1,000,000 pounds, but of measuring with great accuracy the magnitude of the effect it exerts. Two special blocks were made between which to

¹⁴This experience, and the conclusion derived from it, agrees with that of Muttimann and Fraunberger (*Sitzber. Akad. der Wiss. München*, 34, 201) (1904). Their investigation was published after this part of our research had been completed, and was wholly independent.

compress the iron. In order to resist such enormous pressures they were made of the very finest tool steel, and after the lathe-work was finished they were quenched to a condition of maximum hardness. They were frustra of cones, the diameters of the bases being about 16 cm. and those of the tops, between which the iron was compressed, about 3 cm. Their heights were about 8 cm. The pressures exerted were 500,000 pounds and 700,000 pounds. Exactly how much of this pressure bore on the iron test-piece it is impossible to say, for the soft iron was pressed so deeply into the hard steel that there was some possibility of the whole top surface (7 sq. cm.) receiving part of the pressure. On the other hand, if, as is probable, the test-piece alone bore the stress, the maximum pressure was at least 350,000 kilograms per sq. cm., for the surface of the soft iron was never 1 sq. cm.

In order to make more striking any differences which might result from these pressures, samples 13 and 14 had each been broken in two, and one piece of each was kept in a spongy condition, in order to compare with the other compressed one. Thus it was certain that all treatment previous to measurement¹⁵ had been precisely the same, except for this one matter of compression. Other pieces of porous iron gave essentially the same results.

As in the previous experiments, the edges of the compressed iron were protected with paraffin, so that the exposed surface should be that alone which had been compressed.

TABLE 3.—*The effect of previous compression on the electromotive force—Iron electrode against decinormal electrode.*

Time elapsed after immersion.	Sample 13, porous.	Sample 13 after subjection to 250,000 kg. pressure.	Sample 14, porous.	Sample 14 after subjection to 350,000 kg. pressure.	Sample 15 after subjection to 350,000 kg. pressure.	Sample 16 after subjection to 350,000 kg. pressure.
	Volt.	Volt.	Volt.	Volt.	Volt.	Volt.
0 ^h 11 ^m	0.731	0.722
0 28	0.775	0.755	0.786	0.744
6 0	0.781	0.781	0.787	0.770	0.783	0.750
21 0	0.780	0.782	0.787	0.782	0.788	0.751

The results with samples 13 to 15, inclusive, lead to the conclusion that no permanent change in free energy had resulted from the compression. They are exactly similar to those obtained with the lower pressures. The apparently contradictory result of sample 16 will be shortly explained.

As a step toward this explanation, it is necessary to call attention once

¹⁵ Including the temperature to which it had been exposed, the importance of which will shortly be pointed out.

more to the fact that the compressed pieces at first yielded too low an electromotive force, although the value afterwards rose to equal that of the uncompressed pieces. An explanation for these low values is to be found in the idea already mentioned on page 13, there advanced to explain the lag of porous iron which had been kept for some time in a desiccator. It is that an exceedingly thin coating of oxide is formed on the iron by exposure to the air and thus the true electromotive force is masked until this coating is dissolved. Most of the samples of porous iron had been kept a whole day in a desiccator after reduction before immersion, while sample 14 in table 3 had been kept only three hours. The difference in the speed of attaining the maximum value is very marked. This theory not only seems to account for the effect of long exposure to air, but also offers a simple explanation for the slightly lower initial potential of the compressed samples. The length of time during which the compressed pieces were exposed to the air before measurement was exactly the same as that of the parallel porous ones, but the former were inevitably heated somewhat in the act of compression, and thus an oxide coating might well have been formed which would equal in effect one of long, slow formation in a desiccator. The theory probably also offers the most satisfactory explanation of the exaggerated deficiency exhibited by No. 16 in table 3. The blocks between which No. 16 was compressed had been three times subjected to such enormous pressures that they were beginning to fail, and this fourth and last time the blocks split with bright sparks and loud reports, and threw small pieces in all directions. Under such treatment the blocks undoubtedly became warm, and it is quite to be expected that this last sample should possess the heaviest and firmest coating of oxide.

Thus it is fairly safe to conclude that even such enormous pressures as 300,000 kilograms per square centimeter produce no permanent change of free energy in iron.

It is interesting to compare this constancy with the behavior of other properties of metals on subjection to great stress. Since this work was done, Dr. Stull and one of us has found, in the work already referred to, that after subjection to pressures up to 500 atmospheres all of thirty-odd elements examined regain precisely the original volume. The method used is unique and allows of the detection of volume changes of 0.000,01 milliliter in a sample of 10 milliliters.

After this work was done we became acquainted with two pertinent papers by W. Spring,¹⁰ in which he proves the same fact by still another method, the one, in fact, which would most naturally be adopted if that were the main object of the research, namely, the determining of the spe-

¹⁰ Bull. Acad. Roy. de Belg. (3), 6, 509 (1883); Ibid. (1903), p. 1066.

cific gravity before and after compression. He first submitted to pressures up to 10,000 atmospheres more than eighty solids of the most diverse chemical nature, and found that powders weld together perfectly under pressure, as we found with iron. In order to do this, he found it necessary to compress in a vacuum, because imprisoned air not only prevented contact of the particles, but also tore them apart again when pressure was released. All of his work was performed with the care which this precaution indicates. The result of one investigation, entitled "L'élasticité parfaite des corps chimiquement définis," is best given in his own words:

La plupart des corps examinés ont manifesté une petite augmentation permanente de densité après avoir subi une pression d'environ 20,000 atmosphères, mais, celle-ci une fois réalisée, ils ont résisté opiniâtrement à toute diminution permanente ultérieure de leur volume. Pour tous la densité a atteint bientôt *un maximum*. La faible augmentation de densité permanente observée n'a cependant jamais eu pour cause une contraction réelle de la matière. Toujours elle a été due à l'écrasement, par pression, des cavités existant d'avance dans le corps examiné, ou bien à la disparition de fissures plus ou moins évidentes. En un mot, on s'est trouvé en présence d'un fait accidentel, pouvant facilement amener une erreur, mais non d'un phénomène physique essentiel.

Thus the present work on the electromotive force of iron subjected to great stress confirms the very different work of Spring on densities. In so far as these data show that when no change of specific gravity is effected by a given application of energy, no change in the free energy of the system results, they support the theory of compressible atoms.

TENSION EXPERIMENTS.

Although it thus appears to be impossible to produce permanent free energy changes in pure iron through pressure alone, it appeared possible that measurements of electromotive force made while the metal was under tensile stress might show varying values, because tension produces marked physical changes in the metal. These changes are as follows: (1) A strain which immediately disappears on release of the tension, inside the elastic limit. (2) Beyond the elastic limit a permanent strain, with increasing stress needed to produce equal increment of strain, up to the ultimate resistance. (3) Beyond the ultimate resistance, with ductile metals, there is a region before the actual break occurs, where, for increase of strain, decreasing stress is required, until failure takes place. It seemed reasonable to expect that such decided and sudden changes in the cohesion would be accompanied by free-energy changes.

While under stress, or after a "permanent set" has been produced by strain beyond the elastic limit, the iron is in unstable equilibrium. Sufficient proof that it is so within the elastic limit lies in the fact that it returns of

itself to its original dimensions. Beyond the elastic limit, the custom in wire manufacture, of returning the wire perhaps half a dozen times to the annealing pots to be softened, speaks for itself. By heating to 300° to 400° for several hours "the molecular tension in the wire caused by drawing" is released.¹⁷ The molecules, given the opportunity through increased mobility at higher temperatures, may be supposed to return to their normal relations to each other and plasticity is restored to the iron.

Further evidence in this direction is furnished by a piece of work done by Barus, entitled "The Energy Potentialized in Permanent Changes of Molecular Configuration."¹⁸ He pulled wires of various metals to the point of failure, determined their rise in temperature by means of a thermopile, and subtracting the heat evolved from the total work done on the wires, obtained values for the amounts of energy which had become potential in the metals. He says:

To summarize, it appears that as much as one-half of the work done in stretching up to the limit of rupture may be stored up permanently; that the amount of work thermally dissipated varies considerably with the metal acted upon, being very large, for instance, in copper (75 per cent) and smaller in the case of iron (50 per cent); that in the case of the same given metal the work is largely potentialized during incipient stages of strain, and very largely dissipated during final stages of strain. When stress of a given kind is applied to different metals, the total amount of energy which can be stored per unit section, per unit of length up to the limits of rupture, may therefore be looked upon as a molecular constant of the metal.

In a table he gives results showing that in an iron wire of 0.136 cm. diameter, stretched almost to the limit of rupture, at least 2 megergs per centimeter are potentialized, about the same amount having been dissipated as heat. Knowing this value, it is possible to calculate the maximum rise in electromotive force theoretically required by such an increase in the free energy of the metal, supposing that all this work were available as free energy. The general formula for such a calculation is:

$$\Delta\pi = \frac{WE}{96580m}$$

in which

W = the work in joules done per centimeter of the wire;

E = the electrochemical equivalent of the metal, in grams;

m = the weight of the metal per centimeter of wire; and

$W \times E/m$ = the work done per gram equivalent of the metal.

