

March 31, 1887.

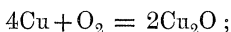
Professor STOKES, D.C.L., President, in the Chair.

The Presents received were laid on the table, and thanks ordered for them.

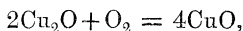
The following Papers were read:—

- I. "Note on the Development of Voltaic Electricity by Atmospheric Oxidation." By C. R. ALDER WRIGHT, D.Sc., F.R.S., Lecturer on Chemistry and Physics, and C. THOMPSON, F.C.S., Demonstrator of Chemistry, in St. Mary's Hospital Medical School. Received March 10, 1887.

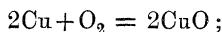
It is well known that when metallic copper is brought into contact simultaneously with atmospheric air and aqueous solution of ammonia, rapid oxidation is set up, the copper oxide formed dissolving in the liquid, producing a *blue* solution of ammoniacal cupric oxide, or cuprammonium hydroxide. Whilst investigating processes for the manufacture of this fluid (now used commercially on a considerable scale) we noticed that if the air supply be greatly in deficiency relatively to the bulk of the copper, under certain conditions the solution is but little coloured, containing copper dissolved principally as cuprous, and not as cupric, oxide. This might, perhaps, be anticipated *a priori*, inasmuch as it is well known that blue cupric solution in ammonia, when digested with metallic copper in the absence of air, takes up a second equivalent of copper, becoming colourless cuprous solution; but further experiments seem to indicate that the production of cuprous oxide under the oxidising influence of a limited supply of air is the primary action, and not merely a secondary result; in short, that the first step in the change is expressed by the reaction—



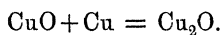
cuprous oxide being formed, which then (under favourable conditions) becomes further oxidised to cupric oxide, thus—



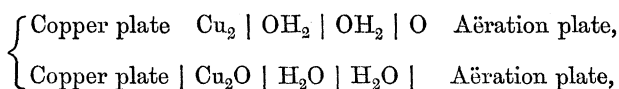
and not by the reaction—



the cupric oxide thus formed as the first product becoming subsequently reduced (in the absence of air) to cuprous oxide, thus—



When a sheet of copper is kept out of direct contact with air by being immersed in ammonia solution, oxidation of the metal is gradually effected by virtue of the dissolving of oxygen from the air at the surface of the fluid, and diffusion of the oxygen solution to the vicinity of the copper. This action is an extremely slow one if the copper be covered by some depth of fluid, and if the setting up of convection currents through heating or evaporation be prevented by keeping the vessel perfectly at rest and at an equable temperature, and well closed to prevent escape of ammonia; but if these precautions be neglected it goes on much more rapidly, and the liquid comparatively soon becomes blue; it can, however, be also materially accelerated by arranging horizontally on the surface of the fluid a plate of platinum or other electrically conducting material not chemically acted upon by the fluid, and connecting this by means of a wire, &c., with the copper plate. The upper conductor, or *aëration plate* as it may be conveniently termed, being simultaneously in contact with the atmosphere and fluid, attracts to its surface a film or aura of condensed gases, the oxygen of which becomes gradually transferred to the copper, a voltaic current circulating through the fluid and connecting wire. Cuprous, and not cupric, oxide thus results, dissolved in the ammonia solution in contact with the copper plate, the mechanism of the reaction being conveniently represented by the scheme—

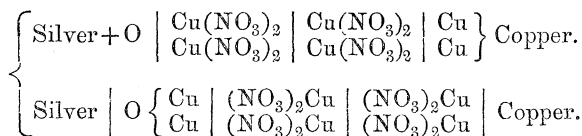


water being represented as the electrolyte for simplicity's sake. The air film on the aëration plate being constantly renewed by absorption from the atmosphere, the process goes on continuously as long as the two plates are connected together by the wire. This wire may be lengthened at will so as to make the current which passes through it whilst the action goes on relatively stronger or weaker according to the amount of resistance introduced into the circuit; and by including a galvanometer or silver voltameter in the circuit the ordinary phenomena due to the passage of currents are readily recognisable.

A voltaic cell thus produced "runs down" very rapidly when the resistance in circuit is diminished, more or less recovering when the resistance is again increased; with a large resistance (*e.g.*, sufficient to reduce the current density to a micro-ampère or less per square centimetre of aëration plate surface), a very notable E.M.F. is main-

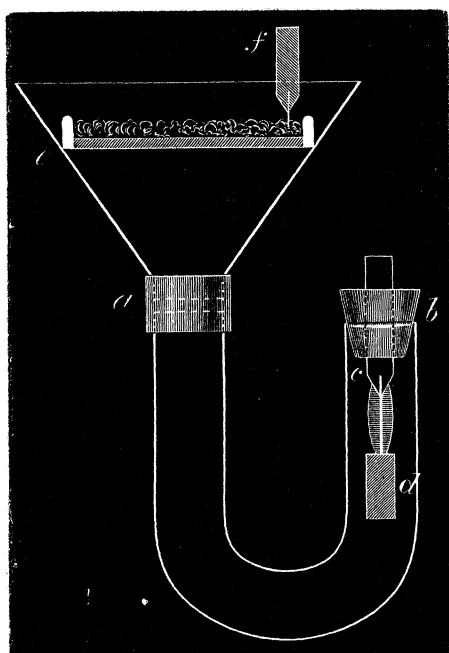
tained, amounting under favourable conditions to 0·5 or 0·6 volt. The maximum E.M.F. thus capable of development varies considerably with the strength of the ammoniacal solution, being the less the weaker the fluid; addition of common salt or of sal-ammoniac to the liquid notably increases the E.M.F. and diminishes the internal resistance of the cell. Spongy platinum in a thin layer as the aëration plate gives higher values than thin platinum foil; the highest numbers thus obtained, using pretty concentrated ammoniacal brine, fell but little short of 0·8 volt; or somewhat less than the E.M.F. corresponding with the heat of formation of cuprous oxide,* since, according Julius Thomsen, $\text{Cu}_2\text{O} = 40810 = \text{about } 0\cdot88 \text{ volt}$.

