ART. XXXV. — *Contributions to Physics from the Lawrence Scientific School.*—No. 1. By S. P. SHARPLES, S.B.

On some forms of the Galvanic Battery.

WHILE making some experiments as to the best method of determining nitrous acid, Dr. Gibbs had his attention called to the fact that nitrous acid is instantly oxydized by an acid solution of potassic bichromate to nitric acid.

This result he communicated to me in the early part of 1870, saying, at the same time, that he thought it might be advantageous to use a mixture of nitric and sulphuric acids and potassic bichromate, as the absorbing liquid in the porous cell of the Bunsen battery. The chromic acid would prevent any evolution of nitrous acid by oxidizing it as soon as formed to nitric acid. The nitric acid being the active fluid in the combination would prevent the polarization which is continually taking place in the ordinary bichromate battery, and would be constantly renewed.

Having occasion to use a battery, a few days after, I tried the mixture with such satisfactory results that it seemed desirable that the subject should be more fully investigated. The electro-motive force and internal resistance of the battery were therefore determined.

The apparatus used was one of Poggendorff's rheostats, which was furnished with sixteen meters of German silver wire, the resistance of this being but little affected by changes of temperature. By means of clamps, any number of centimeters of wire could be introduced into the circuit. When the needle of the galvanometer was deflected to forty or fifty degrees a change of one centimeter in the length of the resistance could be readily seen. The galvanometer was an ordinary one in which the coil was replaced by a broad, thick, copper band, passing once around and close to the needle, which was suspended by a filament of silk and so adjusted that it was at the zero of the scale when it came to rest in the meridian.

In order to determine the internal resistance, I made use of two elements of the same construction, which could be thrown into the circuit either singly, or side by side. I found when all my connections were bright, that there was no appreciable difference between the two elements, that is, either element when connected with the galvanometer would deflect it the same number of degrees.

The zincs were about four inches high, and two and a half inches internal diameter, with a slit in one side. The porous cups filled the internal space almost entirely. The carbons

used were those manufactured by Chester of New York for ordinary medical batteries and had a section of about a square inch. The exciting liquid was a mixture of sulphuric acid with nine times its volume of water; this was found to be without action on the zincs when the battery was not running. The zincs were kept well amalgamated.

The electro-motive force was determined by Wheatstone's method,* as follows: One of the cells was thrown into the circuit; the rheostat was then adjusted until the needle stood at 40° ; the resistance was then decreased, until the needle rose to 50 ; the length of wire removed was noted. The second cell was then placed by the side of the first and the resistance increased until the needle again stood at 50° , and the added length of wire noted. While both cells were connected the needle was brought again to 40° , by removing part of the resistance, this length was also noted; it should correspond exactly to the first length. One of the cells was then removed and the resistance again adjusted; the wire removed should exactly equal the second length noted above. The second cell was now substituted for the first, and if the needle still remained at a constant point, the measure was considered satisfactory. If there was any discrepancy in the measurements, or if the needle stood at a different point with one cell, from what it did with the other, the connections were all examined and the measurements repeated. It was rarely found necessary to make more than one trial.

The formulas used were those given by Wheatstone (loc. cit.), as follows: For electro-motive force $\frac{E}{E'} = \frac{l}{l'}$ in which E = the electro-motive force of a standard battery, and l the length of wire necessary to reduce the needle of the galvanometer from one given point to another given point. E' = the electro-motive force of the battery to be determined, and l' the length of wire which was required to be removed to change the needle from one of the given points to the other.

For the internal resistance of the battery, $R = 2l$, in which formula R = the internal resistance, and l = the length of wire which must be added when a second cell is placed by the first to bring the needle to the same point where it stood when only one cell was in circuit. After making one series of measurements, the needle was brought to 40° , and allowed to remain at that point for twelve hours if the battery remained constant for that length of time; the measurements were then repeated, and compared with those of a Bunsen cell made under the same circumstances.

* Phil. Trans., 1843, Part II, p. 313.

The first measurements, made in March, 1870, were merely to determine the electro-motive force. In the rest of the experiments, made in December, 1870, and Jan. 1871, the internal resistances were also determined.

1st Experiment. For purposes of comparison, a Daniell's cell was fitted up, using the same zinc and porous cup, and the same exciting liquid, but substituting for the carbon a hollow cylinder of copper open at one side and using a saturated solution of cupric sulphate as the absorbing liquid. The mean of six comparisons of this with a Bunsen's cell gave 169 for the electro-motive force of the latter, that of Daniell's being 100. Latimer Clark* gives the number 175.

Ex. No. 2. The porous cell was filled with a saturated solution of potassic bichromate in a mixture of equal parts of nitric and sulphuric acids, diluted with four times their volume of water. This gave a constant battery working without giving off acid fumes until the exciting liquid was exhausted. Its electro-motive force was the same as that of the ordinary Bunsen cell.

Ex. No. 3. The porous cell was filled with coarse fragments of potassic bichromate, and then saturated with nitric acid. The electro-motive force was the same as in the last experiment, but the battery was not quiet so constant, and there was a great waste of bichromate, there being much more than was requisite to saturate the nitric acid.

Ex. No. 4. The cell was filled as in the last experiment, only the liquid used was a mixture of equal parts, nitric and sulphuric acids. The electro-motive force was the same, but trouble was experienced from the formation of crystals of chromic alum which encrusted the carbons and porous cells and stopped the working of the battery.