Substituting values found by Barus, we have:

$$\Delta\pi = 0.432 \times 27.95/0.1114 \times 1/96580 = 0.0011 \text{ volt.}$$

(The radius of the wire was 0.068 cm. and its density 7.68.)

¹⁷ "Wire, its Manufacture and Uses," J. B. Smith, pp. 30, 54, and 56.

¹⁸ Amer. Journ. Sci. (3), 38, 193 (1889); also U. S. Geological Survey Bulletin No. 94, p. 101 (1892).

Two other calculations will be given to illustrate more fully the changes to be expected. The data for these were found in a book¹⁹ which is still quoted as an authority by engineers, although published as long ago as 1879.

In the first of these (p. 24) the test-pieces were taken "from a bar of remarkably pure, refined, and uniform iron." The average of nine tests, very uniform in their results, gave: Breaking stress per square inch, 55,489 pounds; elongation, 23.9 per cent. The diameters of the test-pieces were 0.974 inch. Calculating as before, we get 0.0034 volt as the change to be expected.

In the second one the iron is described as "very soft and ductile." The average of four tests gave: Stress per square inch, 45,873 pounds; elongation, 29.7 per cent. The diameters were 1.000 inch. These data give 0.0035 volt as the expected rise.

The results of all these calculations should be divided by 2, since Barus showed that only 50 per cent of the work done becomes potential. These calculated values, never exceeding 1.8 millivolts, represent the maximum values for the increase of potential—values which may not be actually attained, because it is by no means certain that all the energy thus stored is available as free energy. Moreover, the distribution of the strain between surface and interior is uncertain. This is indicated by the following statement of Burr:²⁰

It has been found by experiment that bars of wrought iron which are apparently precisely alike in every respect, except in area of normal section, *do not give the same ultimate tensile resistance per square inch*. Other things being the same, *bars of the smallest cross section give the greatest intensity of ultimate tensile resistance*.

This is due to the fact that shearing strains increase with greater cross section. And also,²¹

If the tensile stress is uniformly distributed over each end of the test-piece, it will not be so distributed over any other normal section. Since lateral contraction takes place, the exterior molecules of the piece must move toward the center; but if this motion exists, the molecules in the vicinity of the center must be drawn farther apart, or suffer greater strains, than those near the surface. Hence the stress will no longer be uniformly distributed, but the greatest intensity will exist at the center and the least at the surface of the piece. These effects will evidently increase, with a given form of cross section, with the area.

Smith,²² in pointing out the strengthening effect of drawing wire has said: "In the case of the wire drawn through three holes the tenacity of the

¹⁹ "Experiments on the strength of wrought iron." Report of the Committee of the United States board appointed to test iron, steel, and other metals. Commander L. A. Beardslee, U. S. N. Abridged by William Kent. New York, 1879.

²⁰ Elasticity and resistance of the materials of engineering, p. 218. New York, 1903.

²¹ Ibid., p. 206.

²² "Wire, its manufacture and uses," p. 58.

metal was increased 95 per cent above that of the billet;" and Burr says:²³ "Wire is the strongest form in which iron can be used to resist tensile stress."

It is evident, then, that by pulling a wire of small cross-sectional area it is possible to exert the maximum of stress on the surface of a test-piece.

The apparatus (shown in figure 4, page 10) employed in our experiments was exceedingly simple. The upper end of the wire was twisted around an iron support and the pull was exerted by weights in a basket attached to the lower end. In the middle the wire was narrowed at one place, and this was surrounded by a tube of normal ferrous sulphate and connected with a normal calomel electrode. The results were at first highly irregular. The electromotive force of the wires used (pure piano wire and pure soft iron wire) varied over a range of 0.005 volt without apparent cause. Merely tapping the stretched wire sometimes caused a momentary rise of from 0.003 to 0.004 volt. Such electrical disturbances from mechanical jarring have been observed by von Helmholtz. In one case the addition of 5 kilograms to the load caused a net rise of about 0.0007 volt and the next 5 brought it down again by the same amount, while one more brought it up again by 0.0005.

Calculating the theoretical change of potential, we get 0.0017 volt for the total work done, and half of this, or 0.0009 volt, as the change to be expected according to Barus. The data for this calculation are: Tensile strength, 25 kilograms; elongation, 9.3 per cent; diameter of wire, 0.08 cm.

Hence the accidental disturbances exceeded the maximum theoretical effect and entirely masked the latter.

Only one regularity was noticeable, namely, that at the instant at which the load was increased there was a momentary drop in electromotive force. Starting with no load at all and the potentiometer reading 0.7145 volt,²⁴ a 10 kg. load was applied, and at the same instant the galvanometer swung 18 to 20 divisions to the right, and then instantly swung back again very rapidly to the permanent reading, 0.7125 volt. Exactly how much fall of potential this swing to the right indicates could be determined only with a ballistic galvanometer, but it may have been as much as 0.015 volt. The addition of another kilogram had a similar effect, except that the swing was only 12 to 15 divisions to the right and it returned more slowly to 0.7125. The third 10 kg. caused a smaller swing still, and a much slower return to 0.7125. About that value was always reached after standing a few minutes.

²³ Elasticity and resistance of the materials of engineering, p. 241.

²⁴ This reading, being taken with the help of a *normal* calomel electrode, must have 0.052 volt added to it in order to be comparable with the other potentials recorded in the paper. It thus becomes 0.766, the same as before. The normal electrode has less resistance and allows more sensitive readings than the decinormal.

The weights were then added to 48 kg., the last ten still causing a slight swing to the right. A 13 kg. weight was then added to the load, and the wire lengthened rapidly and would have undoubtedly broken had not the support stopped the basket. The galvanometer swung 8.5 divisions to the *left*, indicating a *rise* of about 0.004 volt, and quickly swung back again.

These temporary changes and the change in sign which they undergo are highly interesting. The most obvious explanation of the first effect of diminished potential is to ascribe this to heating incidental to pulling, and experiment gave the idea some support. Heating the wire to redness with a small gas flame just above the surface of the liquid gave a somewhat variable electromotive force, the mean value being about 0.015 volt *below* the initial one—an effect about like the first effect noted above. When cold the wire returned to the initial value. This is advanced as a suggestion rather than a definitive explanation, however.

The decreasing temperature effect due to the successive additional stresses may have been due to the larger percentage of storing as potential energy as the elastic limit is approached—and the final excess of potential may have been due to the sudden manifestation of this increased potential at the point of fracture.

Nevertheless, these conclusions are highly hypothetical. The results do not permit of conclusions broader or more definite than these. On the other hand, they afford the opportunity of correcting two pieces of work which have been widely published and whose incorrect results have been given general credence. The subject is of such great importance to modern engineering that, naturally enough, engineers were the ones attracted to its investigation. M. P. Wood, in his book "Rustless Coatings; Corrosion and Electrolysis of Iron and Steel,"²⁵ under the heading "Corrosion Increased by Stress" (p. 348), quotes three men as entitled to a hearing on this subject.

The first of these, Thomas Andrews,²⁶ carried out experiments far from satisfactory from the electrochemical point of view, because he used a solution of common salt as an electrolyte, and prepared the two pieces of iron for comparison in different ways. The observed difference in potential is quite as probably to be ascribed to the oxidation effect already discussed as to the effect of strain, although a part of the effect may have been due to strain.

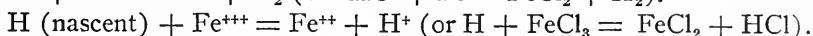
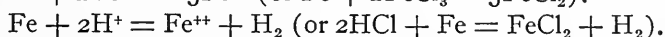
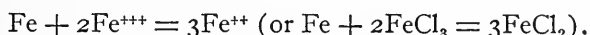
The second paper quoted by Wood is "An Experimental Study of the Corrosion of Iron under Different Conditions," by Carl Hambuechen.²⁷ Of

²⁵ Wiley & Sons, N. Y., 1904.

²⁶ Proc. Inst. Civil. Engin. 118, 356-374 (1894).

²⁷ Trans. Amer. Soc. Mechan. Engin., 22, 816-821 (1901); or Bull. Univ. Wisconsin, Engin. Series, vol. 2, No. 8, (1900).

this paper the section on "Corrosion of Strained Metal," which is the only part to be discussed here, is no more conclusive than Andrews's work, although Hambuechen states his conclusions in unqualified terms. The work was very carefully performed in every particular except one, namely, the fact that he chose ferric chloride solution as the electrolyte in which to measure the electromotive force of the iron test-pieces. This unfortunate choice completely invalidates all the results. The reason is very simple. Ferric chloride is always hydrolyzed to a considerable extent—that is, it contains acid. When such a solution comes in contact with iron the three following reactions take place:



There exists, then, at the electrode a continually changing concentration of ferric, ferrous, and hydrogen ions, and reliable work is out of the question. The effect of all these influences combined would cause the electromotive force to change steadily, quite independently of any stress and strain effects. The rate of this change would depend on such indeterminate and chance relations as the area of the iron surface to the volume and the concentration of the solution, and on the mechanical arrangement, allowing more or less rapid diffusion, etc. The following experiments are enough to show this. Wires of pure iron were cleaned with fine emery cloth, carefully wiped, and simply immersed in a ferric chloride solution.²⁸ They were under no artificial strain of any kind when measured.