It is obvious that this copper atmospheric oxidation cell has a close connexion with the "air-battery" described in 1873 by Gladstone and Tribe ('Roy. Soc. Proc.,' vol. 21, p. 247) in which what is virtually an "aëration plate," consisting of a tray full of crystals of silver is used, opposed to a copper plate immersed in a solution of copper nitrate. Cuprous oxide is formed in both cases, in virtue of the indirect combination brought about between the oxygen of the air and the copper: but there is this great difference between the two (apart from the cuprous oxide being deposited as such in Gladstone and Tribe's arrangement, and being kept in solution in ours), that in the one the cuprous oxide is formed *at the surface of the copper plate* itself, and in the other *at the surface of the aëration plate*. This essential difference is embodied in the above depicted scheme as compared with the following one which represents the action in Gladstone and Tribe's cell:—



One result of this difference is that the surface of the aëration plate in the ammonia cell is kept constantly the same, whereas in the nitrate cell it is continually changing its character through deposition of solid cuprous oxide on the silver: in consequence of this deposition, whilst the E.M.F. of the ammonia cell, *cæteris paribus*, is constant, that of the nitrate cell is continually varying. Gladstone and Tribe, moreover, only obtained an E.M.F. of $\frac{8}{13}$ of a Daniell, or about 0·104 to 0·143 volt, even under the most favourable conditions, viz., when the cell was connected with an electrometer; whilst four or five times this amount is indicated by the cells examined by us.

* The actual chemical change going on in the cell is the synthesis of cuproso-ammonium hydroxide, so that the (unknown) heat of solution of cuprous oxide in ammonia should be added to this to obtain the total heat development.



In order to examine separately the fluids collecting round the two plates after action had gone on for some time, we employed cells of U-shape; and to obtain as large an aëration surface as possible, we adapted to one leg of the U a funnel (as indicated in the figure) with the stem cut off, and united to the U-tube by a piece of india-rubber tubing, *a*, slipped tightly over the junction. The other end of the U-tube was closed with an india-rubber cork, *b*, through which passed a piece of glass tubing with a platinum wire, *c*, sealed into it at the lower end and filled with mercury, thus forming a mercury cup, and serving to make contact with the copper plate, *d*, which was soldered to the end of the platinum wire, the soldering and platinum being coated with gutta-percha, so that only the copper plate was in contact with the fluid with which the U-tube was subsequently filled. A similar glass tube and platinum wire mercury cup, *f*, served to make contact with the aëration plate, which was conveniently supported horizontally at the surface of the fluid in the funnel by means of a disk of porous earthenware, *e*; by fixing a rim of gutta-percha round this disk so as to convert it into a sort of tray like the lid of a pill-box, and filling this tray with platinum sponge, an aëration plate of spongy metal was readily obtained. By interposing suitable resistances, galvanometer, silver voltameter, &c., in the external circuit

obtained on connecting the two mercury cups by a wire, the current passing could be modified at will, and shown to exhibit all the ordinary phenomena of moderately weak currents.

After continued action with small resistance only in circuit, the liquid in the funnel was found on analysis to contain no copper whatever, whilst that surrounding the copper plate, though colourless before removal from the tube, speedily became blue on exposure to air, and contained more or less considerable amounts of copper in solution, obviously originally in the condition of *cuprous* oxide, Cu_2O .

Following up the ideas suggested by the above observations, we are making a number of experiments with a variety of analogous combinations, in which atmospheric oxidation constitutes the essential chemical action taking place; by varying the nature of the aëration plates, the metals dissolved, and the liquids employed (as also by substituting other gases, *e.g.*, chlorine, for air), a large number of combinations are obviously obtainable. Some of those which we have so far examined present points of considerable interest, the oxidising action exerted under favourable conditions being strongly marked, so much so that certain metals, *e.g.*, mercury and silver, not ordinarily prone to atmospheric oxidation, can under suitable conditions be gradually oxidised and dissolved in appropriate liquids, just as the copper is dissolved in the ammonia in the cell above described; these actions, moreover, being accompanied by the development of currents of strength sufficient to cause measureable amounts of electrolytic decomposition outside the cell, *e.g.*, in a silver voltameter.

II. "Clausius's Formula for the Change of State from Liquid to Gas applied to Messrs. Ramsay and Young's Observations on Alcohol." By GEO. FRAS. FITZGERALD, M.A., F.T.C.D., F.R.S., Erasmus Smith's Professor of Natural and Experimental Philosophy in the University of Dublin. Received March 14, 1887.

Clausius, in Wiedemann's '*Annalen*,' vol. 14, 1881, pp. 279—290, and '*Phil. Mag.*,' vol. 12, 1881, p. 381, and vol. 13, 1882, p. 132, has given an empirical formula for calculating the relation between the volume, pressure, and temperature of a substance in both liquid and gaseous states. The equation he gives is a continuous one for an isothermal, and he determines the pressure at which evaporation takes place by considering that the work done in the transformation from liquid to gas at a constant pressure must be equal to what would be done if the transformation took place along the continuous isothermal. He requires, for convenience in applying this to actual cases, to calcu-

