reports, or in any journal which might not come to the attention of the abstractors.

It is expected that the publication of the tables will, after three or four years, become self-supporting. In the meantime, generous subscriptions have been made by governments, academies, scientific societies and individuals throughout the world; but further subscriptions must be obtained before the continued success of the project is assured. The general secretary, Dr. Charles Marie, 98 Rue du Cherche-Midi, Paris, and the members of the International Commission serve without remuneration.

Information concerning the "Annual Tables" or the work of the international committee will be gladly furnished by the undersigned American members of the committee.

G. N. LEWIS,
Massachusetts Institute of Technology, Boston, Mass.
G. F. HULL,
Dartmouth College, Hanover, N. H.
J. STIEGLITZ,
The University of Chicago, Chicago, Ill.

SPECIAL ARTICLES

CHEMISTRY OF THE SILVER VOLTAMETER[1]

AMONG the questions relating to the chemistry of the silver voltameter which have been investigated more or less in detail are the following: (1) Effect upon electrolyte of the various septa employed in the different types of voltameters to separate the anode electrolyte from that of the cathode; these septa include (*a*) filter paper, (*b*) silk, and (*c*) porous pots of unglazed porcelain; (2) the effect of various kinds of impurities upon the weight of the silver deposit and the explanation of this effect; (3) the preparation and testing of pure silver nitrate free from traces of impurities which produce disturbing effects in the voltameter; (4) anode secondary reactions; (5) cathode secondary reactions; (6) preparation of the silver anode; (7) purity of the silver deposit.

Of these, the first question has been studied in greatest detail, principally because of the fact that it includes the cardinal differences between the various types in use by national standardizing laboratories. It early became evident that the different results obtained with the various types was due principally to the effect produced by these septa, and that two of them introduced errors of much greater magnitude than any ordinary variations in the conditions or in the purity of different samples of even commercially pure silver nitrate. However desirable it might have been to have devoted every energy to the preparation of pure electrolyte and to its protection from contamination during the experiments, it was nevertheless necessary first to show, *if possible,* just what the nature of the action of the septa might be, since the primary object of the work was a *study of the silver voltameter as actually used,* and especially as used by the various standardizing laboratories, with a view of determining a uniform type if possible. The results of the investigation of the effect of filter paper seem to show that ordinary filter paper is superficially covered with oxycellulose, which can be extracted with water but which again forms spontaneously when the filter paper is allowed to remain in contact with the air. This oxidation is probably due to fermentation. This oxycellulose solution (colloidal) very readily reduces silver nitrate solution to colloidal metallic silver, which is very similar in properties to the colloidal silver of Carey Lea. Permanent colloidal solutions of silver have been prepared from concentrated aqueous extracts of filter paper. This reduction of silver nitrate is probably due to the intermediate formation of *furfuraldehyde* since the oxycellulose solution is readily decomposed into this aldehyde by the action of exceedingly dilute nitric acid of no greater concentration than that which is probably present in neutral silver nitrate solution (due to slight hydrolysis). Furfuraldehyde, especially the polymerized variety, produces all the *peculiar* effects which have been observed with filter paper, *e. g.,* imparts to the electro-

---

[1] Read before the Philosophical Society of Washington, May 20, 1911.

deposited silver a strongly striated and noncrystalline appearance. Other *strong* reducing agents produce similar effects, but to a less extent. Cane sugar and starch do not produce these effects.

It is very probable that the final effect of the filter paper in increasing the weight of the silver deposit is principally due to the deposition of the *colloidal* silver (by cataphoresis) and also some of the protective or "schutz" colloid-oxycellulose upon the cathode along with the electrolytically deposited silver, resulting in a breaking up of the usual crystalline form of the silver so that it occludes greater amounts of electrolyte. Thus, an unweighable amount of colloid can increase the weight of the silver deposit by a quite appreciable amount. Of course, the weight is further increased by the actual mass of the colloid deposited, but this seems to be a small per cent. of the total increase.

Silk when first used produces an effect very similar to that of filter paper, due to the ease with which it is partially decomposed into aldehydes. After repeated use in the voltameter, this aldehyde decomposition ceases, and it renders the electrolyte strongly acid, probably due to its decomposition into amino-acids. Since, in general, the effect of acid is to decrease the weight of the silver deposit, this fact probably accounts for the progressively decreasing values obtained with a voltameter with silk septa as compared to those obtained with the porous pot type.

Porous pots, when prepared according to certain specifications, have practically no effect upon the electrolyte so far as could be determined. If not so prepared, they render the electrolyte slightly acid and very faintly reducing in character. This *very slight* action is probably catalytic in character, and probably consists in a slight reduction of the silver nitrate to colloidal silver with the formation of an equivalent amount of nitric acid. This action lies at the basis of electrostenolysis. Of all the septa, the porous pot is by far the most inert.

In addition to colloidal silver, certain other colloids produce similar effects, as colloidal silica and colloidal silver hydroxide, whereas other colloids like hydrocarbons and starch do not. It is evidently a matter of whether the colloid migrates to anode or cathode *under the conditions* which *obtain in the voltameter.* This direction of migration may of course be different under other conditions.

Next to the presence or absence of strongly reducing impurities or certain colloids, the condition of *neutrality* of the electrolyte has the greatest effect upon the results. A method has been developed for defining the neutrality to within a part in a million of nitric acid. Fused silver nitrate when prepared according to the methods described in the literature is both slightly basic and also contains minute traces of reducing impurities which are very objectionable in voltameter work. Recrystallized silver nitrate (from neutral solution) is slightly basic, consequently the recrystallization must be made from acid solutions. This acid may be removed by recrystallization or by careful fusion, but the neutrality must be tested in either case.

There is no evidence of any secondary reactions at the cathode. The anode solution remains practically neutral, but if appreciably acid at the start tends to become neutral. The same is true when no septum is used. This indicates a secondary reaction of some sort at the anode. No evidence was found of the formation of reducing substances at the anode, such as a sub-silver nitrate. The evidence obtained by other investigators of the formation of such substances seems to be at least partially vitiated by the fact that in some cases at least the anode solution was filtered through filter paper. In other cases, the character of the filter is not mentioned.

No considerable work has as yet been done on the last question (7).

In the future work, the electrolyte will be subjected to ultramicroscopic examination for the presence of colloids.

A. S. McDaniel

Bureau of Standards,
Washington, D. C.