TABLE 4.—*The electromotive force of iron in ferric chloride against the decinormal electrode.*

Piano wire (20).		Soft wire (21).	
Elapsed time.	E. M. F.	Elapsed time,	E. M. F.
	Volt.		Volt.
0 ^h 0.5 ^m	0.550	0 ^h 1 ^m	0.595
0 5	0.5725	0 5	0.608
0 10	0.576	0 10	0.610
0 30	0.585	0 15	0.610
0 40	0.588	15 55	0.718
17 0	0.743	16 40	0.716

During the first day hydrogen was steadily evolved from both wires, but the second day this side reaction was greatly diminished. As is seen in the table, the electromotive forces rose in these cases respectively 0.192 and 0.123

²⁸ Similar results were found by Finkelstein in 1902. (*Z. phys. Chem.*, **39**, 91).

volt. This rise would have been ascribed by Hambuechen to strain. Further experiment could add nothing to the argument. It will be noticed that even finally the potential was very far from the value in ferrous sulphate, 0.765.

Hambuechen's results are quite as irregular, as one would infer from these considerations. For example, the change in electromotive force, caused supposedly by tensile stress, varies in two cases from 0.004 to 0.056 volt, and yet in the former case the load per square inch was actually 600 pounds greater than in the latter. Hambuechen realized that some of his observed potentials were much larger than were to be expected, and therefore explained that "One of the assumptions it was necessary to make is that the stress equally affected the entire cross section, which is by no means the case, for it is the outside layer which is affected the most and would therefore give higher values of electromotive force than the calculated amounts." This is exactly the opposite assumption to that demanded by the reasonable explanation of Burr already quoted (p. 18).

From the theoretical point of view, the matter appears, then, to be more complicated than might be inferred from a hasty survey of it. One can not safely conclude that the potential on the surface of a wire is an index of the free-energy change in the interior of the wire; and one can not assume that the electrochemical behavior of wire while under stress is the same as when the stress is removed. Still further, one can not but believe that the permanent strain caused by a stress (that is to say, the energy potentialized by a stress) will differ in the case of impure iron from that in the case of pure iron. Moreover, it is by no means certain that energy stored in iron by change of internal structure is available as free energy.

Taking all these considerations together, and weighing also the electrochemical defects in some of the papers just discussed, it is apparent that none of these investigations furnish conclusive evidence concerning the magnitude of the changes of potential to be noticed on stretching a rod or wire. It is apparent, moreover, that this change is smaller than is usually supposed, although it is probable that a slight change of electromotive force is caused by a tensile strain of impure iron.

Qualitative evidence on this point is furnished by a paper entitled "The Effect of Strain on the Rate of Solution of Steel," published by Barus in the Bulletin 94 of the U. S. Geological Survey (p. 61), already quoted. He experimented with soft steel, hard-drawn steel, and the latter annealed; he determined the rate of solution by loss of weight, and he concluded his report as follows: "Summarizing the above results as a whole, it follows that the rate of solution of drawn steel is greater than the rate of the same homogeneous metal similarly circumstanced." In applying the results it

should be noted that steel alone, not pure iron, was experimented upon; that any speed of reaction in which two phases are involved is complicated by many disturbing factors; and that the tendency of iron to occlude hydrogen, discussed in a later section of this paper, must have added another complication.²⁹

Because our results obtained by applying both compressing and distending stresses upon pure iron had been chiefly negative, indicating very slight changes of free energy for large stresses, attention was now directed to the change of the other conditions of experiment, with the hope of tracing to these other conditions the fairly large changes of electromotive force actually to be observed in specimens of pure iron prepared in different ways.

THE EFFECT OF VARYING THE TEMPERATURE OF IGNITION.

It will be noticed on studying tables 2 and 3 that the electromotive forces of cells made from different samples of iron which were chemically alike varied between such wide limits as 0.780 to 0.794 volt, a range far beyond the limits of experimental error.

In tracing these differences back to their fundamental cause, the first clue was furnished by the different degrees of cohesion or compactness exhibited by the several specimens. When the four pieces of porous iron, the results from which are given in table 3, were removed from the cells at the completion of the electrochemical experiments, they were examined with regard to their cohesion by the simple method of resistance to pressure and to fracture between the fingers. It was thus found that No. 2 iron felt softest, No. 3 the hardest and firmest, and Nos. 1 and 4 somewhere between. Reference to the table shows that No. 2 had the highest electromotive force and No. 3 the lowest; hence a more powdery structure evidently went with greater tendency to dissolve. Repetition with other samples confirmed this view.

What, now, could be the cause of this difference in compactness of the different samples? It is well known that many substances, on being heated, begin to cohere at temperatures far below their melting-points, exhibiting the shrinkage commonly called "sintering." It is also well known that this effect becomes more and more noticeable as the melting-point is approached. Probably, then, these different samples had been subjected to different temperatures during their reduction. This relationship was easily confirmed by further experiment. Iron reduced at high temperatures was found to be far firmer in structure than that reduced at low temperatures. In order thus to find the highest potential attainable in this way, iron should obviously be

²⁹ In this connection attention is called to the interesting work of C. S. Burgess on the effect of impurities on the rate of solution, read at the recent meeting of the American Electrochemical Society, May, 1906.

reduced at the lowest possible temperature. Accordingly two samples were prepared, the first being very slowly reduced at a temperature well below 800° . In the second of these reductions the temperature was measured by a Le Chatelier thermopile laid under the boat containing the iron, and the highest temperature it indicated through a reduction lasting three days was 615° . The iron in boat No. 1 was of a clear gray color in those parts where the temperature became highest and dark blackish gray on the surface. All the iron in boat No. 2 was like the top of boat No. 1. Even the firmest iron in boat No. 1 could easily be crushed between the fingers.

Two samples of the light-gray material from boat No. 1 gave the following measurements:

TABLE 5.—*The electromotive force of porous iron reduced at low temperature.*

Sample 22.			Sample 23.		
Elapsed time.		E. M. F.	Elapsed time.		E. M. F.
		Volt.			Volt.
0 ^h	8 ^m	0.796	0 ^h	14 ^m	0.797
0	30	0.800	1	0	0.797
1	0	0.798	24	5	0.799
24	0	0.799	70	40	0.800
70	10	0.796	92	0	0.800

These values are somewhat higher (0.002 and 0.006 volt) than any obtained in previous work, and are further evidence in favor of believing that the low temperature of reduction really causes a product having a higher potential. The contents of boat No. 2 were found to contain much hydrogen, and will be discussed later.

Having thus shown that iron reduced at low temperature may give in combination with the decinormal electrode a potential as high as 0.800 volt, and that increasing temperature of reduction causes a steady decrease in this value until the metal prepared at perhaps $1,200^{\circ}$ gives a value as low as 0.776, it became a matter of interest to discover if iron subjected to a still higher temperature might not give a still lower value. The obvious subsequent step was therefore to test iron which had been fused, and accordingly several specimens of the purest commercial iron (Swedish bar iron and pure piano wire) were tested in preliminary experiments. The Swedish bar iron was very pure, and soon reached a constant value. The piano wire was less regular, and hence was examined more thoroughly. The wire was "hard drawn," and its purity was indicated by the fact that when heated to $1,000^{\circ}$ in hydrogen and quenched in ice-water it was as soft and pliable as the purest iron. Two pieces of this wire were scraped bright and clean with a

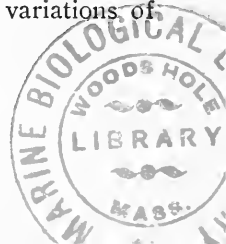
dull knife and measured as usual in a cell shown in figure 3, page 10. The potential of these cells began at very low value, and gradually rose to a constancy at about 0.76 volt. It was evident that the end-point is reached only after a long time; and accordingly six wires were sealed up in ferrous sulphate solution. Three of these had been scraped as before to clean them and the other three were rubbed with fine emery cloth, all of them being carefully wiped with a cloth before immersion. Below are given the final constant values attained by these samples:

TABLE 6.—*The electromotive force of commercial iron of moderate purity.*

Elapsed time.	Swedish bar iron.	Piano wire (hard drawn).					
		Sandpapered.			Scraped.		
	No. 24.	No. 25.	No. 26.	No. 27.	No. 28.	No. 29.	No. 30.
	Volt.	Volt.	Volt.	Volt.	Volt.	Volt.	Volt.
3 hours....	0.765
1 day.....	0.770
3 days....	0.770	0.762	0.762	0.762	0.767	0.769	0.765
4 days....	0.762	0.762	0.762	0.763	0.767	0.765
7 days....	0.763	0.763	0.763	0.765	0.767	0.763

Thus all these samples yield a result lower than the most compact of the sintered samples. The results show excellent agreement, and the number 0.765 volt may be taken as the true electromotive force of the cell made from this wire. The Swedish iron gave a slightly higher value, about 0.770. A third sample of commercial iron, the softest and purest wire obtainable, was next examined. It was cleaned with fine emery cloth and wiped with a clean cotton cloth. Two specimens after two days gave respectively 0.760 and 0.771 volt, or in mean 0.766, essentially the same as before.

