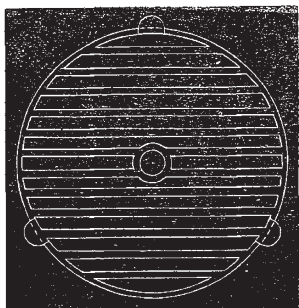


A CONSTANT FORM OF DANIELL'S  
BATTERY\*

GRAHAM'S discovery of the extreme slowness with which one liquid diffuses into another, and Fick's mathematical theory of diffusion, cannot fail to suggest that diffusion alone, without intervention of a porous cell or membrane, might be advantageously used for keeping the two liquids of a Daniell's battery separate. Hitherto, however, no galvanic element without some form of porous cell, membrane, or other porous solid for separator, has been found satisfactory in practice.

The first idea of dispensing with a porous cell, and keeping the two liquids separate by gravity, is due to Mr. C. F. Varley, who proposed to put the copper-plate in the bottom of a jar; resting on it a saturated solution of sulphate of copper; resting on this a less dense solution of sulphate of zinc; and immersed in the sulphate of zinc, the metal zinc-plate fixed near the top of the jar. But he tells me that batteries on this plan, called "gravity batteries," were carefully tried in the late Electric and International Telegraph Company's establishments, and found wanting in economy. The waste of zinc and of sulphate of copper was found to be more in them than in the ordinary porous-cell batteries. Daniell's batteries without porous cells have also been tried in France, and found unsatisfactory on account of the too free access of sulphate of copper to the zinc, which they permit. Still, Graham's and Fick's measurements leave no room to doubt but that the access of sulphate of copper to the zinc would be much less rapid if by true diffusion alone, than it cannot but be in any form of porous-cell battery with vertical plates of copper and zinc opposed to one another,



GROUND PLAN OF NEW BATTERY

as are the ordinary telegraphic Daniell's batteries which Mr. Varley finds superior to his own "gravity battery." The comparative failure of the latter, therefore, must have arisen from mixing by currents of the liquids. All that seems necessary, therefore, to make the gravity battery much superior instead of somewhat inferior to the porous-cell battery, is to secure that the lower part of the liquid shall always remain denser than the upper part. In seeking how to realise this condition, it first occurred to me to take advantage of the fact that saturated solution of sulphate of zinc is much denser than saturated solution of sulphate of copper. It seems† that, at 15° temperature, saturated aqueous solution of sulphate of copper is of 1.186 sp. gr., and contains in every 100 parts of water 33.1 parts of the crystalline salt; and that at 15° the saturated solution of sulphate of zinc is of sp. gr. 1.44, and contains in every 100 parts of water 140.5 parts of sulphate of zinc, both results being from Michel and Krafft's experiments.‡ Hence I made an element with the zinc below; next it saturated solution of sulphate of zinc, gradually diminishing to half strength through a few centimetres upwards; saturated sulphate of copper resting on this; and the copper-plate fixed above in the sulphate of copper solution. In the beginning, and for some time after, it is clear that the sulphate of copper can have no access to the zinc otherwise than by true diffusion. I have found this anticipation thoroughly realised in trials continued for several weeks; but the ultimate fate of such a battery is that the sulphate of zinc must penetrate through the whole liquid, and then it will be impossible to keep sulphate of copper separate in the upper part, because saturated solution of sulphate of zinc certainly becomes denser on the introduction of sulphate of copper to it. To escape this chaotic termination, I have introduced a siphon of glass with a piece of cotton wick

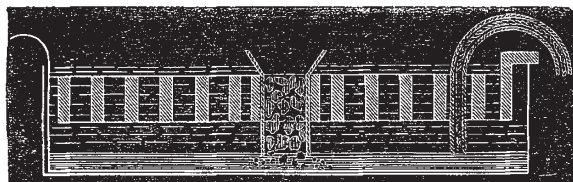
\* From the Proceedings of the Royal Society.

† Storer's Dictionary of Solubilities of Chemical Substances. Cambridge, Massachusetts: Sever and Francis, 1864.

‡ Ann. Ch. et Phys. (3) vol. xli. pp. 478, 482, 1854.

along its length inside it, so placed as to draw off liquor very gradually from a level somewhat nearer the copper than the zinc; and a glass funnel, also provided with a core of cotton wick, by which water semisaturated with sulphate of zinc may be continually introduced at a somewhat lower level. A galvanic element thus arranged will undoubtedly continue remarkably constant for many months; but it has one defect, which prevents me from expecting permanence for years. The zinc being below, must sooner or later, according to the less or greater vertical dimensions of the cell, become covered with precipitated copper from the sulphate of copper which finds its way (however slowly) to the zinc. On the other hand, if the zinc be above, the greater part of the deposited copper falls off incoherently from the zinc through the liquid to the copper below, where it does no mischief, provided always that the zinc be not amalgamated,—a most important condition for permanent batteries, pointed out to me many years ago by Mr. Varley. Placing the zinc above has also the great practical advantage, that, even when after a very long time it becomes so much coated with metallic copper as to seriously injure the electrical effect, it may be removed, cleaned, and replaced, without otherwise disturbing the cell; whereas if the zinc be below, it cannot be cleaned without emptying the cell and mixing the solutions, which will entail a renewal of fresh separate solutions in setting up the cell again. I have therefore planned the following form of element, which cannot but last until the zinc is eaten away so much as to fall to pieces, and which must, I think, as long as it lasts, have a very satisfactory degree of constancy.

