



## XL. On the prepared or peculiar voltaic condition of iron

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XL. *On the prepared or peculiar Voltaic Condition of Iron.*  
By Sir JOHN F. W. HERSCHEL, K.G.H., M.A., F.R.S.\*

IN the Number of the *Annales* for the month of March of the present year, (1833, vol. lii. p. 288,) which I have recently received, I find a remark of M. Braconnot upon the manner in which concentrated nitric acid acts, when brought into contact with iron, which brings to my recollection some experiments made several years ago upon the same subject, presenting particularities sufficiently curious to merit a closer examination. I am at present unable to resume my researches, but I think that an account of them will not be uninteresting to your readers, and that it may induce one of them, perhaps M. Braconnot himself, to study in detail the very remarkable phænomena of the action in question, and to connect them with the usual laws of chemical action.

M. Braconnot says, “filings, or if they be preferred, plates of iron immersed in concentrated nitric acid, do not experience the slightest alteration, and retain all their metallic lustre, so that they are thus preserved from rust. If the same acid be made to boil upon these plates, and it be afterwards supersaturated with ammonia, it scarcely deposits a few insignificant flocks of oxide of iron.” The following are my own observations. (I extract the experiments from a journal dated August 1825.)

\* From the *Annales de Chimie et de Physique*, vol. liv. p. 87, being the paper alluded to by Mr. Faraday in *Lond. and Edinb. Phil. Mag.*, vol. ix. p. 122.; and now inserted to complete the series of papers on the subject to which it relates.

If a piece of soft iron wire, well brightened, be immersed in nitric acid of the density 1.399, the iron instantly becomes brown, and an effervescence more or less lively takes place, attended with the disengagement of red vapours; but this effervescence only lasts a few moments. It very soon ceases, when the iron immediately recovers its metallic lustre, and afterwards remains tranquil and intact at the bottom of the acid for any length of time that may be desired.

Iron thus treated, (which for the sake of brevity, I shall in future call *prepared iron*,) may be withdrawn from the acid and exposed to the air, or immersed in pure water or in ammonia, without by these means regaining the property of being attacked by nitric acid. In its prepared state it may be touched (gently) either in the air or in acid, with gold, silver, platina, mercury, glass, and several other substances without destroying this state. But if its surface be rubbed with force, so as to establish an intimate contact; if, for example, it be scraped with the edge of a piece of glass, upon a glass plate, its state of preparation is then destroyed, and if it be again immersed in the acid, the effervescence followed by total inaction again occurs, and the metallic lustre reappears: in a word, this is a complete renewal of the prepared state. If, on the other hand, prepared iron be touched either with copper, zinc, tin, bismuth, antimony, lead or iron not prepared, when either in the air, water or acid, the prepared state is destroyed, and the action of the acid commences again with effervescence, &c., as usual.

If a rather long piece of iron wire, prepared and moistened with acid, be touched with copper at one of its extremities while it is held suspended in the air over a glass plate, the surface may be seen to become brown, not instantaneously, and all over at once, but successively and by a movement, so to speak, propagated (with rapidity certainly) from the extremity touched to the other extremity. When, in the progress of this embrowning, the limit of the brown colour reaches a drop of acid suspended at an inflection of the wire, effervescence and the complete decomposition of the drop of acid take place. But if a wire immersed in the *acid* be thus touched, the action is instantaneous throughout its whole length.

If these experiments be performed in a capsule containing only a small quantity of acid, and many times repeated, the acid becomes incapable of producing the prepared state in the iron. This effect appears to arise partly from the heat evolved, and partly from the presence of nitrous gas; for having impregnated pure acid with this gas until it acquired

a green colour, it was found incapable of communicating the prepared state to iron. A piece of iron, immersed in acid thus impregnated, continued to produce a lively effervescence until it was entirely destroyed.

A piece of prepared iron was immersed in a solution of nitrate of copper. No precipitate resulted, but when it was touched in the solution with a piece of copper, the surface became instantly covered with a thick layer of metallic copper.

Between those states of the acid, in which it is capable and incapable of preparing iron, several intermediate states intervene, in which the preparation of it is effected with more and more difficulty, and the effervescence lasts longer and longer. In these intermediate states the following remarkable phenomenon sometimes occurs: the action ceases for an instant, and then recommences, and that several times in succession, and with convulsive intermittences, which sometimes succeed each other at intervals of  $\frac{1}{2}$  to  $\frac{2}{3}$  of a second, sometimes with an extraordinary rapidity, so that they cannot be counted. When they are slow, it is easy to see that the cessation of the action is propagated from one extremity of the wire to the other, though a reason cannot always be assigned why it ceases at one extremity rather than at the other.

It often happens that the iron, without acting with vivacity, does not cease to have a brown surface, to colour the surrounding acid, and to give off gaseous bubbles: this slow action may be arrested immediately in a singular manner, by withdrawing the iron from the acid, holding it for an instant in the air, and then letting it fall suddenly with a little shock. In half a second afterwards it seldom fails to shine with all its brilliancy.

