

II. "Note on Electrolytic Experiments." By JAMES DEWAR, M.A., F.R.S., Jacksonian Professor, University of Cambridge. Received February 10, 1880.

Having had occasion to employ the intermittent current of the de Meritens magneto-electric machine arranged for intensity in connexion with spectroscopic work, the following notes of electrolytic experiments made by means of it may not be without some interest.

The number of intermittent currents taking place in the circuit during the course of the following experiments may be taken as about 300 per second, and as the amount of energy in circulation is very considerable, an examination of its action on electrolytes was of some interest.

Dilute sulphuric acid, of about 1 of acid to 6 of water, used as the electrolyte in a large circular glass vessel, gave the following results:—

On placing two rather large platinum poles, each exposing a surface of about 32 square centims., no decomposition took place, a few bubbles of gas came off at one pole for a short time, which soon ceased. The current was proved to be passing by placing a telephone near the side of the glass vessel, and also by the rapid increase in the temperature of the acid, which very soon reached the boiling point. The absence of decomposition was due to the rapidity with which the current in the de Meritens machine is alternated, the gases given off at each pole being rapidly superposed and combining immediately to form water.

Decomposition was immediately produced by making and breaking the current rapidly with the hand, or better still, by placing a large tuning fork in the circuit, to which was attached a copper rod which dipped in and out of mercury at every vibration of the fork.

When two poles were used, consisting of platinum wire, decomposition went on without intermission at both poles, but on the other hand, when one pole was a plate of platinum and the other a platinum wire, the mixed gases were given off at the wire pole only.

The spectrum of the platinum poles, viewed with a small direct vision spectroscope, was very complicated, showing the H and air lines.

Platinum wire of about .5 millim. in diameter used as one pole, readily fused when held close to the surface of the liquid, and remained white hot when immersed below the surface, with a continual ejection of the particles of the fluid, and successive small explosions of the mixed gases.

Aluminium wire behaved in a remarkable way when used as one of the poles, the other pole consisting of a large surface of platinum.

On first plunging the wire beneath the surface nothing is observed; almost immediately, however, it becomes intensely illuminated all over the surface. The light seems to emanate from an immense number of points which look like lit up gems. This appears to be due to the formation of oxide of aluminium, which offers a great resistance to the passage of the current and consequently becomes intensely heated, and is pierced or disintegrated at certain points, and this supposition seems to be confirmed by the absence of any incandescence of the wire when hydrochloric acid, caustic potash, or any other medium which dissolves the oxide as soon as formed, is used. If another aluminium wire is substituted for the platinum plate, then either the one or the other becomes illuminated according to the extent of surface of metal immersed, but they are generally not illuminated at the same time, the largest surface always remaining dull; gases are now freely given off, being chiefly hydrogen.

The luminosity of the aluminium wire becomes very much diminished after a short time, as the wire becomes almost completely covered with a uniform layer of the white oxide, and is gradually eaten away. The luminosity can again be produced by cleaning the poles. The same effects took place when dilute hydrochloric acid, or saturated chloride of sodium was substituted for the dilute sulphuric acid. After the current had passed for some time gas was given off at both poles.

The light evolved from the surface of the poles below the surface of the electrolyte was intensely white, and on spectroscopic examination, proved to be the characteristic channeled spectrum of oxide of aluminium, first described by Thalèn. The characteristic metallic lines between the two H lines were faint.

On bringing a piece of thin foil aluminium as one pole near the surface of the acid it is immediately fused, globules of the melted metal flying about in all directions; the aluminium wire is also fused after a short time, and falls through the liquid in white hot globules.

Magnesium wire at one pole, the other being the platinum plate as before, gave an intense green colour below the surface, a spectroscopic examination showing the combined spectrum of the metal and oxide.

It burnt on the surface of the liquid in the same manner as the aluminium, showers of melted metal being thrown off; the action when a saturated solution of chloride of sodium was employed was, if anything, more intense. Similar actions took place with other metals, such as copper and zinc.

A solution of chloride of sodium was rapidly decomposed, abundance of chlorine being set free, when a platinum wire was used as one pole, the larger platinum plate being used for the other. A solution of iodide of potassium behaved in the same way, but was decomposed at a very much slower rate when both the poles were of large surface. A saturated solution of sulphate of copper deposited hardly a trace of

copper, when the platinum plate and a thick platinum wire were used as the two poles. Various modifications of these experiments may be made by employing different metals. The intensity current used with a saturated solution of nitrate of potash, has the power of engraving on glass, as described by von Plante.

The determination of the heat evolved from the Jablochhoff candle in the annular calorimeter formerly described, amounted to about 6,000 gram-units per minute, or in other words, it is about $\frac{1}{6}$ th of the total radiation of the Siemens machine when the small resistance of the electric arc is alone in the circuit.

On introducing into this circuit containing a Jablochhoff candle the voltameter which was formerly used, and in which no decomposition was apparent when used alone, the total radiation of the candle was very slightly diminished, but the cell showed intermittent bursts of electrolytic gas just as when the tuning fork was used as formerly described. This seemed to be always associated with any quality of intermittence due to the want of regularity in the action of the candle. Assuming that the whole work of the intermittent current was exhausted first in electrolysis, and then in recombination of the separated electrolytes, and that recombination resulted solely in a heating effect localised in the cell, then the elevation of temperature would be a measure of the chemical work done. As, however, the amount of this heating is relatively small in comparison with the current circulating, we must suppose that a considerable portion of the energy of recombination is thrown into the circuit as a new electromotive force. The chief interest in these experiments is the value of the de Meritens machine, as having many of the advantages from Plante's secondary piles, and the facility and ease with which this power can be used. Mr. Spottiswoode's recent experiments have shown that the character of the arc obtained from the de Meritens machine is intermediate in qualities between that of the ordinary arc and that of the induction spark, and may be employed with great advantage in exciting the induction coil. The use of it in spectroscopic work has been fully detailed to the Society in conjoint communications with Professor Liveing. The luminous discharge obtained below the surface of fluids shows another valuable use of the machine in connexion with this subject.