It may be interesting to note the discrepancies between the weights of hydrogen and chlorine and the hydrochloric acid formed in the individual experiments.

In these eleven experiments there were seven with an apparent loss of weight and four with an apparent gain, the total loss being 1 in 35,000.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE BUREAU OF STANDARDS No. 5.]

PREPARATION OF CHLORPLATINIC ACID BY ELECTROLYSIS OF PLATINUM BLACK.

BY H. C. P. WEBER.

Received October 9, 1907.

In the work[1] on the atomic weight of chlorine it was necessary to prepare considerable quantities of chlorplatinic acid free from nitric acid. When using aqua regia to dissolve platinum, considerable difficulty was experienced in removing the last traces of nitric acid by evaporation. When working with as much as 100 grams of platinum, the oft-repeated evaporation to dryness of the solution becomes exceedingly tedious and even at best, yields uncertain results. If the evaporation is carried on with strong hydrochloric acid considerable quantities of material become necessary, while with the use of water there is danger of hydrolytic decomposition of the chlorplatinic acid and consequent contamination of the chlorplatinate with hydroxychlorplatinates.

The process here described overcomes these difficulties and yields a pure solution of chlorplatinic acid. The platinum is prepared for electrolysis by dissolving platinum scraps or platinum sponge in aqua regia. The excess of acid is removed either by neutralization or evaporation, and the platinum solution is reduced by zinc or an alkaline formate, preferably the latter. The solution is decanted from the precipitated platinum, which is then warmed with a little dilute hydrochloric acid to remove iron. The platinum is then transferred to the electrolytic apparatus, the washing of the precipitated platinum being completed in this apparatus, which is constructed as follows:

It consists of a cylindrical tube about 4 cm. in diameter and 35 cm. long, which ends in a narrow glass tube, about 4 mm. bore, which is given the form of a siphon. The anode is a thin disk of sheet platinum which just fits into the tube and is perforated with numerous small pinholes. A small piece of platinum wire is welded to the disk and carried through the glass tube by means of sealing glass. The other end of the platinum wire ends in a glass tube which is carried to the top of the ap-

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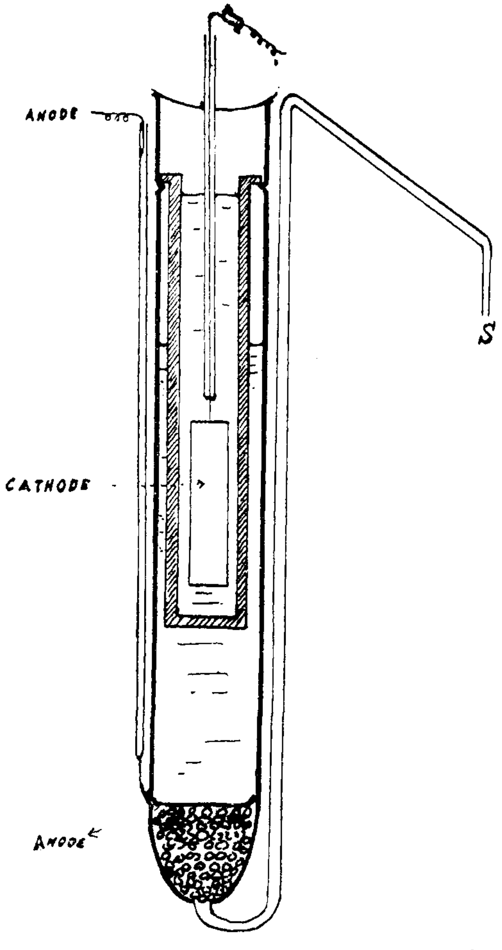
[1] Noyes and Weber: See preceding article.

paratus and is filled with mercury to make connection for the current. The platinum disk should be about 30 cm. from the top of the apparatus at that point where the tube commences to narrow. After the anode has been sealed into the tube the space below it is filled with glass beads to support the platinum disk, which should rest firmly and evenly upon them. About 5 cm. from the top of the tube three notches are pressed into the glass. From these the cathode chamber is suspended. This consists of a porous porcelain filter about 18 cm. long and 25 mm. in diameter. It is well that the rim of the filter fit snugly in the glass tube so that the filter cap hangs in the tube fairly rigidly.



The cathode consists of a sheet of platinum 4 to 5 cm. long and 2 to 3 cm. wide. To it is connected a platinum wire passing through a glass tube. It is suspended from a perforated watch glass, which serves as a cover for the apparatus.

The whole apparatus is suspended in a long cylinder by means of a large cork for the purpose of cooling it by running water when necessary. This is not shown in the diagram and may be dispensed with when low currents are used. The apparatus has been used with a current up to 10 amperes. With a current of this strength the cooling jacket is essential, as the apparatus gradually becomes hot.

The platinum is transferred to the tube, being dropped on the anode plate, and is here washed with dilute hydrochloric acid until clean. The wash waters are drawn off by gentle suction at the siphon end S. The platinum is then covered with concentrated hydrochloric acid. There should be such a quantity of hydrochloric acid that the liquid stands on a level with *S* when the porous cylinder is inserted. The porous cylinder is then inserted and filled to the top with hydrochloric acid. After the cathode is inserted the apparatus is ready for electrolysis.

The current may be taken from a 120 volt direct current, lighting circuit with a number of incandescent lamps in parallel with each other and in series with the cell. The cell may be run continuously on 8-10 amperes. The current is used quantitatively in dissolving platinum. During a run of four and a half hours at 8 amperes, 64 grams of platinum were dissolved. The theoretical quantity for 36 ampere hours is 65 grams. While the apparatus is in operation the hydrochloric acid travels from the cathode cell to the anode under the influence both of gravity and electric endosmoses. With the proper adjustments of height of hydrochloric acid in the anode cell, the heavy layer of chlorplatinic acid solution is delivered at the tip of the siphon *S*, drop by drop. If the flow of concentrated solution ceases for any reason it may again be started by gentle suction at *S*. For this purpose it is best to have the siphon tip *S* connected with a receiving flask by means of a double perforated stopper. The acid in the cathode chamber is replenished from time to time as it becomes necessary.

If towards the end of the operation, when the amount of platinum remaining upon the perforated disk becomes small, bubbles of chlorine commence to rise through the liquid, it is an indication that the current density is becoming too great. In this case, bringing fresh acid into the neighborhood of the platinum black and decreasing the current will remedy the chlorine evolution.

In concentrating the solution of chlorplatinic acid after it is so prepared, chlorine is passed through it for a short while. This insures freedom from platinous compounds in case any have been formed during the electrolysis.

[Contributions from the Research Laboratory of Physical Chemistry of the Massachusetts Institute of Technology, No. 20.]

THE THEORY AND PRACTICE OF THE IODOMETRIC DETERMINATION OF ARSENIOUS ACID.

By Edward W. Washburn.

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1. Introduction.—The first application of arsenious acid solution in titrametric analysis was made by Gay Lussac,[1] who used it in chlorimetry with an indigo indicator. Penot[2] later improved the method by the use of strips of starch iodide paper as the indicator and the use of caustic soda as the solvent for the arsenious acid, instead of hydrochloric acid,

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[1] Gay Lussac, Ann., **18**, 18.

[2] Penot, Dingl. Pol. J., **127**, 134 and **129**, 286.