

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

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THEODORE WILLIAM RICHARDS & GUSTAVUS EDWARD BEHR

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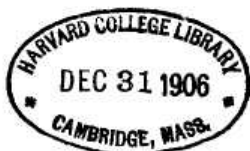
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THE ELECTROMOTIVE FORCE OF IRON UNDER VARYING CONDITIONS, AND THE EFFECT OF OCCLUDED HYDROGEN.

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° 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 Baxter¹ 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.

¹Baxter, Am. Chem. Journ., 22, 363 (1899).