

### 7. Summary.

Using a slightly modified form of Lamb and Larson's "flowing" junction apparatus, reproducible values were obtained, within a few hundredths of a millivolt, of the potentials of the liquid junctions between equi-concentrated solutions of a series of monovalent chlorides. The Lewis and Sargent form of Planck's original equation,  $E_i = RT/F \ln \Lambda_c/\Lambda'_c$ , expresses the results for junctions involving most of the ions studied, and gives qualitative agreement in all cases. The experimentally determined potentials can, however, be obtained from the differences between numbers, one for each ion at each concentration. This is equivalent to the expression given above, except that, for the potassium and lithium ion, values of  $\Lambda$  which are slightly different from those obtained from conductance measurements would have to be used.

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### NOTES.

**A Simple Method for the Preparation of Sodium Hydroxide free from Carbon Dioxide.**—Having recently had occasion to prepare solutions of sodium hydroxide free from carbon dioxide, the method of preparation here described was evolved and in use found simpler than most methods commonly used.

**Method.**—Distilled water contained in an Erlenmeyer flask is boiled to remove any carbon dioxide present, after which, when the water is cooled enough, ethyl ether is added to form a layer 3 or 4 cm. in depth. Pieces of metallic sodium, not exceeding about 1 cm. in diameter are then dropped into the flask. They will fall no further than the ether layer where they remain suspended. The water contained in the ether layer causes the slow formation of sodium hydroxide, which readily passes below to the water layer. Meanwhile the ether prevents the results usually observed when metallic sodium is brought in contact with water in the presence of air. After the desired quantity of metallic sodium has reacted, the larger portion of ether is removed by a pipet, and the last traces by boiling the solution. Various modifications and adaptations will suggest themselves to the reader.

**Fire Hazard.**—It would seem that the above procedure is fraught with considerable danger from fire and explosions. Particular effort was made to cause explosions. As a result it was observed that none occurs so long as the depth of the ether layer is great enough so that the suspended sodium cannot simultaneously come in contact with both air and water. When the quantity of sodium to be dissolved is rather large in proportion to the quantity of ether present it sometimes happens that the heat evolved by the reaction is sufficient to evaporate the ether sufficiently to cause

fire hazard. Obviously, this condition is easily corrected by the addition of more ether to the flask. Of the explosions resulting by intentionally adding large quantities of sodium to a shallow ether layer, none was of sufficient violence to break the containing flask which, of course, was unstoppered. With the care ordinarily exercised in handling ether and by keeping the ether layer as thick as 3 or 4 times the diameter of the largest piece of sodium being dissolved, the reaction is carried out easily and without danger. A further advantage of the method arises from the fact that the greater part of any kerosene adhering to the sodium is removed with the ether.

**Purity of Product.**—No precipitate is formed when a solution of barium hydroxide is added to a solution of sodium hydroxide prepared by this method; but further than this, no critical examination has been made to learn whether or not this product is of sufficient purity for purposes requiring high precision. It is hoped to extend the work to include a study of the applicability of this method to the preparation of the hydroxides of all the alkalis and alkali earth metals and to a critical examination of the purity of the resulting products.

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**The Nesslerization of Ammonia Solutions.**—In using the Folin-Bell<sup>1</sup> method for the determination of ammonia in urine and the Folin-Youngburg<sup>2</sup> method for the determination of urea in urine, we found trouble in keeping the product of the nesslerizations dissolved. This uncertainty concerning clouds and precipitates forming in nesslerized mixtures had been mentioned by Allen and Davisson<sup>3</sup> in a paper on colorimetric work. We set out to find what were the necessary conditions for a successful nesslerization that would give a solution yielding no precipitate on standing for the usual time required for the colorimetric determination.

We have found several precautions necessary. When any of these are not carefully observed the product of the nesslerization will be partly dissolved and partly precipitated. If the following precautions are taken the product of the nesslerization will be a clear sparkling solution with no visible precipitate

1. All dilutions must be made with distilled water. Tap water, even though ammonia-free, has not been found advisable.
2. The flasks in which the nesslerizations are made should be well rinsed with c. p nitric acid and then with distilled water to remove the mercury film that may have separated from a previous nesslerization.

<sup>1</sup> Folin and Bell, *J. Biol. Chem.*, **29**, 333 (1917).

<sup>2</sup> Folin and Youngburg, *ibid.*, **38**, 111 (1919).

<sup>3</sup> Allen and Davisson, *ibid.*, **40**, 196 (1919).

3. The Nessler solution used should be the one recommended by Folin in his later paper.<sup>4</sup> Folin's earlier Nessler solution<sup>5</sup> was not found to work as well.

4. The given amount of Nessler solution (10 cc. to 20 cc.) must be added rapidly all at once. We found that a wide-mouthed pipet or cylinder worked very well. Slow addition of the reagent was not good.

5. After the addition of the Nessler solution, the mixture must not be shaken or stirred. It must be left perfectly quiet for at least 20 minutes. When the reagent is added, the solutions mix instantly as intimately as is possible with shaking. Any dilution with water to a definite volume must be done gently and only after the 20 minutes' standing period.

6. The solution to be nesslerized should not contain over 1.0 mg. of ammonia nitrogen for 150 cc. of solution. On nesslerization and dilution of the product to 200 cc., the brown color is very intense, and with such concentrated solutions part of the product tends to deposit on the walls of the flask and interfere with the colorimetric work.

After determining the necessary precautions we tried some 200 nesslerizations, leaving out some one or another of the above precautions. Only very rarely were we able to obtain successful results. Using the precautions mentioned, in more than 200 nesslerizations, we did not meet with a single failure. We therefore believe that the method outlined above affords complete control and gives solutions that are clear and remain so for hours. The necessary precautions are not bothersome.