The cell is of glass, in order that the condition of the solutions and metals which it contains may be easily seen at any time. It is simply a cylindrical or rectangular jar with a flat bottom. It need not be more than ten centimetres deep; but it



SECTION

may be much deeper, with advantage in respect to permanence and ease of management, when very small internal resistance is not desired. A disc of thin sheet copper is laid at its bottom. A properly shaped mass of zinc is supported in the upper part of the jar. A glass tube (which for brevity will be called the charging-tube) of a centimetre or more internal diameter, ending in a wide saucer or funnel above, passes through the centre of the zinc, and is supported so as to rest with its lower open end about a centimetre above the copper. A glass siphon with cotton-wick core is placed so as to draw liquid gradually from a level about a centimetre and a half above the copper. The jar is then filled with semisaturated sulphate of zinc solution. A copper wire or stout ribbon of copper coated with india-rubber or gutta percha passes vertically down through the liquid to the copper plate below, to which it is riveted or soldered to secure metallic communication. Another suitable electrode is kept in metallic communication with the zinc above. To put the cell in action, fragments of sulphate of copper, small enough to fall down through the charging tube, are placed in the funnel above. In the course of a very short time the whole liquid below the lower end of the charging tube becomes saturated with sulphate of copper, and the cell is ready for use. It may be kept always ready by occasionally (once a week for instance) pouring in enough of fresh water, or of water quarter saturated with sulphate of zinc at the top of the cell, to replace the liquid drawn off by the syphon from near the bottom. A cover may be advantageously added above, to prevent evaporation. When the cell is much used, so that zinc enough is dissolved, the liquid added above may be pure water; or if large internal resistance is not objected to, the liquid added may be pure water, whether the cell has been much used or not; but after an interval, during which the battery has not been much in use, the liquid added ought to be quarter saturated, or even stronger solution of sulphate of zinc, when it is desired to keep down the internal resistance. It is probable that one or more specific gravity beads kept constantly floating between top and bottom of the heterogeneous fluid will be found a useful adjunct, to guide in judging whether to fill up with pure water or with sulphate of zinc solu-

tion. They may be kept in a place convenient for observation by caging them in a vertical glass tube perforated sufficiently to secure equal density in the horizontal layers of liquid to be tested by the floaters.

An extemporised cell on this plan was exhibited to the Royal Society, and its resistance (measured as an illustration of Mance's method, described in the first of his two previous communications) was found to be  $\cdot 29$  of an Ohm (that is to say, 290,000,000 centimetres per second). The copper and zinc plates of this cell, being circular, were about thirty centimetres in diameter, and the distance between them was about  $7\cdot 5$  centimetres. A Grove's cell, of such dimensions that forty in series would give an excellent electric light, was also measured for resistance, and found to be  $\cdot 19$  of an Ohm. Its intensity was found to be  $1\cdot 8$  times that of the new cell, which is the usual ratio of Grove's to Daniell's. Hence seventy-two of the new cells would have the intensity of forty of Grove's. But the resistance of the seventy-two in series would be 209 Ohms, as against 76 Ohms of the forty Grove's; hence, to get as powerful an electric light, threefold surface, or else diminished resistance by diminished distance of the plates, would be required. How much the resistance may be diminished by diminishing the distance rather than increasing the surface, it is impossible to deduce from experiments hitherto made.

Two or three cells, such as the one shown to the Royal Society, will be amply sufficient to drive a large ordinary turret-clock without a weight; and the expense of maintaining them will be very small in comparison with that of winding the clock. The prime cost of the heavy wheel-work will be avoided by the introduction of a comparatively inexpensive electro-magnetic engine. For electric bells, and all telegraphic testing and signalling on shore, the new form of battery will probably be found easier of management, less expensive, and more trustworthy, than any of the forms of battery hitherto used. For use at sea, it is probable that the sawdust Daniell's first introduced on board the *Agamemnon* in 1858, and ever since that time very much used both at sea and on shore, will still be found the most convenient form; but the new form is certainly better for all ordinary shore use.

The accompanying drawing represents a design suitable for the electric light, or other purposes, for which an interior resistance not exceeding  $\frac{1}{10}$  of an Ohm is desired. The zinc is in the form of a grating, to prevent the lodgment of bubbles of hydrogen gas, which I find constantly, but very slowly, gathering upon the zincs of the cells I have tried, although the solutions used have no free acid, unless such as may come from the ordinary commercial sulphate of copper and commercial sulphate of zinc crystals which were used.

