II. *On Metallic Titanium.* *By* W. H. WOLLASTON, *M. D. V. P. R. S.*

Read December 12, 1822.

THE evidence that we yet possess of the reduction of titanium to its metallic state, is not altogether satisfactory; for even LAUGIER, (who has described a valuable series of experiments made upon it in 1814, and who had the advantage of all the previous knowledge acquired by the labours of VAUQUELIN and HECHT, in 1796, of LOWITZ, in 1798, and of LAMPADIUS, in 1803), could only say that he thought himself justified in considering certain parts of his product which were of a golden colour as really reduced; adding in confirmation, that Messrs. VAUQUELIN and HAÜY, to whom he had shown them, "appeared disposed to adopt his opinion."*

As M. LAUGIER had not the means of confirming his opinion by analysis, I may presume that an account of some experiments which I have recently made upon this substance, will be acceptable to chemists in general; and that in proportion to the degree of doubt they may entertain, they will feel interested to examine scrupulously the evidence I shall adduce as to the metallic state of the subject of my experiments.

* Je me crois fondé à regarder cette couche mammelonnée comme la portion réellement réduite - - - - - - - - - - - - - - - - -
M. M. VAUQUELIN et HAÜY m'ont paru disposées à adopter cette opinion.
Ann. de Chimie, V. 89, p. 317.

My attention has been directed, by various friends, especially by Professor BUCKLAND, who gave me the subject of my experiments, to certain very small cubes, having the lustre of burnished copper, that occasionally are found in the slag of the great iron-works at Merthyr Tydvil, in Wales, which, from their hue, have, by some persons, been imagined to be pyritical. Their colour, however, is not truly that of any sulphuret of iron that I have seen; and though the form be cubic, it is not the striated cube of common iron pyrites, which so often passes into the pentagonal dodecahedron, but similar to that of common salt; for any marks, that are to be discerned on their surfaces, appear as indented squares instead of striæ.

Their hardness also is totally different from that of pyrites, and is such as, when combined with the preceding characters, marks a substance wholly unknown to mineralogists. By selecting a sharp angle of one of these cubes, I found that I could not only write upon the hardest steel, or upon crown glass, but could even visibly scratch a polished surface of agate or rock crystal.

Having broken out some of these crystals for experiment, I found them all apparently attracted by a magnet; but observing that they had still small portions of slag adherent to them, they were next digested in muriatic acid, which, by dissolving the iron from their surfaces, soon freed them from their deceptive appearance of magnetism.

The cubes thus purified are not acted upon by muriatic acid.

Nitric acid has no action upon them.

Nitro-muriatic acid does not dissolve them.

Boiling sulphuric acid does not affect them.

Before the blow-pipe they are utterly infusible. A con-

tinued heat oxidates them, and they become purple or red at the surface, according to the degree of oxidation, or depth to which it penetrates.

Borax has no action upon them, but only cleans the surface from any oxide that may be formed. Neither does the addition of subcarbonate of soda produce more effect than borax alone.

Nitre, aided by a strong heat, oxidates them rapidly; but unless the heat be long continued, the effect is only superficial.

The combined action of nitre and borax together, soon effects their solution, as the latter dissolves the oxide as fast as it is formed, and presents a clean surface for fresh oxidation. But as these salts do not unite by fusion, the addition of soda, as a medium of union, considerably shortens the process. The fused mass becomes opake in cooling, by the deposit of a white oxide, which may either be previously freed of the salts by boiling water and then dissolved in muriatic acid, or the whole mass may be at once dissolved together.

In either case alkalies precipitate from the solution a white oxide, which is not soluble by excess of alkali, either pure, or in the state of carbonate. By evaporating the muriatic solution of the oxide to dryness, at the heat of boiling water, it is freed of any redundant acid, and the muriate which remains is perfectly soluble in water, and in a state most favourable for exhibiting the characteristic properties of the metal.

Infusion of galls gives the well known colour of gallate of titanium. The colour occasioned by adding triple prussiate of potash is red, as observed by LAUGIER, and so nearly re-

sembling that of the gallate, that I do not think any difference that I can discern is to be depended upon as constant. It differs from prussiate of copper by inclining to orange instead of purple, while the colour of prussiate of uranium is rather brown than red.

Since the oxide thus examined agrees in its characteristic properties with that of titanium procured from Anatase, I cannot entertain a doubt as to the general nature of the substance under consideration. I believe it to be pure, for I find no trace of any other substance combined with it, not even of iron, although the crystals are found imbedded in an iron slag, in the presence of metallic iron; nor yet of silica, for which the oxide has a strong affinity. Neither is there any sulphur present, as the salt which remains after oxidation of it by nitre, contains no trace of sulphuric acid.

That the cubes are in the metallic state, is nearly proved by their lustre, by the effect of nitre upon them, and by the failure of borax to act upon them, till they have been subjected to the action of nitre. It may be farther observed, that, when the action of nitre is rapid, heat is evidently generated, as by the combustion of other metals; but as I acted upon them in their solid state, and did not pulverise them, I did not witness what could properly be called detonation, as described by LAMPADIUS.

The property which may be regarded as most decisive of the metallic state of these cubes, is the power which I find them to possess of perfectly conducting the most feeble electricity.

If a slip of zinc and another of copper be placed in contact, and immersed together in dilute sulphuric acid, bubbles of

gas are seen to rise from the surfaces of both the metals; but, if a piece of paper be interposed between them, then no gas is given off by the copper. In a piece of paper, so placed between zinc and copper, I made a small hole, and after inserting in it one of the cubes so as to be in contact with both the metals, I had the satisfaction to find an electric communication completely established by this interposition, for gas was now given off from the surface of the copper.

From the situation in which this metal is found, it evidently has no affinity for iron in the metallic state, and it seems equally indisposed to unite with every other metal that I have tried. Though it is evidently impossible to measure with precision the specific gravity of such specimens as I first received for analysis, I was in hopes of trying whether one of the largest of the cubes would sink or swim in melted tin, and for that purpose endeavoured to tin its surface, but I could not succeed in uniting it with either tin or lead, with silver or copper, and had no encouragement to prosecute farther a series of negative results, in search of metals for which it may have an affinity.

From the extreme infusibility of these cubes, it seems probable that they have not been formed by crystallization in cooling from a state of fusion, but have received their successive increments by reduction of the oxide dissolved in the slag around them: a mode of formation to which we must have recourse for conceiving rightly the formation in nature of many other metallic crystals.

Since the date of this communication, the liberality of Mr. ANTHONY HILL, of Merthyr Tydvil, has supplied me with a

larger quantity of the slag which formed the subject of my first experiments, and has enabled me to determine the specific gravity of metallic titanium to be 5.3. For this purpose, the vitreous part was fused with a mixture of borax and subcarbonate of soda in about equal quantities, and was then dissolved in muriatic acid, which also removed a quantity of metallic iron, and left the titanium freed from extraneous matter. Though great part of what was thus obtained from the interior of the slag was in a pulverulent state, the quantity, which amounted to 32 grains, and displaced 6,04 of water, was sufficient to preclude any considerable error.

I have moreover learned that metallic cubes, similar to those which I have above described and examined, were, more than 20 years since, observed in a slag at the Clyde iron-works in Scotland; that a small quantity has also been met with at the Low Moor iron-works, near Bradford, in Yorkshire; and at the Pidding iron-works, near Alfreton, in Derbyshire; and that some good specimens have been obtained from Ponty-pool, in Monmouthshire; but it does not appear that any one has ascertained, or even suspected, the real nature of this singular product.