Thus all the commercial compact samples of iron showed a distinctly lower solution tension than any of the spongy pure samples. Before this difference could be certainly ascribed to any peculiarity in the freshly reduced spongy iron, proof must be afforded that it was not due to impurities in the commercial samples. This possibility was most conveniently subjected to trial by fusing a sample of pure reduced iron, and comparing the product with the commercial sample. At first an attempt was made to prepare pure fused iron by fusing a small quantity in a small lime crucible in an oxyhydrogen flame. The hydrogen used was very pure, having been made by electrolysis, for impurities would be taken from the gas by the fused iron. The flame was so directed as to cover the iron completely and was provided with excess of hydrogen, but nevertheless all the iron oxidized. The oxide unfortunately did not act as a protection to the iron underneath, because it fused and was absorbed by the porous lime. No acceptable variations of



apparatus or manipulation greatly bettered the result, which could have been easily accomplished with larger quantities of material. Therefore another method was tried, namely, the melting of the iron in a vacuum by means of the heat generated by its own resistance to a great electric current. Besides an apparatus suitable for exhaustion, the essentials for success were iron electrodes, a suitable crucible, and a sufficiently high current. Bundles of piano wire provided the electrodes, and a nest of powdered iron, supported on a crucible of lime made from the purest marble, was used to contain the melted particles. In order to increase the resistance of the metal it was powdered in the Hempel steel mortar, and the current was passed through this powder. The arrangement of the apparatus and its description are given in figure 5.

The operation of the experiment was as follows: After everything was arranged as shown in the figure, the Sprengel vacuum-pump was started and the stoppers thus firmly forced in. This, however, disarranged the electrodes and air was again admitted, so that they could be carefully placed at the desired places in the lime boat. The apparatus was now evacuated a second time and the current turned on. For some time nothing happened, but finally the metal fused with the help of vigorous jarring. More and more powder was added from above as the fusion progressed. There were brilliant flashes of violet light with each addition of powder, followed by bright-red glowing. By feeding powder into the open spaces left by the fused material it was possible to maintain the fusion almost continually until the supply was exhausted. The product consisted mainly of small pellets about the size of the head of a pin or a little larger, resting in the nests of pure powdered iron. Only one was large enough to use conveniently in a cell. Nevertheless, this gave a result agreeing so well with that from the commercial materials that a duplicate seemed unnecessary. The sample was covered with soft paraffin on those parts which did not have a smooth fused surface.

TABLE 7.—*Pure iron fused in vacuum.* (33).

Elapsed time.	E. M. F.	Elapsed time.	E. M. F.
	Volt.		Volt.
0 ^h 7 ^m	0.745	40 ^h 40 ^m	0.761
0 9	0.750	41 30	0.759
0 20	0.757	72 10	0.763
0 40	0.760	90 25	0.761

Thus this sample of exceedingly pure iron fused in vacuum gave essentially the same potential as good quality commercial material (0.765).

This iron must have been wholly free from carbon, from any other metal, and indeed even from all but the merest trace of hydrogen. It is hence clear that the impurities in the commercial iron could not have been enough to affect its electromotive force, and that pure, compact iron really gives a lower value than the same iron reduced by hydrogen. To what cause, then, is this difference to be ascribed? Is the higher solution tension of the spongy iron due to the traces of hydrogen within it, or to difference of internal structure, or to the disposal of its external surface?

The first of these three possible causes of an extraordinarily high potential does not seem to be a very probable one; nevertheless, it seemed worthy of test, especially in view of the results on occluded hydrogen to be recorded later. Accordingly, several samples of spongy iron were ignited for varying lengths of time at varying temperatures in a vacuum, while inclosed in a stout porcelain tube. It was thus found that while short ignition or ignition at a low temperature left much of the gas in the metal, treatment at a higher temperature for a longer time seemed to remove nearly all of it, while causing the iron to sinter into a compact mass. Iron thus treated at $1,160^{\circ}$ gave in conjunction with the decinormal electrode the usual potential 0.787 in a few hours, a value which remained unchanged even in the last decimal place after ninety hours. Even this iron, however, undoubtedly contained traces of hydrogen, although much less than at first.

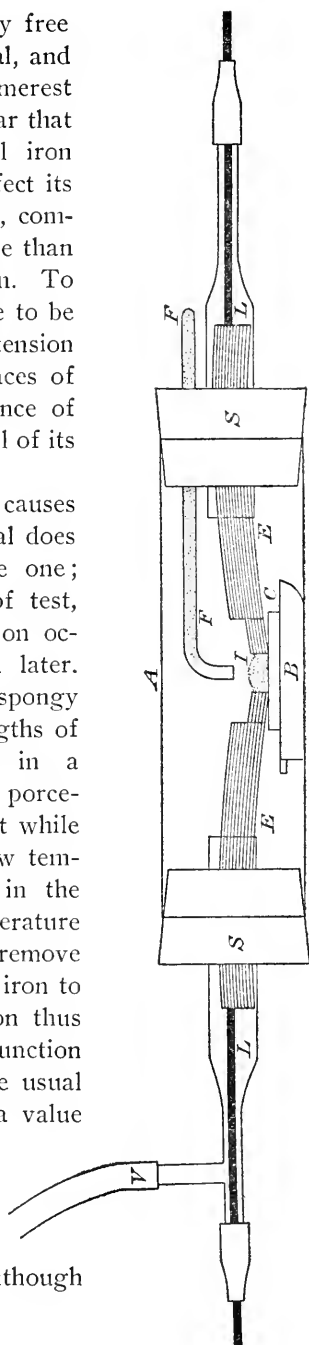


FIG. 5.—APPARATUS FOR FUSING IRON IN VACUUM.

- A, Lamp chimney.
- V, Tube to vacuum pump.
- L, L, Leads to dynamo.
- Z, Z, Piano-wire electrodes.
- S, S, Rubber stoppers (these were protected by several thicknesses of asbestos board).
- B, Porcelain boat.
- C, Lime crucible.
- F, Iron powder to be fused.
- F, Feed glass tube filled with powder, operated by jarring.
- Scale about one-third natural size.

The permanence in the value in the potential is in itself the best evidence that the hydrogen, even if present, is so shielded from the electrolyte as not to affect the measurement of electromotive force. It is improbable that a trace of occluded gas could exercise a lasting effect in maintaining the potential above that of the reversible electrode of iron in its sulphate. This matter will be discussed in detail in the second section of the paper.

There are two other hypotheses capable of explaining the abnormal potential of the spongy iron. It is certain that the "sintering" is increased and the surface of the iron diminished in this way; and it is possible that change in the degree of polymerization of the iron, resulting in the formation of a more stable modification, is likewise effected.³⁰ Either of these changes might affect the electromotive force. A method of deciding between these two would demand either the formation of compact iron at low temperature, or else of loose spongy iron at high temperature—and neither is capable of certain preparation. The former was nearly obtained in the experiment first recounted, in which the spongy iron was rendered compact by great pressure; the latter can hardly be obtained by mechanical subdivision.

It is to be noticed that of the first three specimens used in the experiments recorded in table 3, the untouched porous pieces gave an average potential of 0.783, while the same pieces after cold-welding at very high pressure gave the essentially identical value 0.782. The cold-welded pieces were very hard and tenacious, and appeared qualitatively in every way similar to iron which had been fused (which gave only 0.765 volt); but it is not certain that some particles on the surface were not as loosely coherent as in the sponge, and hence capable of giving as high a potential. It is true that one fact militates against this possibility—the fact, namely, that the compressed pieces steadily rose to the maximum potential and staid there a long time, which could have hardly been the case if the high potential had depended upon a few particles.

Because of the experimental difficulties it is impossible now to decide definitely between these possible causes of difference between the spongy and compact metal. It is possible that all three are superposed; but of the three,

³⁰ The allotropic theory of iron need not be discussed here. It has satisfactorily explained so many phenomena and has had such wide usefulness that it is universally accepted by scientific metallurgists. Its theoretical side from the standpoint of the phase rule is thoroughly treated by Roozeboom, *Z. f. Phys.*, ch., 34, 436 (1900). The metallurgist's use of it is shown by Baron von Jüptner in his work "Grundzüge der Siderologie," vol. 2, 1901. See also *Berichte der d. Chem. Gesell.*, 39, 2381 (1906).

A short explanation of the terminology may not be out of place. Pure iron has at least two well-defined transition points. Iron stable below 766° is known as alpha iron, between 766° and 895° as beta iron; and the phase formed above 895° is called gamma iron.

the writers are rather inclined to believe that the chief cause is probably the state of subdivision—the very finely divided particles giving a higher electromotive force than the fused mass.²¹ If this is true, the case is one of great interest because of the magnitude of the effect, corresponding as it does to a tenfold greater solubility of the finest particles.

In this connection it was deemed worth while to test the electromotive force of iron which had been suddenly cooled or quenched. In this way it might be found whether or not pure iron, when suddenly cooled, could be caught in a condition of internal structure less stable than when cooled slowly.

