PRELIMINARY NOTICE ON THE COMPOSITION OF THE BLACK DEPOSIT WHICH ATTACHES ITSELF TO THE POSITIVE ELECTRODE OF THE BATTERY ON ELECTROLYSING SOLUTIONS OF ARGENTIC NITRATE.

By J. W. GATEHOUSE.

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THE composition of this substance is generally stated in our text books to be such that its formula is Ag_2O_2 . The few experiments, however, which I have been able to perform indicate that its composition varies both with the battery power used and with the strength of the solution. In all cases it appears to contain a very large amount of absorbed gas, consisting principally of oxygen, but in no case free from nitrogen.

With a saturated solution of silver nitrate, or so nearly saturated as not to deposit crystals during the process of electrolysis, and a current proceeding from two pint Grove cells, the deposit at the positive pole is almost black, highly crystalline, and fairly coherent, so that, although much may have fallen to the bottom of the cell, the remainder can be withdrawn attached to the platinum electrode.

During the process a purple tint first pervades the solution, gradually turning to a deep brown; this, first appearing at the positive pole, gradually stretches through the solution till it reaches the negative electrode, which also consists of platinum.

The silver deposited on this electrode gradually stretches through the solution in a fine arborescent form till it meets the deposit on the opposite side. Although some of the black deposit adheres to the electrode, much drops to the bottom of the cell, and this, in addition to the oxygen gas given off from the positive electrode itself, yields a constant stream of gas, whether in solid connection with the electrode or not. This evolution of gas proceeds at ordinary temperature, even after all silver nitrate has been removed by washing, and the finer the state of division in which the deposit is formed the greater appears to be the amount of gas absorbed by it. After being heated to 212°F . its composition is constant. The deposit evolves oxygen freely when treated with concentrated sulphuric acid, and chlorine when treated with hydrochloric acid.

2.42 grains of the crystalline deposit obtained by using two Bunsen cells was heated for an hour to 120°F ., the gas evolved was not measured with great accuracy, but consisted of about 2 c.c., of which approximately nine-tenths were oxygen and the remainder nitrogen.

These 2.42 grains raised to a white heat were reduced to pure silver, the weight of which was 1.985 grains; loss of gas, .435 grains. On the supposition that the whole of the gas thus lost was oxygen, this gives the composition of the substance at 120°F ., as silver, 82.02 per cent.; oxygen, 18.00 per cent.; and leads to the formula Ag_2O_2 being the correct one at this temperature.

With a power of four Bunsen cells, and a slightly acid solution, a fine black powder was obtained, from which volumes of gas continuously ascended as it lay at the bottom of the decomposing cell. There was no trace of adherent crystals, the platinum electrode being merely covered with a fine black powder, and the solution itself took a magnificent violet tint, soon passing to a deep brown, from all parts of which the brown deposit seemed to form; but it was difficult to distinguish whether this was actually the case or not, as the evolution of gas from the deposited powder was so rapid as to produce currents which carried particles around from bottom to the top, exactly as we see in the case of convection currents.

A portion of this brown powder was washed as rapidly as possible, transferred to a graduated tube fitted with a cork, and small tube at the bottom, but with the small tube reaching some two inches into the larger graduated one. We thus have a species of Ure's audiometer, with the open limb small, and entering the large one.

The deposit lies at the bottom of the large tube, between it and the small one, and can be thus conveniently heated in a water-bath.

Three c.c. of gas were thus collected; of this 2.75 c.c. were absorbed by pyrogallie acid and soda, leaving .25 c.c. of nitrogen. The total amount of solid matter remaining after expulsion of the gas was only .23 grains, of which only .06 grains remained as silver after being heated to redness. The amount here being very small, and the chances of error great, I do not place much reliance on the composition of the substance, as deduced from this experiment, but merely give it as showing the enormous comparative quantity of gas which may, under certain circumstances, be occluded by a small amount of this solid.

In a third experiment, where the deposit was crystalline, and the total solid weighed 6.73 grains, 4 c.c. of gas were collected, of which 3.7 were absorbed by soda and pyrogallie acid, and .3 c.c. of nitrogen remained unabsorbed.

These experiments (which are, indeed, only preliminary work on the subject, and as such I take the liberty of placing them before the Society) do not, indeed, settle the composition of this interesting deposit, nor throw any light on that still more unknown subject of the formation of the purple colour in the solution of the nitrate during the electrolysis; yet I hope they indicate a field of interesting study which I trust may be entered into by men abler than myself, and with more time to devote to the subject.