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**The Preparation of Chloroplatinic Acid by Means of Hydrogen Peroxide.**—Since the use of concentrated hydrogen peroxide and hydrochloric acid instead of aqua regia for solution of platinum black in the preparation of chloroplatinic acid was first described,<sup>1</sup> the technique has been improved in several details, and it seems worth while at this time to describe briefly the method developed after several years of experience.

The presence of organic compounds, other than sodium formate, was avoided from the start and for this reason the difficulty with acetanilid

<sup>4</sup> Folin and Wu, *J. Biol. Chem.*, **38**, 89 (1919).

<sup>5</sup> Folin, *ibid.*, **26**, 473 (1916).

<sup>1</sup> Rudnick and Cooke, *THIS JOURNAL*, **39**, 633 (1917).

mentioned by Braley and Shaffer in their paper<sup>2</sup> was never encountered. The peroxide used in this work was, from the very first concentrated from a commercial product stated to be free from acetanilid, alcohol, etc.

Platinum black seems to dissolve more readily if it is not allowed to become dry after reduction. In order to combine this advantage with the necessity of keeping account of yields and of the amount of platinum in stock, the purified potassium chloroplatinate rather than the dried platinum black was chosen as the starting point for the preparation of the final solution. This offers the further advantage of starting with a pure compound for reduction and so obtaining a clean, quick and perfect separation of the platinum black.

Another important point developed was the use of hydrogen chloride instead of the strong aqueous acid. Hydrogen chloride is so easily made by the usual method of adding conc. sulfuric acid to conc. hydrochloric acid that this point offers no difficulty to offset the advantage of concentration and increased speed of solution.

The method, then, as at present used may be briefly described as follows.

The potassium chloroplatinate residues accumulating from the determinations of potash are extracted with the smallest possible quantities of boiling water and filtered while hot so as to separate all asbestos and paper fibers of the filter pads. The pure chloroplatinate crystals obtained on cooling are dried and form a part of the material for preparation of the reagent.

The filtrate and all other aqueous filtrates, including the spent Lindo-Gladding solution, are reduced with zinc and hydrochloric acid. All filtrates from this reduction are allowed to stand exposed to sunlight as much as possible for several weeks. Sometimes additional platinum black is obtained in this way.

The alcoholic filtrates are evaporated until the alcohol is driven off as judged by the odor. The residue is then reduced with zinc and hydrochloric acid and further treated in the same manner as the aqueous filtrates referred to in the preceding paragraph.

Whenever platinum black comes down in the form of a mirror, or otherwise does not lend itself readily to solution with hydrogen peroxide in a small volume, it is best to dissolve such deposits with a little nitro-hydrochloric acid. The nitric acid is evaporated and the remaining solution is added to the next lot of filtrate to be reduced with zinc and hydrochloric acid.

The more or less granular crude platinum black thus obtained is thoroughly washed by decantation and is then treated with hydrogen chloride.

<sup>2</sup> The Interaction of Platinum, Hydrochloric Acid and Hydrogen Peroxide. Presented at the April, 1921, Meeting of the American Chemical Society, Rochester, N. Y.

To this in suspension conc. hydrogen peroxide<sup>3</sup> is added and hydrogen chloride is bubbled through simultaneously in such manner that the bubbles keep the platinum black well agitated. After the flow of gas and of peroxide have been properly regulated, the process needs very little attention and solution is complete in the course of some hours, the time depending on the amount of platinum black to be dissolved.

The solution thus obtained is treated with the necessary amount of pure potassium chloride and the potassium chloroplatinate crystals are filtered off, dried and added to the stock of pure chloroplatinate on hand.

From a weighed amount of this stock the reagent is prepared by reduction with alkaline sodium formate, washing the platinum black obtained and dissolving it as described above. This solution is then made up to the proper volume as calculated from the weight of chloroplatinate taken, so that 10 cc. of the reagent contains 1 g. of metallic platinum, as required by the official methods of the A.O.A.C.<sup>4</sup>

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**FRIEDEL AND CRAFTS' REACTION. SOME SUBSTITUTED  
PHTHALIC ANHYDRIDES WITH TOLUENE AND  
ALUMINUM CHLORIDE.**

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As pointed out in a previous paper<sup>1</sup> an unsymmetrical phthalic anhydride with benzene and aluminum chloride may give two acid products. In some of the reactions described in this paper two acid products were obtained, in others only one. With the symmetrical tetrahalogenophthalic anhydrides only one acid product was obtained as was to be expected.

The physical properties of the toluyl-nitrobenzoic acids are very similar

<sup>3</sup> The conc. hydrogen peroxide should be freshly prepared immediately before use. Commercial peroxide, free from preservatives, is concentrated by distillation at reduced pressure to  $\frac{1}{10}$  its volume. The reservoir of commercial peroxide is connected to a Pyrex distilling flask, holding about twice the volume of conc. peroxide to be prepared, and the initial volume in the flask, which is the final volume desired, is maintained. The distillation is carried on under a pressure of 50 mm. of mercury or less and the bath is kept at a temperature 5° to 10° higher than the boiling point of water at the pressure in the flask.

Hydrogen chloride is prepared in the usual manner by adding conc. sulfuric acid to conc. hydrochloric acid in a suitable generator.

<sup>4</sup> Official Methods, A.O.A.C., 1920, p. 12.

<sup>1</sup> Lawrence, *THIS JOURNAL*, 42, 1871 (1920).