The principle which I have adopted for keeping the sulphate of copper from the zinc is to allow it no access to the zinc except by true diffusion. This principle would be violated if the whole mass of the liquid contiguous to the zinc is moved toward the zinc. Such a motion actually takes place in the second form of element (that which is represented in the drawing, and which is undoubtedly the better form of the two) every time the crystals of sulphate of copper are dropped into the charging-tube. As the crystals dissolve, the liquid again sinks, but not through the whole range through which it rose when the crystals were immersed. It sinks further as the sulphate of copper is electrically precipitated on the copper plate below in course of working the battery. Neglecting the volume of the metallic copper, we may say, with little error, that the whole residual rise is that corresponding to the volume of water of crystallisation of the crystals which have been introduced and used. It becomes, therefore, a question whether it may not become a valuable economy to use anhydrous sulphate of copper instead of the crystals; but at present we are practically confined to the "blue vitriol" crystals of commerce, and therefore the quantity of water added at the top of the cell from time to time must be, on the whole, at least equal to the quantity of water of crystallisation introduced below by the crystals. Unless a cover is added to prevent evaporation, the quantity of water added above must exceed the water of crystallisation introduced below by at least enough to supply what has evaporated. There ought to be a further excess, because a downward movement of the liquid from the zinc to the level from which the syphon draws is very desirable to retard the diffusion of sulphate of copper upwards to the zinc. Lastly, this downward movement is also of great value to carry away the sulphate of zinc as it is generated in the use of the battery. The quantity of water added above ought to be regulated so as to keep the liquid in contact with the

zinc, a little less than half saturated with sulphate of zinc, as it seems, from the observations of various experimenters that, the resistance of water semisaturated with sulphate of zinc is considerably less than that of a saturated solution. A still more serious inconvenience than a somewhat increased resistance has been pointed out to me by Mr. Varley as a consequence of allowing sulphate of zinc to accumulate in the battery. Sulphate of zinc crystallises over the lip of the jar, and forms pendants like icicles outside, which act as capillary siphons, and carry off liquid. Mr. Varley tells me that this curious phenomenon is not unfrequently observed in telegraph batteries, and sometimes goes so far as to empty a cell and throw it altogether out of action. Even without this extreme result, the crystallisation of zinc about the mouth of the jar is very inconvenient and deleterious. It is of course altogether avoided by the plan I now propose.

In conclusion, then, the siphon-extractor must be arranged to carry off all the water of crystallisation of the sulphate of copper decomposed in the use of the cell, and enough of water besides to carry away as much sulphate of zinc as is formed in the use of the battery. Probably the most convenient mode of working the system in practice will be to use a glass capillary siphon, drawing quickly enough to carry off in a few hours as much water as is poured in each time at the top; and to place, as shown in the drawing, the discharging end of the siphon, so as to limit the discharge to level somewhat above the upper level of the zinc grating. It will no doubt be found convenient in practice to add measured amounts of sulphate of copper by the charging-tube each time, and at the same time to pour in a measured amount of water, with or without a small quantity of sulphate of zinc in solution.

As 100 parts by weight of sulphate of copper crystals contain, as nearly as may be, 36 parts of water, it may probably answer very well to put in, for every kilogramme of sulphate of copper, half a kilogramme of water. Experience (with the aid of specific-gravity beads) will no doubt render it very easy, as a perfectly methodical action involving very little labour, to keep the battery in good and constant action, according to the circumstances of each case.

When, as in laboratory work, or in arrangements for lecture-illustrations, there may be long intervals of time during which the battery is not used, it will be convenient to cease adding sulphate of copper when there is no immediate prospect of action being required, and to cease pouring in water when little or no colour of sulphate of copper is seen in the solution below. The battery is then in a state in which it may be left untouched for months or years. All that will be necessary to set it in action again will be to fill it up with water to replace what has evaporated in the interval, and stir the liquid in the upper part of the jar slightly, until the upper specific gravity-bead is floated to near the top by sulphate of zinc, and then to place a measured amount of sulphate of copper in the funnel at the top of the charging-tube.

W. THOMSON

#### NOTES

AT the Anniversary Meeting of the Geological Society, held on the 17th ult., the Wollaston Gold Medal was presented to Prof. Ramsay in recognition of his many researches in practical and in theoretical geology; and the balance of the proceeds of the Wollaston Donation Fund was given to Mr. Robert Etheridge in aid of the publication of his great stratigraphical "Catalogue of British Fossils." A report of the interesting proceedings on the occasion will be found in another column. Mr. Prestwich was re-elected President of the Society for the ensuing year.

A STATUTE was promulgated last week in Convocation at Oxford enlarging the powers of the delegates of "unattached students," whom it is proposed to allow to admit students after examining them in one of the subjects already permitted (*i.e.*, Classics and Mathematics), "together with some other subject recognised in the schools of the University" (*e.g.*, Physical or Natural Science).

We are indebted to *Harper's Weekly* for some of the interesting notes on science in America, which we are able to furnish this week, in advance of their publication there. This magazine provides its readers with an important and interesting summary in each issue of the progress of science on that side of the Atlantic.