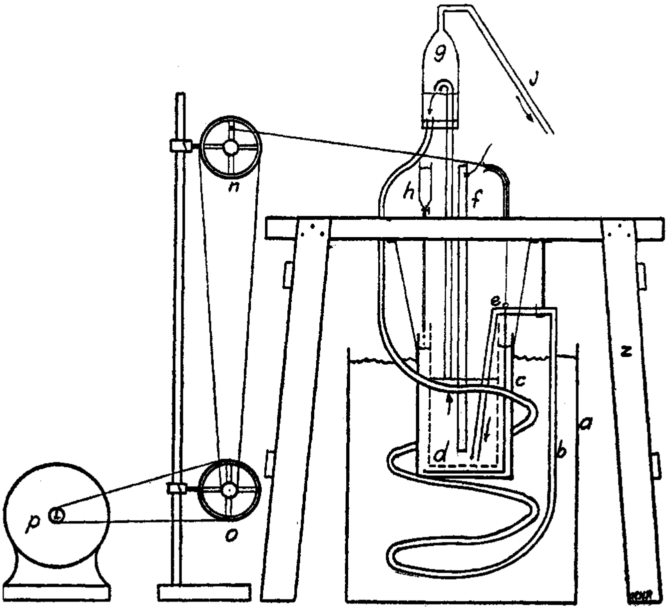
NOTES.

The Electrolytic Preparation of Hydroxylamine Hydrochloride.—The extensive use of hydroxylamine hydrochloride in the electroanalytical determination of metals according to the methods devised in this laboratory (see Schoch and Brown, This Journal, **38,** 1660 (1916)), and the utter absence of this substance in the market at present rendered it necessary for us to prepare hydroxylamine hydrochloride in lots of several hundred grams. After trying various other methods, we found its preparation by electrolytic reduction from nitric acid according to the method of Julius Tafel[1] to be very convenient. Since, under the present circumstances, others may desire to make this material, we thought they might wish to learn how the method works, and to benefit by the changes in procedure which we have made.

The apparatus shown in the accompanying sketch is identical with that used by Tafel except that the anode (*f*) is a lead rod or pipe, about one inch in diameter; this was used in place of the graphite anode employed by Tafel because we found it necessary to use dilute sulfuric acid in the anode compartment. The lead cup or cathode (*c*) has a diameter of 10 cm. and a height of 18 cm. Its inner surface was well amalgamated. When used continuously, it had to be re-amalgamated once a week. The porous cup (*d*) has an internal diameter of 6.5 cm. and a height of 19 cm.



Apparatus for electrolytic preparation of NH_2OH, HCl.

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[1] *Z. anorg. Chem.*, 31, 289.

The space between these (the cathode compartment) holds about 400 cc., and is filled with a mixture of three volumes of water to one volume of hydrochloric acid (sp. gr. 1.20). Although the cathode liquid is kept cool by surrounding the lead cup with a freezing mixture (in the pail *a*), yet the anode liquid has to be cooled also; this is accomplished by connecting (*j*) to a suction pump and drawing the anode liquid through the glass tube (*s*) into the glass "adapter" (*g*). The latter is closed at the bottom by a two-holed rubber stopper; a $^1/_2$ in. lead pipe ($^1/_4$ in. bore), 10 ft. long, has one end thrust through one of these holes at the bottom of (*g*) and is bent into a coil placed in the freezing mixture as shown. The anode liquid flows, by gravity, from (*g*) through the lead pipe, and then, through a glass tube extension to the bottom of the porous cup. A glass stirrer serves to stir the cathode liquid; its upper end is shown at (*e*). Its lower end is bent into circular form so as to fit between the lead cup and the porous cup. The stirrer is raised and lowered by the mechanical arrangement shown. The nitric acid is dropped in through the dropping funnel (*h*).

To operate the apparatus, the anode compartment is filled with dilute sulfuric acid, the cathode compartment with hydrochloric acid of the required concentration, and the pail with a freezing mixture. When the liquids in the cell has attained a temperature of 15° or less, a current of 50 amperes is turned on (pressure, 25 volts!), and then a mixture of nitric acid (sp. gr. 1.40) with one volume of water is allowed to drop into the cathode compartment through (*h*) at such a rate that 2$^1/_2$ hrs. are required to add 75 cc. of the nitric acid mixture. After this amount of nitric acid had been added, the current is allowed to continue to flow for 30 minutes longer, or a total of three hours. The current density in the above procedure is 8 amps. per 100 sq. cm.