Ex. No. 5. The absorbing liquid was a saturated solution of potassic bichromate in hydrochloric acid. The electro-motive force of this battery rapidly declined; starting with the same force as Bunsen's, in the course of $2\frac{1}{2}$ hours it ran down to two-thirds of that force; its internal resistance at the start was 1.7 that of Bunsen's; at the end of $2\frac{1}{2}$ hours it was 3.6. It gave off chlorine during the whole time it was in action.

Ex. No. 6. The absorbing liquid was a saturated solution of potassic bichromate in nitric acid. It gave the same electro-motive power as the ordinary Bunsen cell, but the internal resistance was about 2.3 as much. The battery was sensibly constant for twelve hours.

Ex. No. 7. Ex. No. 1 was repeated under slightly different circumstances. The saturated solution of bichromate, used in the last experiment, was mixed with $\frac{1}{3}$ its own volume of strong

* On Electric Measurements, p. 108.

sulphuric acid, and enough water-added to take up the precipitated chromic acid. This formed the most satisfactory battery tried; it was perfectly constant during twelve hours. The internal resistance was only about $1\frac{1}{2}$ times that of an ordinary Bunsen's cell of the same construction, and not the slightest odor could be perceived in the room. The electro-motive force was the same as that of the Bunsen cell.

Ex. No. 8. Having seen in the American Chemist* a notice of a new battery by Prof. Bunsen, mentioned in an address by Prof. Roscoe, before the Chemical Section of the British Association for the Advancement of Science, I made a trial of it. This battery consisted of two metals, platinum and zinc, with a single fluid, namely, a solution of chromic acid in dilute sulphuric acid; I tried it in a small cell in which equal surfaces of zinc and carbon were opposed to each other. The electro-motive force was twice that of a Daniell's cell, or 1.2 that of a Bunsen's; but it was not very steady, and the chromic acid acted strongly on the zinc.

Ex. No. 9. Dr. Gibbs suggested to me to try a solution of chromic acid in nitric acid in the porous cell, using sulphuric acid in contact with the zinc. The electro-motive force was the same as in the last experiment, and the internal resistance was the same as in the Bunsen cell. The battery was perfectly constant. Two cells very slowly decomposed pure water and gave vivid flashes of light when the connections were made.

Ex. No. 10 was undertaken to determine the effect of replacing the bichromate by manganic oxide. The porous cell was filled around the carbon with manganic oxide; nitric acid was then poured on it until it was completely saturated. This gave very poor results; the electro-motive force was about 1.43 times that of a Daniell's cell. The battery was not very steady, and after running some time began to give off fumes of nitrous acid.

Ex. No. 11. Joule† gives an experiment with a battery in which platinum in nitric acid is used as the negative, and zinc in caustic potassa as the positive electrode, and gives the electro-motive power as equal to 2.41 Daniell's. I repeated the experiment, using a solution containing $\frac{1}{5}$ of its weight of potassic hydrate in the outer cell, and a saturated solution of chromic in nitric acid in the inner cell. I found the electro-motive force at first about 2.35 that of Daniell's cell, the internal resistance being that of a Bunsen's cell. It was rather unsteady at first, and then began to gradually decline. No odor was perceptible.

Several experiments were tried, with the hope of obtaining a single fluid battery with the following results.

Ex. No. 12. A strong solution of caustic potassa was made, saturated with ferricyanide of potassium and used in the cell

* Vol. i. p. 209.

† Phil. Mag., vol. xxiv. p. 113, 1844.

employed in experiment No. 8. This gave a feeble current and the carbon was rapidly polarized.

Ex. No. 13. As solutions of sulphurous acid and acid sulphites dissolve zinc without evolution of hydrogen, forming hyposulphites, it was thought that these might be used as the exciting liquids. They gave a very feeble current and the carbon was soon polarized; the sulphite of zinc formed also adhered to the zinc and prevented further action.

Ex. No. 14. Iodide of potassium saturated with iodine was tried; this also gave a feeble current and the carbon soon became polarized.

Ex. No. 15. A cell of the Maynooth battery was fitted up and a saturated solution of potassic bichromate in nitric acid used as the absorbing liquid; the battery was not very constant, and the iron was soon attacked; no fumes, however, were given off. The electro-motive power was about .55 of a Daniell's cell.

The result of these experiments seem to show that the battery used in experiment No. 7 is the best for ordinary use, since it costs but little, if any more, than the Bunsen battery charged with nitric acid alone, and is entirely free from fumes until exhausted. If the following directions are observed in preparing the fluids, it cannot fail, I think, to give satisfaction.

To prepare the exciting liquid, sulphuric acid of 1.84 sp. gr. is mixed with nine times its volume of water and allowed to stand until the precipitated lead has all settled. The clear acid is then decanted and is fit for use. This plan of preparing the acid has been in use in this laboratory for some years and gives very good results, local action being almost entirely prevented by the removal of the lead.

To prepare the absorbing fluid, ordinary commercial nitric acid is saturated with potassic bichromate; this should be done in a warm room, as it takes up much more when warm than when cold. The solution thus prepared is mixed with one-third of its volume of sulphuric acid and enough water added to re-dissolve the chromic acid precipitated.

Two objects are gained by adding the sulphuric acid. The mixture is less expensive than if pure nitric acid is used and the internal resistance is decreased. If the internal and external cells are properly proportioned this battery will run until the exciting fluid is exhausted, without giving off any fumes of nitrous acid. If crude chromic acid could be obtained at a sufficiently low rate, No. 9 would be a very powerful and convenient battery for many purposes.

My thanks are due to Dr. Wolcott Gibbs for many valuable suggestions made during the progress of this investigation and for the use of the apparatus employed.

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