Preliminary experiments, to be recounted later in another connection, showed that in order to obtain significant results for this purpose the heating and sudden cooling must occur in the absence of any foreign substance capable of reacting upon the iron; therefore the metal must be quenched in the absence of any gas or water.

The apparatus needed was not complex. A stout tube of Berlin porcelain was clamped in a vertical position, closed at both ends by Hempel water-cooled stoppers, and was heated in the middle by an encompassing perforated Fletcher furnace. The temperature was registered by a platinum-rhodium thermopile. The porcelain plate on which the test-pieces of iron were laid was suspended in the middle of the tube by an iron wire on one side and a small silver wire on the other. On the lower Hempel stopper lay a smooth, thick iron plate, and ice-cold water was circulated through the stopper, while the whole lower end of the tube was packed in ice. The apparatus was now evacuated with a Sprengel mercury pump, and when the pressure had fallen to less than 1 mm. the tube was heated. For ten minutes the temperature was kept above $1,000^{\circ}$; the silver wire was melted and one side of the porcelain plate was dropped. The iron of course fell from this region of high temperature to the cold iron plate. The apparatus was left to cool over night, without the admission of a trace of air. The two pieces of iron when put in had been blackish-gray and very loosely knit together; when taken out they were quite cohesive and of a clear-gray color, exactly resembling iron which had been reduced in hydrogen above 700° . This illustrates the effect of sintering and proves that the original dark color of the iron powder was not due to incomplete reduction, but solely to its state of division. One surface of one of the two pieces was found lying flat on the cold iron plate and this one was immersed in ferrous sulphate and measured. It gave in eight minutes a potential of 0.788, which slowly rose to 0.805 in an hour, and then settled down to constancy at the value of 0.795.

²¹ Ostwald, *Zeitschr. für Phys. Chem.*, **34**, 45 (1900); Hulett, *ibid.*, **37**, 385 (1901).

In repeating the experiment two improvements were introduced. For fear that some silver might have volatilized and contaminated the iron, the silver-wire support was replaced by a simple mechanical device, one side of the porcelain plate supporting the iron being held in place by a pipe-stem, while the other side was attached to an iron wire running through a lubricated hole in the stopper. By pulling the wire the iron could be dropped. Furthermore, quick and effectual cooling was obtained by surrounding the outside of the base of the porcelain tube, containing the iron cooling-plate, by a mixture of chloroform and solid carbon dioxide. Time was allowed for the thorough cooling of the inclosed iron plate. The temperature of porous iron was thus almost instantaneously lowered from $1,100^{\circ}$ to -75° or thereabouts. Great pains was taken to exclude the vapor of water, which would have condensed in the cold part of the tube and vitiated the experiment. This was accomplished by running a stream of pure dry hydrogen through the tube for many hours.

As soon as possible after the fall of the porous iron, which took place this time in an atmosphere of hydrogen, the pieces were taken out, immersed in ferrous sulphate, and measured in the usual way. In six minutes after immersion the potential was 0.790, in twenty minutes 0.796, and in an hour 0.798. After a day it settled down to perfect constancy at 0.793 volt, essentially identical with the result of the previous experiment. This is not enough above the usual value (0.787) obtained from iron slowly cooled from the same high temperature to allow the conclusion that the sudden cooling had made any considerable difference in the potential or difference in internal structure.

It becomes now an interesting question as to which of the many values for the gradually changing potential of the cell $\text{Fe}, n\text{FeSO}_4, n/10\text{KCl}, \text{HgCl}, \text{Hg}$ correspond to the true values of the solution tension of the different forms of iron. Consideration shows that the final high values are probably to be taken in each case, for several reasons. In the first place, these values are approached asymptotically, and are then maintained at a constancy for a long time. For example, one sample of iron which in 16 hours had given in the cell a potential of 0.793 volt, after 150 hours more was still practically unchanged at 0.792 volt. In the next place, the different kinds of iron, although sometimes beginning at impossibly low values, all finally rise to nearly the same point. Again, it is not conceivable that the iron should gradually raise itself to a potential above its true value and maintain itself there in a reversible reaction with a large excess of both iron and ferrous sulphate at hand, while it is easy to see that a coating of oxygen would lower the potential at first. The conclusion is, moreover, reinforced by the fact that the same potential is attained from the opposite direction by the gradual

falling off of a higher potential artificially and temporarily created in the metallic electrode with the help of hydrogen conveyed to the system from without, as will be explained in the succeeding section of the paper. Hence there can be little doubt that the potential of porous iron reduced at about $1,000^{\circ}$ and immersed in normal ferrous sulphate is really as high as $0.79 - 0.612 = 0.18$ volt, if the decinormal calomel electrode is taken as 0.612, the normal calomel electrode being taken as 0.56. Pure iron which has been fused in a vacuum gives a value nearly 0.03 volt lower, or about 0.15 volt. This latter value, corresponding to the flat surface of a coherent mass, is the one to be chosen ordinarily as the normal value. Even this is nearly twice as large as that usually ascribed to it. The errors of the work of others were probably insufficient time of immersion and the presence of acid in the electrolyte, both of these tending to lower the observed value, as is shown above.

PART II. THE ELECTROMOTIVE FORCE OF IRON CONTAINING OCCLUDED HYDROGEN.

The fact that hydrogen freely penetrates iron at red heat and that iron retains some of this hydrogen on cooling was discovered as long ago as 1866 by Graham; but the more detailed study of this and related phenomena has been undertaken only in recent years, after its importance in the metallurgy of the metal had been established. Many papers have been published on this topic, but the field has been by no means thoroughly treated.

Our attention during this research was first directed to the well-known affinity of iron for hydrogen by observing the copious evolution of this gas from metal reduced at a low temperature.⁸² Iron obtained from the oxide at 570° is, as well known, a fine powder, which oxidizes easily, and hence after even a short exposure to the air gives a low electromotive force. In order to test properly the free energy of such iron, it must be cooled in pure hydrogen and tested instantly after opening the reduction-tube. In this way it was found that the potential is not essentially different from iron reduced at 700°, being about 0.795 volt in conjunction with the decinormal electrode.

Nevertheless, such powder, upon immersion in ferrous sulphate evolved copious bubbles of gas, which were proved to be hydrogen. That this hydrogen was not in any extraordinary condition is shown by the fact that it neither altered the potential of the iron nor caused the iron containing it to produce any unusual reducing effect on mildly oxidizing solutions. It is probable that the hydrogen thus held by the fine powder was merely adsorbed, as the gas is adsorbed by charcoal.

That the gas could exist in the metal in a radically different condition we did not at first suspect; but this conclusion was forced upon us by the surprising and quite unexpected results of several other experiments.

In the first place, several pieces of porous iron which had been reduced at high temperature, slightly oxidized by long standing in the air, and then reheated in hydrogen at 575° gave at first an extraordinarily high value for the usual cell couple, namely 0.825. In seven hours this had decreased to 0.810, and in five days became constant at 0.798, essentially the normal value.

⁸² Baxter has shown that pure iron reduced at a high temperature contains but little occluded hydrogen. *Am. Chem. Journ.*, **22**, 363 (1899).

A slight indication of an excessive value of this kind had already appeared in other previous samples, many of which after a short immersion in ferrous sulphate showed a slight maximum. This was noticeable even in samples which had been ignited in a vacuum. In the cases mentioned at the beginning of this paragraph, after standing some time, bubbles of hydrogen appeared around the metal, as the electromotive force decreased. This seemed to show that in some way the excessive electromotive force was connected with hydrogen. But hydrogen gas has a lower, not a higher potential than iron. Therefore, it is clear that if the abnormality is produced by hydrogen, this impurity must exist in the metal in a different form—no longer as merely adsorbed gas on the surface of the fine powder, but in some new state, inclosed in the less open structure of the sintered iron.

More light was thrown upon all these matters by interesting series of experiments which showed that the dissolved active hydrogen could be more easily introduced into the iron in other ways. There follows a brief description of these experiments.

The first series furnishing this further light was a set of experiments originally begun as a preliminary attempt to cause a change in the internal structure of iron by quick cooling. In it iron was plunged while hot into water.

In order to quench iron suddenly from a high temperature without coating the metal with a hardly soluble film of oxide, it was clearly necessary to conduct in an atmosphere free from oxygen both the heating of the metal and the transference to the cooling agent.

An atmosphere of hydrogen was first used for this purpose. As before, a stout tube of Berlin porcelain was erected in a vertical position, the middle portion being heated by a Fletcher furnace. Pure electrolytic hydrogen, thoroughly washed and dried, was supplied at the top of the tube through a cooled Hempel stopper, which was further protected against the rapid convection of hot hydrogen by a pipe-bowl suspended at the upper limit of the heated zone by means of an iron wire. The iron was heated at first in an unglazed basket of the best porcelain, and in the later experiments on a shelf or disk of the same material. Simple mechanical devices as before enabled the iron to be plunged or dropped quickly into the cooling agent at the base of the tube. The temperature of heating was determined by a Le Chatelier platinum-rhodium thermoelectric junction. Cold boiled water was used as the cooling agent at the base of the tube, the operation being, therefore, merely the quenching of pure iron without exposure to oxygen gas.

