

VI. *On the corrosion of copper sheeting by sea water, and on methods of preventing this effect ; and on their application to ships of war and other ships. By Sir HUMPHRY DAVY, Bart. Pres. R. S.*

Read January 22, 1824.

1. **T**HE rapid decay of the copper sheeting of His Majesty's ships of war, and the uncertainty of the time of its duration, have long attracted the attention of those persons most concerned in the naval interests of the country. Having had my enquiries directed to this important object by the Commissioners of the Navy Board, and a Committee of the Royal Society having been appointed to consider of it, I entered into an experimental investigation of the causes of the action of sea water upon copper. In pursuing this investigation, I have ascertained many facts which I think not unworthy of the notice of the Royal Society, as they promise to illustrate some obscure parts of electro-chemical science ; and likewise seem to offer important practical applications.

2. It has been generally supposed that sea water had little or no action on pure copper, and that the rapid decay of the copper on certain ships was owing to its impurity. On trying, however, the action of sea water upon two specimens of copper, sent by JOHN VIVIAN, Esq. to Mr. FARADAY for analysis, I found the specimen which appeared absolutely pure, was acted upon even more rapidly than the specimen which contained alloy : and, on pursuing the enquiry with specimens of various kinds of copper which had been collected by the

Navy Board, and sent to the Royal Society, and some of which had been considered as remarkable for their durability, and others for their rapid decay, I found that they offered very inconsiderable differences only in their action upon sea water ; and, consequently, that the changes they had undergone must have depended upon other causes than the absolute quality of the metal.

3. To enable persons to understand fully the train of these researches, it will be necessary for me to describe the nature of the chemical changes taking place in the constituents of sea water by the agency of copper.

When a piece of polished copper is suffered to remain in sea water, the first effects observed are, a yellow tarnish upon the copper, and a cloudiness in the water, which take place in two or three hours : the hue of the cloudiness is at first white ; it gradually becomes green. In less than a day a bluish-green precipitate appears in the bottom of the vessel, which constantly accumulates ; at the same time that the surface of the copper corrodes, appearing red in the water, and grass-green where it is in contact with air. Gradually carbonate of soda forms upon this grass-green matter ; and these changes continue till the water becomes much less saline.

The green precipitate, when examined by the action of solution of ammonia and other tests, appears principally to consist of an insoluble compound of copper, (which may be considered as a hydrated sub-muriate) and hydrate of magnesia.

According to the views which I developed fourteen years ago, of the nature of the compounds of chlorine, and which

are now generally adopted, it is evident that soda and magnesia cannot appear in sea water by the action of a metal, unless in consequence of an absorption or transfer of oxygene. It was therefore necessary for these changes, either that water should be decomposed, or oxygene absorbed from the atmosphere. I found that no hydrogen was disengaged, and consequently no water decomposed : necessarily, the oxygene of the air must have been the agent concerned, which was made evident by many experiments.

Copper in sea water deprived of air by boiling or exhaustion, and exposed in an exhausted receiver or an atmosphere of hydrogen gas, underwent no change ; and an absorption in atmospherical air was shown when copper and sea water were exposed to its agency in close vessels.

4. In the Bakerian Lecture for 1806, I have advanced the hypothesis, that chemical and electrical changes may be identical, or dependent upon the same property of matter : and I have farther explained and illustrated this hypothesis in an elementary work on chemistry, published in 1812. Upon this view, which has been adopted by M. BERZELIUS and some other philosophers, I have shown that chemical attractions may be exalted, modified, or destroyed, by changes in the electrical states of bodies ; that substances will only combine when they are in different electrical states ; and that, by bringing a body naturally positive artificially into a negative state, its usual powers of combination are altogether destroyed ; and it was by an application of this principle that, in 1807, I separated the bases of the alkalies from the oxygene with which they are combined, and preserved them for

examination ; and decomposed other bodies formerly supposed to be simple.

It was in reasoning upon this general hypothesis likewise, that I was led to the discovery which is the subject of this Paper.

Copper is a metal only weakly positive in the electro-chemical scale ; and, according to my ideas, it could only act upon sea water when in a positive state ; and, consequently, if it could be rendered slightly negative, the corroding action of sea water upon it would be null ; and whatever might be the differences of the kinds of copper sheeting and their electrical action upon each other, still every effect of chemical action must be prevented, if the whole surface were rendered negative. But how was this to be effected ? I at first thought of using a Voltaic battery ; but this could be hardly applicable in practice. I next thought of the contact of zinc, tin, or iron : but I was for some time prevented from trying this, by the recollection that the copper in the Voltaic battery, as well as the zinc, is dissolved by the action of diluted nitric acid ; and by the fear that too large a mass of oxidable metal would be required to produce decisive results. After reflecting, however, for some time on the slow and weak action of sea water on copper, and the small difference which must exist between their electrical powers and knowing that a very feeble chemical action would be destroyed by a very feeble electrical force, I resolved to try some experiments on the subject. I began with an extreme case. I rendered sea water slightly acidulous by sulphuric acid, and plunged into it a polished piece of copper, to which

a piece of tin was soldered equal to about one-twentieth of the surface of the copper. Examined after three days the copper remained perfectly clean, whilst the tin was rapidly corroded : no blueness appeared in this liquor ; though, in a comparative experiment, when *copper alone* and the same fluid mixture was used, there was a considerable corrosion of the copper, and a distinct blue tint in the liquid.