The same effect may be produced with greater certainty, if, without withdrawing the iron from the acid, it be touched with a thin plate of platina. The contact of the platina, and, under certain circumstances that of silver also, exercises an inverse influence to that of zinc, &c. &c., in the production of the prepared state, or in its preservation when it exists. Thus, when operating in a capsule of platina, or upon a plate of that metal placed at the bottom of a porcelain capsule, the preparation of iron may be effected, not only with concentrated acid, but with dilute acid, even when diluted with an equal quantity of water. With a larger proportion of water the preparation of the iron is no longer possible, even when there is an intimate contact of the platina; but if a portion of acid be added, the iron resumes its brilliancy and becomes prepared.

Once prepared, the iron resists perfectly the action of an

acid diluted to the same, or even to a greater extent; which proves that these phænomena are owing, not merely to the absence of the water necessary to hold the nitrate of iron in solution, but rather to a certain permanent electrical state of the surface of the metal. This mode of considering the subject is confirmed by the following experiments.

A piece of iron wire was heated, and a small zone of wax placed around the middle of it to divide it into two portions. The wire being immersed in the concentrated acid, the action ceased at the same moment upon each half, and upon touching one of its extremities with copper the action was renewed in each simultaneously. The prepared state being again established, the iron was withdrawn by a glass rod attached to the wax, and one of its extremities was touched while it was in the air. The action commenced as usual at the extremity touched, and was extended through half of the wire, but was then stopped by the wax, so that one half was brown, while the other retained its metallic lustre.

A piece of iron, bent into an arc and divided as I have described by wax, was prepared, and then two-thirds of its length withdrawn from the acid, thus leaving the greater part of one half of it, A, still immersed. The other half (B) while thus in the air was touched with copper, when the action was propagated to the wax, where it stopped. The extremity B was then quickly lowered until it touched the surface of the acid; the action commenced immediately in the portion A, which was immersed, and which had hitherto preserved its lustre.

Prepared iron resists the action of the acid, when at a temperature insupportable to the hand, but not at the temperature of ebullition. When it is let fall into very hot acid, it resists for a few instants, and then begins to cause a violent effervescence. I have never found that iron could be submitted to the action of boiling nitric acid without oxidation, as is remarked by M. Braconnot, but perhaps the acid which he employed was more concentrated than mine. On the other hand I have found it impossible to make acid, of the density of 1.399, either cold or at the temperature of ebullition, act upon softened steel (*acier recuit*), or even upon those plates of steel which are employed for watch-springs. It may be kept boiling upon the plates for any length of time, without producing the least effect. But a circumstance, which to me appears very singular, is that a wholly different effect is produced upon steel which has received the highest temper, so as completely to resist the file, it being attacked with extreme violence by the hot acid, and even with considerable facility by cold acid. But when the acid is cold the steel is easily

prepared and becomes brown, in the same manner as iron when touched with zinc, but slowly, and, so to speak, with resistance. But if it be prepared and touched alternately several times in succession, it finally becomes subject to intermittences of action, becomes heated, and emits torrents of gas, without there being any possibility of calming the effervescence.

Since these experiments were made, I have found a very curious memoir by Keir, in the Transactions of the Royal Society of London for the year 1790, entitled, *Experiments and observations on the dissolution of metals in acids, and their precipitations*; in which several facts of this kind are recorded.

Keir was led to remark the prepared state of iron, when studying the precipitation of silver by that metal, in which Bergman had previously found some anomalies. He even discovered that this singular state may be developed by the action of nitrous acid. But the remarkable effects arising from contact with other metals, by which these facts may be included in the class of electro-chemical phænomena, escaped his observation. That the contact of one metal should protect another from the action of a chemical agent, as long as the contact lasts, does not now surprise us; (it occurs when nitric acid is poured over a piece of copper placed upon platina;) but what to me appears extraordinary in the experiments above described is, that the effect can be indefinitely prolonged after the contact ceases; and that a permanent electrical state may exist on the surface of a metal, and be there maintained by its own power, contrary to that which ordinarily exists in the same metal, and to that which continues to exist in it at a very small depth in its interior, even during the existence of the forced state at the surface.

Slough, Aug. 19, 1833.

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XLI. *A Report on the Progress of Phytochemistry in the Year 1835, in reference to the Physiology of Plants.* By J. C. MARQUART.\*

[Continued from vol. xi. p. 166, and concluded.]

WE have received this year very important additions to the knowledge of the alkaloids. What was formerly described as *Atropia*, *Hyoscyamia* and *Daturia* must, according to the discoveries of Brandes, be expunged. They are not alkaloids; this discovery was left for Mein, Geiger and Hesse†.

\* From Weigmann's *Archiv für Naturgeschichte*, vol. ii., part iv., p. 139 et seq. Translated by Mr. Wm. Francis.

† Geiger and Liebig's *Annalen*, vol. vii. p. 269.