Even the first experiments gave interesting results. Porous iron reduced at 800° was quenched from $1,000^{\circ}$. Twenty minutes afterwards the super-

ficially oxidized sample was immersed in ferrous sulphate and half an hour later it gave the value 0.89 volt against the decinormal electrode, instead of only 0.79 as before. This extraordinary value was only temporary, the electromotive force falling rapidly, at the end of one hour being 0.825 volt and of five hours, 0.803. Three other pieces quenched at the same time gave similar results. Because the electromotive force fell rapidly it appeared possible that an immediate reading might have given even higher results. A repetition of the experiment with frequent readings was evidently very desirable.

The second quenching was a repetition of the first. To remove the adhering water after the operation, the samples of iron were rinsed for a minute or two in ferrous sulphate solution before putting into the cells, thus preventing dilution of the normal solution in which they were measured. The results verified those of the first quenching, but added to them, in that the later ones showed the speed of decrease in potential to be much less in the first half hour than afterwards. The potential started at about 0.9 volt, and after remaining almost constant for thirty minutes began to fall off rapidly. A number of other similar quenchings were made, most of which gave similar results, only a few showing no excess of potential. Typical examples are given in the following table, under the heading, Sample 44.

Further experiments were made to determine if the temperature before quenching caused any considerable effect on the results.

The apparatus used was the same as the one which served in the previous experiments. One sample was quenched from 695° and another from 600° . In both cases the quenched iron rose to a maximum electromotive force less strikingly above the normal value, the former attaining 0.87 volt and the latter 0.82 volt, which potentials, as usual, settled down to the normal values of 0.795 in the course of half a day. These experiments showed that the excessive value of the electromotive force was directly dependent upon the temperature before quenching, a higher temperature giving a greater excess. They added to the evidence already given that the "gamma" or high-temperature phase of iron could have nothing to do with the excessive values, because the latest quenching occurred from a temperature below the recognized transition point. It will be remembered in this connection that pure iron quenched from $1,100^{\circ}$ on a cold iron plate gave normal values for its electromotive force.

The experiment was next made of reheating the quenched iron in hydrogen in order to discover whether or not it would return to its normal condition. Two pieces of this same quenched iron were thoroughly dried in alcohol and ether and three days later were reheated in hydrogen for one hour (the highest temperature being faint redness) and then slowly cooled.

The results, together with those of the previously described quenched iron, are given in the following table:

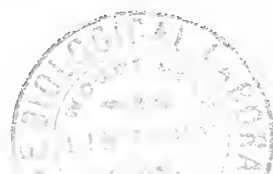
TABLE 8.—*The effect of reheating quenched iron.*

Time elapsed after immersion.	Sample 44, quenched, not reheated.		Sample 45, reheated iron.	Sample 46, reheated iron.
	Fresh.	Exposed to air.		
	Volt.	Volt.	Volt.	Volt.
0h 3m	0.880	0.79	0.796	0.794
0 11	0.910	0.80	0.800	0.801
0 20	0.906	0.90	0.800	0.804
0 45	0.890	0.89	0.797	0.804
2	0.810	0.81	0.797	0.803
4	0.797	0.80	0.797	0.802

It is clear at once that samples 45 and 46 had once more acquired the same condition they possessed before they were quenched—as was to be expected. Thus there can be no doubt that the reheated iron returns essentially to its normal condition.

From these experiments it was clear that something, either chemical or physical, had happened to the iron during its heating and plunge into water which caused it to assume an excessive potential. Two possible causes might underlie these interesting results. Either the sudden cooling might have preserved the iron in an unstable allotropic form yielding a higher electromotive force, or else occluded hydrogen might in some way be responsible for the differences. The former of these explanations was disproved by the already described experiments on cooling iron in a vacuum on a cold iron plate. Hence only the latter explanation remained, and the phenomenon was obviously to be classed with the occlusion of hydrogen from the hot gas.

It now became an interesting matter to find whether this hydrogen came from the hydrogen gas or from the water during the instant of quenching. This was easily decided by an experiment in which the metal was heated in and quenched from an atmosphere of *nitrogen*. The quenching apparatus was exactly the same as that used in all the previous experiments. The nitrogen was prepared by Wanklyn's method of blowing air through aqua ammonia, passing this ammoniacal air over hot copper gauze, and purifying the resulting nitrogen in the usual way. All rubber used in the apparatus had been boiled in caustic solution and was thickly coated on the inside with the semi-solid paraffin. In this apparatus a typical sample of porous iron was heated for twelve minutes in nitrogen at a temperature of 1,040° and was then quenched in ice-water. Of the two pieces thus quenched, one was



immersed in the ferrous sulphate solution five minutes after quenching, while the other was thoroughly dried in alcohol and ether and put into the cell to be measured on the following day.

The results agreed in a general way with those already obtained by quenching from an atmosphere of hydrogen. They differed in two respects. The maximum electromotive force was 0.03 volt higher than any other thus far obtained, rising to 0.94 volt, and this high electromotive force was retained for a much longer period of time. These are differences in degree only, and since the other results differed among themselves, although to a less extent, the higher value is to be ascribed merely to more favorable experimental conditions.

Could the formation of iron nitride in any way have produced the high potential in this case? Reflection promptly decided this question in the negative. Iron nitride is formed only at low temperatures and is decomposed even in a stream of ammonia at higher temperatures; "free nitrogen is not able to unite with iron, even when the latter is reduced in nitrogen, and the formation of nitride is dependent on the coming in contact of nascent nitrogen with iron."³³ Moreover, the nitride begins to decompose in a stream of nitrogen at 600°, and the nitride Fe_2N is an exothermic compound. Hence probably it has a lower electromotive force than iron,³⁴ not a higher one, and the nitride is evidently out of the question.

Upon standing in ferrous solution the quenched iron evolved an appreciable volume of gas, which was shown to be hydrogen by explosion with oxygen in a micro-eudiometer.

In view of this fact, and because iron quenched from nitrogen gave the same high potential as iron quenched from hydrogen, there can be no doubt that the bulk of the occluded hydrogen must have come from the water at the moment of quenching. Some of the iron must have been oxidized, and the resulting nascent hydrogen must have dissolved in the iron, in its active state. No other explanation seemed to be compatible with the extraordinary potential observed.

Other workers on this subject (for example Heyn,³⁵ who found that hydrogen exists in iron quenched from above 730° in an atmosphere of hydrogen) have usually supposed that the occluded impurity was taken from the gas and not from the water, but our experiments show conclusively that the water is the source of the greater part of the hydrogen.

³³ Stahlschmidt, Pogg. Ann., 125, 37 (1865).

³⁴ Assuming total energy change to be an approximate guide to free energy change in reactions of this kind.

³⁵ Stahl und Eisen, 20, 837 (1900). See also Roberts-Austen, Fifth report of the Alloys Research Committee, Proc. Inst. Mech. Eng., 1899, p. 35.

The discovery that in this case nascent hydrogen may be absorbed more freely than the gaseous material by iron at once reminded us of the well-known absorption of the light element by metals used as a cathode in acid solutions. Cailletet³⁶ and Johnson³⁷ showed in 1875 that iron will take up at ordinary temperatures electrolytic hydrogen deposited upon it, while ordinary gaseous hydrogen has no effect. Johnson's work was particularly interesting. His iron was in the form of soft wire and his simple method of testing for hydrogen was to bend the wire to test its brittleness, since he had discovered the interesting fact that hydrogen imparted this property to iron previously tough. Immersing the wire in acids which react on it to form hydrogen uniformly made it brittle. Also when the fractured surface was wetted with water it was seen to froth. Making the wire the cathode in neutral, acid, or alkaline solutions had the same effect, but iron anodes were unaffected even in the acid solution. Other wires were placed in a bottle full of water and hydrogen was made to bubble violently through the water, without any trace of absorption.

Another interesting research yielding similar results was conducted by Bellati and Lussana.³⁸ A barometer was closed at the top by an iron plate, and by cementing a glass ring on this an electrolytic cell was made in which hydrogen was generated at the iron plate; the mercury at once fell by diffusion of the hydrogen through the plate into the barometric vacuum. This work was later confirmed and amplified by Shields.³⁹

In view of these phenomena, it became a very interesting point to discover if the active hydrogen introduced into cathode iron from solution is capable of raising the potential of a normal cell to the value of 0.93, that observed with spongy iron quenched from 1,100° in nitrogen. Shields had already observed that this occluded hydrogen raised the electromotive force of the iron above the normal value, but the maximum had not been determined.

This point was easily tested. In order to obtain satisfactory evidence it is of course necessary that iron alone should be immersed as cathode; the platinum wire supporting it must be above the liquid. Preliminary experiments showed that a large excess of potential is as a matter of fact attained, but that it falls off with very great rapidity. Spongy iron which had been

³⁶ Comptes rendus, 80, 319 (1875).

³⁷ Proc. Roy Soc. (London), 23, 168 (1875).

³⁸ Bellati and Lussana, Z. Phys. Chem., 7, 229 (1891).

