III.—*On the Preparation of the Metals of the Alkalies and Alkaline Earths by Electrolysis.*

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THE following research, carried out at the suggestion of Professor Bunsen, in his laboratory, upon the Electrolytic Decomposition of the Salts of the Alkalies and Alkaline Earths, seems to show that the statements given in the Handbooks concerning the preparation and properties of the metals of the alkaline earths are for the most part false. Indeed, it is more than probable that the metals calcium and strontium have never before been isolated; for all the experimenters who have supposed that they have prepared the metals, describe them as silver-white, whereas the globules of metal as large as a pea, which I have observed, have the colour and lustre of gold alloyed with silver. The preparation of barium, strontium, and calcium, presents many singular difficulties; for if galvanic currents of various intensities be passed through the fused chlorides of these metals, by means of two large carbon poles, as used by Bunsen for the preparation of magnesium,* a number of small flames are observed, not only at the negative, but also at the positive pole, whether at a high or low temperature. These small flames are occasioned by the metal in the form of a powder, burning, rising at the anode, and carried to the cathode by the current of chlorine evolved there. At the same time a small quantity of basic chloride is formed round the anode, which hinders the further passage of the current. No metallic globules are found on opening the cooled crucible, and only exceptionally does a part of the chloride evolve hydrogen on moistening with water. As the mass of chloride surrounding the negative pole had a strongly alkaline reaction, there can be no doubt that the diminution of the strength of the current was owing to the formation of lime. This is explained by the fact that the chlorides, when fused in a vessel composed of a silicate, soon become alkaline under the influence of atmospheric moisture.

Professor Bunsen, in his Electrolytic Researches, has shown that the density of the current is the chief condition under which the electricity is able to overcome the chemical affinities of different substances. It was very probable, therefore, that with a current of greater density the formation of the oxides would be prevented, as Bunsen found in the preparation of chromium in the moist way.† Experiment showed

* Bunsen on Magnesium (Ann. Ch. Pharm. lxxii. 137).

† Pogg. Ann. xci. 619.

that this hypothesis was perfectly correct; for if an iron wire of the size of a needle be used instead of the large carbon negative pole, globules of potassium, sodium, calcium, strontium, &c. &c., are easily reduced; so that in future the preparation of these metals will be an easy experiment for the lecture-table. Although so easily reduced, it is difficult to obtain the metal in a coherent mass, and to separate it from the surrounding chloride. The reduced metal being specifically lighter than the fused salt, it rises to the surface and burns before it can be collected. If one attempts to collect the metallic globules by means of a bell-shaped vessel of glass, the metal reduces the silicon, which separates out in the form of a black powder, and prevents the metal fusing. I propose three methods for avoiding these difficulties,—Firstly, by using a platinum wire as negative pole: this, however, gives an impure metal, or rather an alloy with platinum, which, being specifically heavier than the fused chlorides, sinks to the bottom of the vessel, and is there found as a metallic ball. Secondly, by fusing together the chlorides of two metals mixed in equivalent proportions: these double chlorides melt at a temperature so low, that even potassium and sodium are not volatilised in the melted mass. If the heat is regulated in such a manner that a solid crust is formed on the top of the melted mass, only round the negative pole, a large quantity of metal is found on it after cooling the crucible. The third method consists in the separation of the metal on the immediate surface of the melted chlorides, by means of a pointed iron wire as pole, on to which the fused metal hangs: a thin film of melted chloride serves as a varnish to protect it from oxidation. It naturally depends on the metal to be obtained, which of the three methods is most applicable.

I shall now proceed to describe the preparation and properties of calcium. One method—which is, however, very uncertain, but which, if it succeeds, gives globules of calcium larger than peas—is the following:—A mixture of two equivalents of chloride of calcium and one of chloride of strontium with a small quantity of chloride of ammonium, is fused in a Hessian crucible; an iron cylinder, serving as positive pole, is placed in the melted mass; within the iron cylinder is then placed a small porous cell previously made red-hot, and afterwards filled with the same mixture fused in a porcelain crucible. A thin iron wire or fine carbon point serves as the negative pole in the porous cell. If the porous cell be filled with mixture from $\frac{1}{2}$ inch to 1 inch higher than the outer crucible, it is easy to regulate the fire so that a solid crust shall be formed in the inner cell, whilst the outer mass remains liquid. If a current from six of Bunsen's elements be allowed

