

ing a clear liquid above so that by letting the alkaline sulphide run in slowly the point may be observed where no further precipitate is formed.

After some remarks by the chair, the second paper, "Upon the determination of tannic acid," by Mr. Nelson H. Darton then followed.

Dr. Grothe then stated that he together with Dr. Friedburg had recently observed the formation of a chloroform hydrate.

Some remarks and questions by the Recording Secretary then followed.

Dr. Friedburg then moved that members should be instructed to send all their papers and manuscripts to the Committee on Papers and Publications for their approval before they are read.

Carried unanimously.

Mr. Casamajor then presented the resignation of Mr. W. Schrage which was accepted.

Mr. Casamajor stated that Prof. Mallett had accepted an invitation for our coming annual dinner and moved that a committee of three be appointed to make arrangements for said dinner.

Carried.

The Recording Secretary then moved that the Chair appoint said committee.

Carried.

The Chair, after due consideration, appointed Messrs. Casamajor, Sloane and Stebbins.

Mr. Casamajor further stated that the cost for the dinner would be \$3 per plate.

After which the meeting adjourned.

JAMES H. STEBBINS, JR.,  
*Recording Secretary.*

## X. VOLUMETRIC ESTIMATION OF COPPER AND OF LEAD

BY P. CASAMAJOR.

In this process, copper is precipitated from an alkaline solution by a titrated solution of sodic sulphide. This reagent is used in a process published some thirty years ago by Pelouze, in the *Annales de Chimie et de Physique*. In Pelouze's process, copper is dissolved in a large excess of ammonia, and an intensely blue liquid is obtained. To this a titrated solution of sodic sulphide is added until the blue color disappears.

To titrate the sodic sulphide, one gramme of pure copper is dissolved in nitric acid, and 40 or 50 cubic centimetres of concentrated ammonia are added, the whole being placed in a flask. This liquid is heated to boiling, and the solution of sodic sulphide is dropped in the flask until the blue color disappears. To observe this, the precipitate is allowed to settle, and more ammonia is added if necessary.

The solution of sodic sulphide was found to keep well in tightly stopped bottles.

I have had occasion to use this process several times, and have always found that the end of the reaction is not definite. The brown color of the sulphide, of which particles remain suspended, interferes with the observation of the color of the liquid. After the blue color has disappeared, an addition of alkaline sulphide will show a visible turbidity, even when copper is the only metal present.

Instead of treating a cupric solution by an excess of ammonia, I use an alkaline tartrate, dissolved in an excess of caustic soda. This liquid is the same, which, added to a titrated solution of cupric sulphate, forms Fehling's solution. It is prepared by dissolving 173 grammes of Rochelle Salt in 480 cc. of caustic soda solution, of specific gravity 1.14, and adding water sufficiently to form 1 litre of liquid. This solution is added to the acid solution of copper to be tested, in slight excess of the quantity sufficient to redissolve the cupric oxide, and to obtain a clear blue solution. The liquid in the porcelain dish is then heated to nearly boiling point, and the sodic sulphide solution is gradually added, until no turbidity is produced by the addition of one drop of the reagent.

In this manner of proceeding, the blue color of the solution is not taken into account. The brown cloud which follows the addition of the titrated reagent is the only guide. The first portion of sodic sulphide, added to the alkaline cupric solution, gives rise to an intense black brown precipitate. As soon as this is formed the liquid in the porcelain dish is thoroughly stirred with a glass rod, which has the effect of agglomerating the cupric sulphide into a coarse curdy precipitate, which rapidly settles to the bottom of the dish, leaving the liquid quite clear and nearly colorless. If, after settling, the liquid should not be sufficiently clear, it should be vigorously stirred again, until the desired effect is obtained. After every addition of sulphide of sodium, the thorough agitation of the liquid is repeated until it is sufficiently clear. The degree of turbidity caused

by the addition of the reagent is a guide as to the quantity to be added. At the beginning, the brown color is very intense, and it is useless to wait for a complete clearing up before adding more of the reagent. Towards the end, the brown cloud is very slight, and the sodic sulphide should be added slowly, stirring up after every addition. Finally the sodic sulphide should be added drop by drop, until not the faintest cloud is seen after adding one drop.