³⁹ Shields, Chem. News, 65, 195 (1892). Further discussion of this matter will be found in papers mentioned later; see also Hoitsema, Z. Phys. Chem., 17, 1 (1895); Winkelmann, Drude's Ann., 8, 388 (1902); Richardson, Nicholl and Parnell, Phil. Mag. (6), 8, 1 (1904). St. Schmidt considers the assumption of a split of the hydrogen molecule to be unnecessary and unwarranted. (Drude's Ann., 13, 747 (1904).)

made the cathode of a dense current in an acid solution for an hour was quickly washed with neutral ferrous sulphate, and was measured as soon as possible. In half a minute after immersion it had sunk to 0.822 volt, in four minutes later 0.800, and in an hour to constancy at 0.790. Evidently the hydrogen is only very superficially deposited, and most of it is gone before measurement is possible. Longer exposure as cathode might have more effect. Much more striking results were obtained from electrolytic iron obtained from a neutral solution with the help of a current so dense as to deposit hydrogen with the iron. Such a specimen (sample 48), measured about three seconds after the breaking of the current, gave a potential of 0.93, equal to that observed in the quenched iron. In a minute this had sunk to 0.85 volt; but even after an hour it remained as high as 0.83 volt, not sinking to about the normal value 0.798 for several days.

Thus it is clear that as far as potential measurements can show, the hydrogen driven into iron with the help of electrical energy is essentially similar to that absorbed in the act of quenching, although the latter operation seems to be especially favorable to the occlusion. Probably the action of the red-hot core upon the steam produced by the exterior of the porous metal supplies the nascent hydrogen to the iron at a temperature especially suitable for occlusion.

It is interesting to note that even without outside electrical assistance hydrogen in this active form may be taken up by iron from acid solutions. Upon immersing the metal in an acid solution of ferrous sulphate, hydrogen is of course evolved, and the potential of the iron while still in the acid is lowered as much as two decivolts—evidently by the coating of gas, for hydrogen gas has a potential much lower than iron. But besides this superficial effect, a more deep-seated one is occurring, as is easily shown.

Upon removing this iron quickly to a neutral solution of ferrous sulphate and measuring at once, its potential is found to be above the normal value, the usual cell often reading as high as 0.83 instead of 0.78 or 0.79. In a few hours it settles down as usual to its normal level, evolving in the process bubbles of hydrogen gas. The iron alone could not of course raise the active hydrogen which it absorbs to a concentration above that capable of giving an electromotive force equal to its own (0.79 with the decinormal electrode), but with the help of the osmotic pressure of the ionized hydrogen in the acid more hydrogen is driven in. This excess manifests its potential and changes to hydrogen gas when the surrounding acid is removed. As a change of only tenfold in the concentration of the ionized hydrogen would be expected to produce a change of potential of nearly 0.06 volt, the observed effect is by no means excessively large. Stated in another way, it may be

said that the hydrogen taken in by iron from an acid solution is in equilibrium with *nascent* hydrogen, and therefore possesses a high chemical potential.

In the course of the quenching experiments it was found that iron charged with active hydrogen lost its impurity much more quickly when immersed in ferrous sulphate than when immersed in water or kept in air. This interesting fact seemed worthy of more careful study, because it might be capable of throwing light on the singular occlusion. Accordingly the following series of experiments was instituted upon six pieces of iron, all quenched at once under such conditions that all were exactly alike:

Piece No. 51 was immersed in ferrous sulphate and measured immediately after quenching. Its electromotive force began at about 0.8 volt, gave the maximum value 0.91 volt after a few minutes, and then fell off as before, reaching 0.90 volt in half an hour and 0.793 volt in four hours.

No. 52 was left in the water in which it was quenched for an hour and twenty minutes before measurement. When the electromotive force had reached its maximum of 0.90 volt after 26 minutes subsequent immersion in ferrous sulphate, No. 51 had passed that point over an hour and a half before.

No. 53 was also left in water and was first measured after two hours and forty minutes had elapsed. By the time it gave its highest electromotive force, 0.91 volt, No. 1 had dropped to 0.803 volt.

No. 54 was left in water for 26 hours and then immersed in ferrous sulphate. It behaved but little differently from No. 53, but its maximum was lower, being only 0.85 volt. Before its immersion all the preceding had reached their constant values 0.795.

No. 55 was thoroughly dried in alcohol and ether immediately after quenching and kept in a desiccator an equal length of time (26 hours) before measurement. This specimen began at 0.79 volt, rose regularly to 0.88 volt in two hours, and reached 0.80 volt again in twenty-four hours.

No. 56 also was immediately thoroughly dried and was measured after 73 hours, giving a similar but less marked maximum (0.85 volt).

The whole series of experiments was then repeated with essentially identical results.

The comparison of the results of these series of experiments shows that mere exposure to dry air slowly lowers the high electromotive force due to quenching, that pure water hastens this lowering a very little more than exposure to the air, but that immersion in ferrous sulphate quickly establishes equilibrium. The more typical of these experiments, with some of the previous ones, are plotted in figure 6.

It became now an interesting matter to discover if any other electrolyte

would effect the adjustment of equilibrium as quickly as the ferrous sulphate. In an easily carried out variation on the preceding series, a normal solution of potassic sulphate was used as a typical electrolyte. Brief immersion in this solution seemed to show no more effect in discharging the hydrogen than in water, but long immersion showed a slight difference in favor of the electrolyte. The rate was nevertheless so much slower than that observed in the case of ferrous sulphate as to indicate entirely another mechanism of reaction.

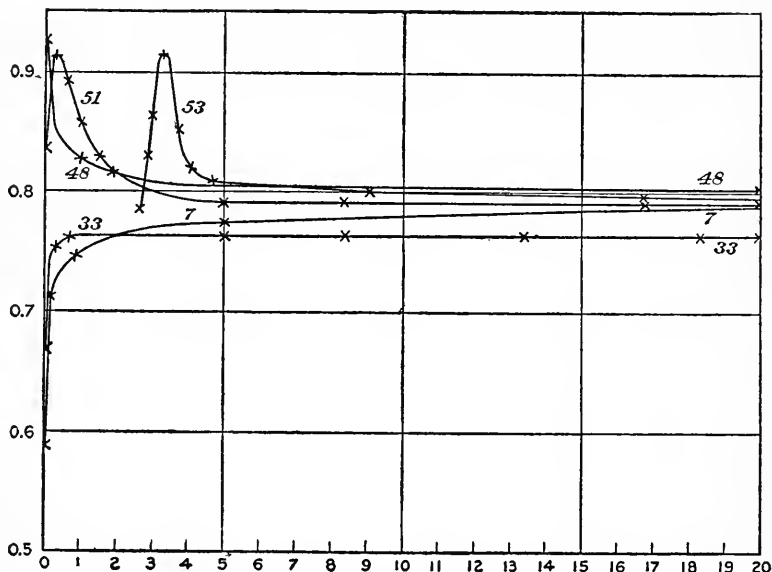


FIG. 6.—THE CHANGING POTENTIAL OF THE IRON ELECTRODE.

In the direction of ordinates are plotted the potentials of the iron electrodes in normal sulphate, in combination with a decinormal calomel electrode. Time in hours is plotted in the direction of abscissae. The curves are typical, No. 7 of porous iron which has been exposed to air, No. 33 of pure fused iron, No. 48 of porous iron which has been made a cathode, No. 51 of porous iron quenched in water, and No. 53 of the same after exposure to air for 2½ hours.

The progress of the evolution of the gas in ferrous sulphate may be supposed to be as follows: The active hydrogen, having a higher potential than the iron, causes metal to deposit from the ferrous sulphate, and the acid thus formed immediately attacks the deposit, or a neighboring portion of metal. Without the interposition of the iron as carrier, the hydrogen seems to find it difficult to go from its occluded to its gaseous state. When an electrolyte which contains no easily deionized cation is substituted for the ferrous sulphate, the reaction involving deposition can not take place, and the hydrogen remains in its occluded condition.

These considerations show further that the final potential which the iron attains after long immersion in ferrous sulphate is probably the true potential, because, since both iron and ferrous sulphate are greatly in excess, the equilibrium finally attained must correspond to these two alone. Even if some dissolved hydrogen is retained by the iron it can not possess a permanent potential above that of the iron. That this is true is shown by the fact that quenched iron finally attains a potential equal to that finally attained by a similar sample which has been long exposed to the air—one approaching this value from above, the other from below.

The attempt to explain the nature and condition of the active hydrogen in iron is assisted by a suggestive paragraph which occurs in a paper by Thos. Graham⁴⁰ "On the relation of hydrogen to palladium and on hydrogenium":

The chemical properties of hydrogenium⁴¹ also distinguish it from ordinary hydrogen. The palladium alloy precipitates mercury and calomel from a solution of the chloride of mercury without any disengagement of hydrogen; that is, hydrogenium decomposes chloride of mercury, while hydrogen does not. . . . Hydrogenium (associated with palladium) unites with chlorine and iodine in the dark, converts red prussiate of potash into yellow prussiate, and has considerable deoxidizing powers. It appears to be the active form of hydrogen as ozone is of oxygen.