After the end of three hours of electrolysis, the cathode liquid is removed by syphoning, and concentrated *in vacuo*, by heating it on top of a water bath; the flask should not be touched by the water in the water bath. The common practice of drawing air through the distilling flask must naturally not be employed. When the liquid has been concentrated to such an extent that crystals are formed in the drops spattered on the sides of the flask, it is removed and cooled in a freezing mixture without stirring (to avoid possible decomposition of the hydroxylamine by the oxygen of the air). The crystals are gathered on a filter paper, and the mother liquor is concentrated further to secure a second crop of crystals, and again a third crop; with the third crop the liquid may be evaporated almost completely.

To free the hydroxylamine hydrochloride from the accompanying ammonium chloride, the crude material is treated with separate small portions of cold absolute alcohol until a test shows that the residue is free from hydroxylamine hydrochloride. In explanation of this procedure, it should be mentioned that one liter of alcohol at 15° dissolves 44.3 grams of hydroxylamine hydrochloride, and only 6.2 grams of ammonium chloride.

The hydroxylamine hydrochloride is obtained from the alcoholic solution by the same procedure as that employed for its crystallization from the cathode liquid above. In one case—which is typical—we obtained 45.7 grams of this "purified" material from 37.5 cc. of nitric acid (sp. gr. 1.40). If we deduct from this the maximum weight of ammonium chloride possibly mixed with it, we find that the yield of pure hydroxylamine hydrochloride is about 80% of the theoretical amount possible.

This work was done by Mr. R. H. Pritchett of this laboratory.

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Inclusions in the Silver Voltameter.—In a very interesting and important paper on the inclusions of mother liquor in the crystals deposited in the silver coulometer[1], Vinal and Bovard have determined the weight of mother liquor thus held, under the most satisfactory conditions which have been worked out with much care by the Bureau of Standards. They find it to be on the average 0.004 %—an amount only about one-quarter of our average value, but identical with the lowest which we found under our conditions. This is a contribution of great importance, for it gives positive information on the only important point previously in doubt about this work of the Bureau as regards the electrochemical equivalent of silver. It seems, indeed, by thus completing the investigation, to place this work of the Bureau, carried out under Professor E. B. Rosa, on a higher plane than any other which has ever been published concerning this important constant.

The small amount of inclusion thus found by the Bureau of Standards justifies the great care taken there to maintain adequate purity of the electrolyte. In this connection we wish to point out again[2] that these investigators were the first to investigate the precise effects of organic impurities on the weight of the deposit. A previous statement of ours[3] was not intended to claim priority of any such detailed knowledge; it was intended only to express the fact that the desirability of purity of electrolyte had been recognized in early work on general grounds. In all of the 56 "standard" electrolytes made at Harvard in 1901[4] with the porous cap coulometer, organic matter of all kinds was scrupulously ex-

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[1] *Bull. Bur. Standards*, Reprint 271 (1916); This Journal, 38, 496 (1916).

[2] Richards and Anderegg, This Journal, 37, 692 (1915).

[3] *Ibid.*, 37, 8 (1915).

[4] Richards and Heimrod, *Proc. Am. Acad.*, 37, 415 (1902).

cluded from the electrolyte, both in preparation and during the electrolysis; but no effort was made to discover the part played by filter paper in affecting the weight of the deposit (recognized as too great) in the filter-paper coulometer. The excess of weight was then ascribed primarily to another cause, namely, the possible existence of a complex ion formed at the anode. The investigators at the Bureau of Standards have shown that the effect of filter paper is considerable, and believe indeed that its presence is the only cause of the excess.