By thoroughly stirring the liquid in the porcelain dish, and thereby causing the precipitate to become agglomerated in heavy clots, the surface of the dish remains very clean. On the white porcelain, as a back ground, the faintest cloudiness is easily observed, and a liquid containing one gramme of copper in 30,000 cubic centimeters, will still give a distinct brown cloud by the addition of one drop of the reagent.

For the volumetric estimation of lead, the same process may be applied. Sulphate of lead is easily dissolved in the alkaline tartrate solution. The sulphide of lead is precipitated in exactly the same manner as sulphide of copper. The precipitate agglomerates into curd as easily as does cupric sulphide, and the end of the reaction is equally definite.

As lead can be separated from other metals as sulphate, which is easily dissolved in the alkaline tartrate solution, we have by this method a rapid way of estimating lead. The precipitation by sodic sulphide is a quick operation, which only takes a few minutes. Sulphuric acid can also be separated as plumbic sulphate and estimated in the same way. Other acids which form insoluble plumbic salts could also be estimated by this process.

Copper can be separated from every other metal as sulphocyanate (Rivot's process). This precipitate may be heated with excess of nitric acid, and the alkaline tartrate solution added, after which the copper can be precipitated as sulphide.

These volumetric processes for copper and lead are founded on the easy agglomeration into heavy clots of the sulphides of these metals by agitation, the liquid remaining perfectly clear. Other metals, whose sulphides agglomerate in the same way in the alkaline tartrate solution, can probably be estimated by this process.

An attempt was made with silver, but chloride of silver was found to be insoluble in the alkaline tartrate solution. Chloride of silver was dissolved in excess of ammonia, and sodic sulphide added, but this did not prove satisfactory as sulphide of silver is sufficiently

soluble in ammonia to give a brown solution in which a faint cloud cannot be seen.

As chloride of silver is agglomerated into heavy clots by agitation, like cupric and plumbic sulphides, the white-cloud obtained, by pouring a titrated solution of sodic chloride into a solution of nitrate of silver, may be observed against a black background. This may be had by carrying on the precipitation in a flat dish of black glass, or in one of clear white glass, the under side of which has been covered with lamp black. The solution never clears up so completely by agitation as the alkaline solutions of copper and lead, but the slight milkiness of the liquid does interfere with the observation of the white cloud due to the formation of even very small quantities of chloride of silver.

The best temperature for the agglomeration of chloride of silver is about 65° C.

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### FOREIGN PATENTS.

Condensed from R. Biedermann's Report to the German Chemical Society, by Otto H. Krause.

A. R. PECHINEY, Salindres : *Manufacture of sodium bicarbonate* (Eng. P. 2098, May 24, 1880). This invention relates to the manufacture of soda by the ammonia process. The apparatus employed consists of a horizontal cylinder, which can be turned upon its long axis, and which is divided, first, by a perforated diaphragm parallel to the latter, and then into several compartments by discs placed at right angles to this. The discs have openings in the centre. The axles upon which the cylinder turns are hollow, to allow the gases and liquids to enter and pass out. Ammoniacal solution of sodium chloride enters, and unabsorbed gases pass out through the axle at one end, whilst the axle at the other end, which has two concentric openings, serves for the exit of the liquid containing the suspended sodium bicarbonate and for the entry of the pure carbonic acid resulting from the calcination of the latter. Impure carbonic acid, from kilns or furnaces, enters the outer concentric opening, and is led by means of pipes through the first three compartments of the cylinder and delivered into the fourth. The cylinder makes half revolutions at regular intervals. Ammoniacal solution of sodium chloride fills the apparatus, flowing through the holes in the discs, and passes into it continuously, whilst carbonic acid enters at the other end. On its way through, the liquid meets a current of gas, which latter gradually becomes richer in carbonic acid, the last three compartments receiving the pure gas.