Of these chemical tests one was easily extended to hydrogen contained in iron. It was found that carefully cleaned pure iron wire, and also porous iron which had been kept for a year in the pure air of a desiccator over potash, had no appreciable tendency to reduce neutral potassic ferricyanide. Even after the iron had stood in a solution of this salt for five days the solution gave no precipitate with ferric chloride. Such iron was evidently practically free from active hydrogen. On the other hand, iron which had been freshly made showed a marked reducing tendency, and this tendency was even greater in quenched iron and iron which had been used as a cathode (or had been simply immersed in acid) and thoroughly washed. These results are quite in accord with the potential measurements already recorded, and furnish additional evidences of active hydrogen in freshly reduced or quenched iron, but point to its absence on the surface of iron long exposed to the air.

In what form may this hydrogen be supposed to exist? Ramsay was perhaps the first to suggest that hydrogen undergoes dissociation when passing through a hot metal, or through one made a cathode in acid solution.⁴² Our experience supports this hypothesis, and seems to be explicable in no

⁴⁰ Proc. Roy. Soc. (London), 17, 219 (1869); Collected Papers, p. 290-299; Pogg. Ann., 138, 49 (1869).

⁴¹ Hydrogenium = hydrogen in a metal.

⁴² Sir William Ramsay, Phil. Mag., 5, 38, 206 (1894).

other way. In one respect only does Ramsay's opinion appear questionable, namely, in his assumption that the dissociated gas is ionized.⁴³ In recent years the word ion has been used in so many senses that an unfortunate vagueness has crept into its definition; but the idea of ionization seems always at least to be associated with electric charges. Now, in this case there seems to be no need of assumption of an electric charge on the occluded hydrogen atom; indeed it is hard to see how much a charge could be held in the midst of so good a conductor as iron. To the writers it appears much more probable that the hydrogen is rather in the condition of nascent hydrogen, set free from the positive charges which had caused it to ionize in the aqueous solution, but not yet consolidated into the form of hydrogen gas. It would appear that iron is permeated with minute cavities into which only this dissociated form of hydrogen is able to enter, and that upon all occasions when the nascent element is liberated in the presence of the iron, the opportunity of entrance is at once seized. In the wording of the atomic hypothesis, the active hydrogen occluded by iron seems to be atomic but not ionized hydrogen, very different in its properties from the molecular hydrogen which is adsorbed by the fine powder reduced at low temperatures.

In conclusion, it is a pleasure to express our gratitude to the Carnegie Institution of Washington for generous pecuniary assistance in this investigation.

SUMMARY OF PART FIRST.

(1) A method, both rapid and convenient, is given for the preparation of iron containing no impurity but hydrogen.

(2) The potential of this spongy iron in ferrous sulphate was measured and found to be at first greatly affected by previous exposure to the air. After long immersion in ferrous sulphate solution a constant and trustworthy value was reached.

(3) Even the enormous pressure of about 350,000 kilograms per square centimeter did not produce any appreciable permanent change in this value, although the masses were effectively cold-welded. Taken in conjunction with the results of Spring, this fact is shown to be consistent with the hypothesis of compressible atoms.

(4) Measurements of the free-energy change in iron during a pull upon a wire great enough to cause rupture gave results showing that this change must be very small, and called attention to regrettable errors in previous work on this subject.

⁴³ Ramsay, "Modern Chemistry," II, 31 (London, Dent, 1904).

(5) Iron reduced at a low temperature was found to have an electromotive force higher by at least 0.02 volt than iron which had been fused. If the normal calomel electrode is taken as having a single potential difference of 0.56, pure compact iron has a single potential difference of 0.15, and spongy or porous iron about 0.17 to 0.18 volt. The former is to be chosen as the normal value. It is pointed out that the much lower results of others are probably to be referred to the acidity of their solutions and to insufficient waiting for equilibrium.

(6) No important change in these values was caused by sudden cooling from a high temperature.

(7) Speculations concerning the relations of these facts to the structure and internal pressure and solubility of iron are tentatively recorded. The difference of potential of the different forms of iron is probably but not certainly to be referred to the different sizes of their separate particles.

SUMMARY OF PART SECOND.

(8) It was found that hydrogen could be taken up by finely powdered iron reduced at low temperatures without affecting the metal's electromotive force. When the metal is wholly coated with hydrogen the electromotive force is diminished. It is probable that hydrogen thus held is merely adsorbed or held as molecular hydrogen.

(9) It was found further that by quenching in water, whether from hydrogen or from nitrogen gas, that iron takes up hydrogen in an active form, raising the single potential by as much as 0.15 volt. This hydrogen is quickly expelled in ferrous sulphate solution, and very slowly in water or potassic sulphate solution, the potential returning to the normal value. The gas thus evolved was proved to be hydrogen gas.

(10) A small amount of hydrogen in the same active form may be taken in from hot hydrogen gas.

(11) Active hydrogen thus occluded by iron seems to be in every way similar to that occluded by iron in the presence of nascent hydrogen, whether this is chemically or electrolytically produced.

(12) It is pointed out that the most reasonable explanation of these facts is to suppose that the active dissolved hydrogen is dissociated but not ionized. The investigation will be continued in the near future.

The Electromotive Force of Iron Under Varying Conditions, and the Effect of Occluded Hydrogen

BY

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AND

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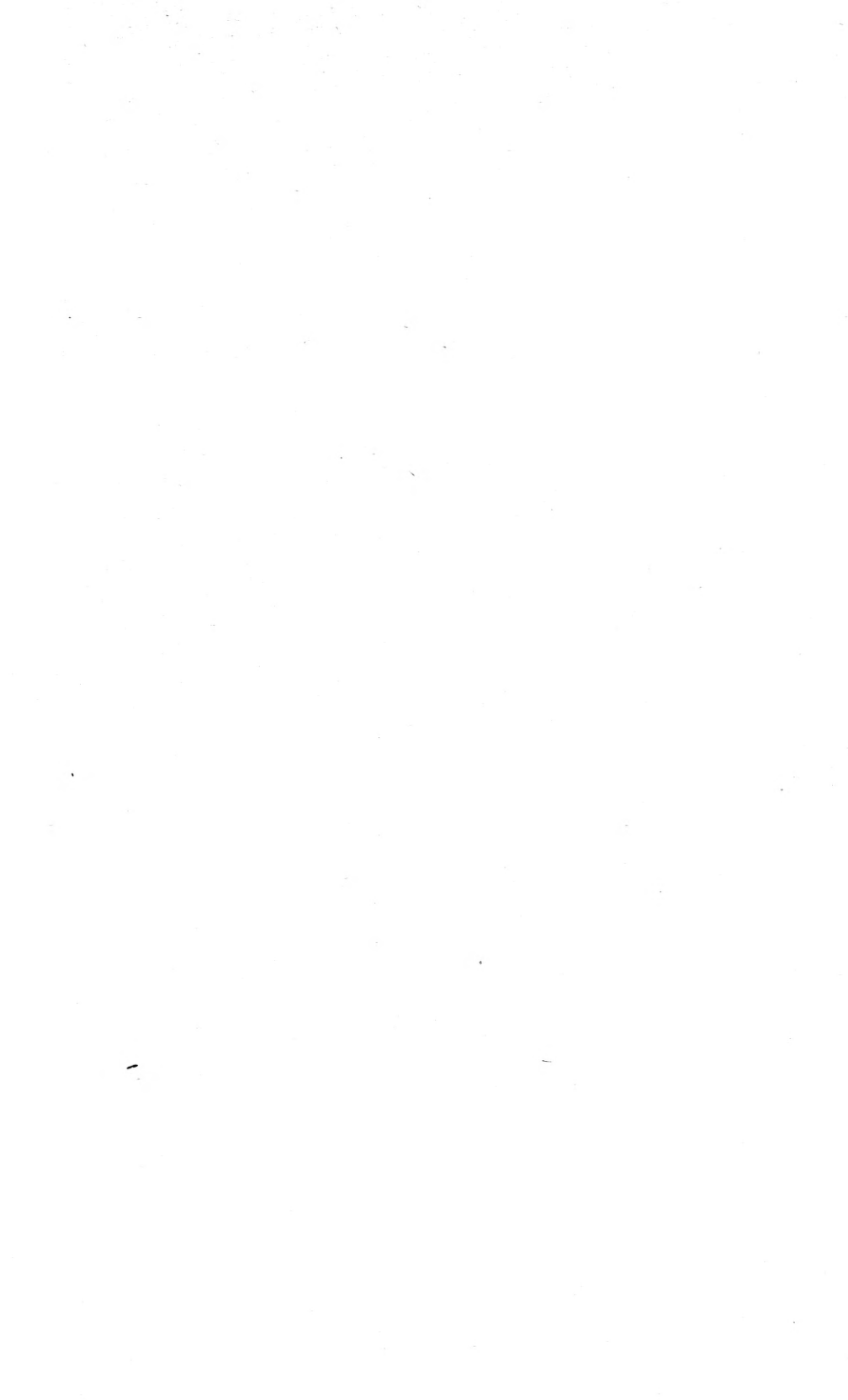


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