If one-twentieth part of the surface of tin prevented the action of sea water rendered slightly acidulous by sulphuric acid, I had no doubt that a much smaller quantity would render the action of sea water, which depended only upon the loosely attached oxygene of common air, perfectly null ; and on trying $\frac{1}{200}$ part of tin, I found *the effect* of its preventing the corrosion of the copper perfectly decisive.

5. This general result being obtained, I immediately instituted a number of experiments, in most of which I was assisted by Mr. FARADAY, to ascertain all the circumstances connected with the preservation of copper by a more oxidable metal. I found, that whether the tin was placed either in the middle, or at the top, or at the bottom of the sheet of copper, its effects were the same ; but, after a week or ten days, it was found that the defensive action of the tin was injured, a coating of sub-muriate having formed, which preserved the tin from the action of the liquid.

With zinc or iron, whether malleable or cast, no such diminution of effect was produced. The zinc occasioned only a white cloud in the sea water, which speedily sunk to the bottom of the vessel in which the experiment was made. The iron occasioned a deep orange precipitate ; but after many weeks, not the smallest portion of copper was found in the

water ; and so far from its surface being corroded, in many parts there was a regeneration of zinc or of iron found upon it.

6. In pursuing these researches, and applying them to every possible form and connection of sheet copper, the results were of the most satisfactory kind. A piece of zinc as large as a pea, or the point of a small iron nail, were found fully adequate to preserve forty or fifty square inches of copper ; and this, wherever it was placed, whether at the top, bottom, or in the middle of the sheet of copper, and whether the copper was straight or bent, or made into coils. And where the connection between different pieces of copper was completed by wires, or thin filaments of the fortieth or fiftieth of an inch in diameter, the effect was the same ; every side, every surface, every particle of the copper remained bright, whilst the iron or the zinc was slowly corroded.

A piece of thick sheet copper, containing on both sides about sixty square inches, was cut in such a manner as to form seven divisions, connected only by the smallest filaments that could be left, and a mass of zinc, of the fifth of an inch in diameter, was soldered to the upper division. The whole was plunged under sea water ; the copper remained perfectly polished. The same experiment was made with iron : and now, after a lapse of a month, in both instances, the copper is as bright as when it was first introduced, whilst similar pieces of copper, undefended, in the same sea water, have undergone considerable corrosion, and produced a large quantity of green deposit in the bottom of the vessel.

A piece of iron nail about an inch long was fastened by a piece of copper wire, nearly a foot long, to a mass of sheet

copper, containing about forty square inches, and the whole plunged below the surface of sea water ; it was found, after a week, that the copper was defended by the iron in the same manner as if it had been in immediate contact.

A piece of copper and a piece of zinc soldered together at one of their extremities, were made to form an arc in two different vessels of sea water ; and the two portions of water were connected together by a small mass of tow moistened in the same water : the effect of the preservation of the copper took place in the same manner as if they had been in the same vessel.

As the ocean may be considered, in its relation to the quantity of copper in a ship, as an infinitely extended conductor, I endeavoured to ascertain whether this circumstance would influence the results ; by placing two very fine copper wires, one undefended, the other defended by a particle of zinc, in a very large vessel of sea water, which water might be considered to bear the same relation to so minute a portion of metal as the sea to the metallic sheeting of a ship. The result of this experiment was the same as that of all the others ; the defended copper underwent no change ; the undefended tarnished, and deposited a green powder.

Small pieces of zinc were soldered to different parts of a large plate of copper, and the whole plunged in sea water : it was found that the copper was preserved in the same manner as if a single piece had been used.

A small piece of zinc was fastened to the top of a plate of polished copper, and a piece of iron of a much larger size was soldered to the bottom, and the combination placed in sea water. Not only was the copper preserved on both sides

in the same manner as in the other experiments, but even the iron ; and after a fortnight, both the polish of the copper and the iron remained unimpaired.

7. I am continuing these researches, and I shall communicate such of them as are connected with new facts, to the Royal Society.

The Lords Commissioners of the Admiralty, with their usual zeal for promoting the interests of the Navy by the application of science, have given me permission to ascertain the practical value of these results by experiments upon ships of war ; and there seems every reason to expect (unless causes should interfere of which our present knowledge gives no indications) that small quantities of zinc, or which is much cheaper, of malleable or cast iron, placed in contact with the copper sheeting of ships, which is all in electrical connection, will entirely prevent its corrosion. And as negative electricity cannot be supposed favourable to animal or vegetable life ; and as it occasions the deposition of magnesia, a substance exceedingly noxious to land vegetables, upon the copper surface ; and as it must assist in preserving its polish, there is considerable ground for hoping that the same application will keep the bottoms of ships clean, a circumstance of great importance both in trade and naval war.

It will be unnecessary for me to dwell upon the economical results of this discovery, should it be successful in actual practice, or to point out its uses in this great maritime and commercial country.

I might describe other applications of the principle to the preservation of iron, steel, tin, brass, and various useful metals ; but I shall reserve this part of the subject for another communication to the Royal Society.