to pass through the mixture thus arranged for half an hour to an hour, a large amount of reduced calcium is obtained. I have, however, only obtained the metal by this method once or twice in globules; in all the other experiments, the metal was reduced in the form of a powder, which was present in some parts of the mixture in such quantity that, upon being scraped with a knife, it showed the colour and lustre of gold alloyed with silver. Such pieces, when thrown in water, cause a violent evolution of hydrogen, and when pulverised under strong alcohol, which dissolves the chlorides, leave a metallic powder only slowly oxidable, which, when rubbed in an agate mortar, gives gold-coloured streaks. This method, on account of its uncertainty, cannot be recommended, and I therefore proceed to describe a more simple and safe one, by which calcium is obtained in small globules. The same mixture of salts is used, and melted in a small porcelain crucible, in which a carbon positive pole is placed, and a thin harpsichord wire (wound round a thicker one), dipping only under the surface of the melted salt, is connected with the zinc of the battery.

In order to obtain the beads of calcium which hang on to the fine wire, the negative pole must be withdrawn about every two to three minutes, along with the small crust which forms around it. The surest method, however, to obtain the metal, although in very small beads, is by placing a pointed iron wire merely so as to touch the surface of the liquid: the great heat evolved, owing to the resistance to the current, causes the reduced metal to fuse and drop off from the point of the iron wire, and the bead is recovered from the liquid by means of a small iron spatula.

The properties of metallic calcium are the following:—It is a light-yellow metal of the colour of gold alloyed with silver; on a freshly filed surface, the lustre somewhat decreases the yellow colour, which becomes more apparent if the light be reflected several times from two surfaces of calcium: a thin film of oxide produces the same effect. The hardness approaches that of gold, being from 2 to 3. It is particularly ductile, and may be cut, filed, or hammered out to plates having the thickness of the finest paper, a piece not larger than a mustard-seed having been flattened to the size of 10 to 15 square millimetres, showing only a few cracks at the border.

Concerning the specific gravity of calcium, I shall return to it shortly in my paper on strontium and barium. In dry air, the metal retains its colour and lustre for a few days only, but in presence of moisture the whole mass is slowly oxidised. Heated on platina foil over a spirit-lamp, it burns at a red heat with an excessively bright flash, about equal in intensity to the voltaic arc. Calcium is only slowly acted upon

by dry chlorine, but, when heated, burns in that gas with a most brilliant light, as also in iodine, bromine, oxygen, sulphur, &c. With phosphorus it combines without ignition, forming phosphide of calcium. Heated mercury dissolves it to a white amalgam. Water is rapidly decomposed by the metal, with evolution of great heat and hydrogen; diluted nitric, hydrochloric, and sulphuric acids cause a still more rapid decomposition, the first acid often causing ignition. Concentrated nitric acid, even when heated almost to boiling, does not attack the metal, the action not beginning till the liquid boils. By using water as the liquid element, calcium is negative to potassium and sodium, but positive to magnesium. Nevertheless, calcium is not reducible by potassium or sodium from its chloride. This is easily proved by the following experiment:—If 1 equivalent of chloride of sodium, and 2 equivalents of chloride of calcium, or equal equivalents of chlorides of calcium and potassium, be melted in a small porcelain crucible over a Berzelius spirit-lamp, owing to the easy fusibility of the mixtures, the metals potassium and sodium may be easily prepared by electrolysis when the following precautions are taken:—The heat must be so regulated that a solid crust forms on the surface around the negative carbon pole, whilst the mixture remains fused, allowing the free evolution of chlorine round the positive pole: by this means, after the decomposition has continued for about twenty minutes, and the cooled crucible has been opened under rock-oil, a large amount of potassium or sodium, almost chemically pure, is generally obtained. If the same experiment be repeated at a white heat in a charcoal fire, with an iron wire as negative pole, small globules of potassium or sodium are seen burning on the surface, which, when analysed, are found to be also almost chemically pure.

From these experiments it appears that the metal formerly obtained by the reduction of chloride of calcium with the alkaline metals, cannot be calcium, but was most probably a mixture of potassium or sodium with aluminium, silicon, &c.