Another important feature of the interesting paper of Vinal and Bovard was the discovery of a hitherto unsuspected source of error in the silver coulometer—namely, the effect of platinum black (remaining from a previous determination) upon the weight of silver deposited and upon the inclusion. Although recognizing the presence of traces of platinum black after the gently ignited silver had been dissolved, we did not suspect that this substance could affect a subsequent trial, because we thought that we were able to remove it wholly by scrubbing. But Vinal and Bovard have shown that even minute traces of platinum black, imperceptible to the eye, may have an appreciable effect upon the new deposit. Our oversight was in omitting to ignite the cathode at a high temperature between each trial[1]—a precaution which we can now see to be essential. On account of this error in experimentation, it is clear that our more subtle conclusions, especially that concerning the "volume effect" and the comparison of the Kohlrausch coulometer with the porous cup form, may have been invalidated. The amount of residual platinum black in our cathodes cannot be decided without further trial (now in progress) under precisely similar conditions; it must have been very small. The uncertainty introduced into our results is perhaps less than one part in ten thousand in the weight of the ignited silver;[2] but, nevertheless, small as the effect is in relation to the weight of silver, it is important in relation to the small divergencies upon which some of our conclusions were based.

Other less important minor points in connection with the irregularities of the coulometer are receiving further experimental attention, here and elsewhere. Discussion of all these points had better await the results. So far as we can see, none of the still unsettled questions affects appreciably the main outcome of the work of the Bureau of Standards, as regards the magnitude of the electrochemical equivalent of silver. This is now established by this recent paper of Vinal and Bovard, in an unusually impregnable position.

In brief, this note is intended to express our satisfaction that the ad-

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[1] In our experiments the crucible was merely heated at 160° until constant in weight between each trial.

[2] This conclusion is based upon preliminary experiments carried out here by N. F. Hall.

mirable work of the Bureau of Standards has been completed by the determination of the actual amount of inclusion in their deposits; to emphasize the fact that in view of the newly discovered effect of invisible traces of platinum black, we overrated the significance and certainty of some of our recent conclusions, reasonable although they seemed at the time; and to state that further experiments are in progress.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

MOLECULAR REARRANGEMENTS OF β-TRIPHENYLMETHYL-β-METHYL HYDROXYLAMINES AND THE THEORY OF MOLECULAR REARRANGEMENTS.[1]

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Received August 1, 1916.

The earliest observations of molecular rearrangements of hydroxylamine derivatives were those of Lossen[3] in the case of hydroxamic acids, $RCO.NHOH$, and of dihydroxamic acids, $RCO.NHOCOR_1$.[4] In explanation of these and similar rearrangements, the one of us proposed the theory[5] that they take place through the intermediate formation of univalent nitrogen derivatives under the influence of the reagent used to effect the rearrangement. Thus, a hydroxamic acid could form such a univalent nitrogen derivative by the loss of water in the presence of dehydrating agents.

$$RCO.NHOH \xrightarrow{-HOH} RCO.N \longrightarrow CO:NR. \qquad (1)$$

Dihydroxamic acids would yield the same products with the loss of a molecule of acid under the influence of bases or heat.

$$RCO.NH.OCOR_1 \xrightarrow{-R_1COOH} RCO.N \longrightarrow CO:NR. \qquad (2)$$

The free or latent valences of the unsaturated nitrogen atom were considered to have the power to take the radical R from the carbon atom. Of the many facts brought out in support of this theory by the one of us and by a number of independent investigators,[6] only the most important need be summarized here: (1) The ready application of the theory

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[1] A brief preliminary report appeared in *Proc. Nat. Acad. Sciences*, **1**, 205 (1915). For literature references to previous papers, see Stieglitz and Leech, THIS JOURNAL, 36, 272 (1914).

[2] The material presented here is used by Stagner in his dissertation in part fulfilment of the requirements for the Ph.D. degree of the University of Chicago.

[3] *Ann.*, 161, 359 (1872).

[4] This is tautomeric with $RC(OH):NO.COR_1$.

[5] See the literature references given by Stieglitz and Leech, *loc. cit.*

[6] Schroeter, *Ber.*, **42**, 2340 (1909); **44**, 1207 (1911); Stoermer, *Ibid.*, **42**, 3133; Wieland, *Ibid.*, 42, 4207; L. W. Jones, *Am. Chem. J.*, 48, 1 (1912); **50**, 440 (1913).