

With the higher concentration the effect of polymerization is very great in cutting down the vapor pressure, and the distillates are always weaker.

There is, therefore, a certain concentration of total formaldehyde at which the amount of simple molecules in equilibrium with the complex ones stays nearly constant with the slowly rising temperature, and since the vapor pressure is dependent almost entirely upon the simple molecules and not the polymer the vapor pressure will be constant and the material will distill over of a constant composition. With concentrations above 15% the formaldehyde is there chiefly as a polymerized form and therefore its vapor pressure is much lower than it would be if it were there as simple molecules. The result is as shown; the distillate is weaker than the original, although the total amount of formaldehyde present is large as shown by the high percentage in the residue.

Conclusions.

1. Distillation curves for solutions of various concentrations of formaldehyde in water have been determined.
2. With low concentrations (below 8%) the distillate is always *stronger* than the original, but with high concentrations the distillate is always *weaker*.
3. With low concentrations the residue is always weaker than the last distillate, but with high concentrations the residue is always stronger.
4. The difference is accounted for by the polymerization of the formaldehyde in water solutions into molecules having a low vapor pressure.

AMES, IOWA.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF AMHERST COLLEGE.]

TRihalogen-Methyl Reactions. III. THE USE OF THE SILVER CATHODE IN ELECTRO-DEPOSITION OF COPPER.

By HOWARD WATERS DOUGHTY AND BENJAMIN FREEMAN.¹

Received January 9, 1921.

The recent advances in the price of platinum, together with the numerous thefts of platinum from college and university laboratories, emphasize the desirability of substituting less expensive metals for it so far as may be practicable, and the writers therefore suggest the use of silver instead of platinum cathodes in the quantitative electro-deposition of copper. Silver cathodes have been used by students in this laboratory during the past year with entirely satisfactory results.

The use of silver cathodes has been suggested by various writers, but has not come into general practice, principally because of the difficulty in removing the deposit of copper after the analysis without also removing

¹ Presented before the Connecticut Valley Section of the American Chemical Society, November, 1920.

an appreciable amount of silver. Smith¹ suggests the removal of the copper by dil. hydrochloric acid to which hydrogen peroxide or a little nitric acid has been added. This suggestion is apparently based on the work of Salkowski,² who showed that silver is not dissolved to any considerable extent by hydrochloric acid and hydrogen peroxide. After removal of the copper the silver cathode is washed with dil. aqueous ammonia to remove any silver chloride that may have formed. The method is quite satisfactory in removing the copper, and if the cathode is removed from the solution promptly after the copper has dissolved there is very little loss of silver. We have tested the method by exposing a cathode made from pure silver foil, having a surface of approximately 70 sq. cm., to the action of a solution composed of 30 cc. of dil. hydrochloric acid and 15 cc. of a 3% hydrogen peroxide solution, with the following results. After 10 minutes the loss of weight of a 3.6 g. cathode was 0.0016 g.; after one hour it was 0.0080.

In 1919, Sand and Smalley³ suggested the use of hot dil. sulfuric acid and hydrogen peroxide to remove copper from a silver cathode. We have found this method much less satisfactory than the use of hydrochloric acid and hydrogen peroxide. In fact, Salkowski² states that silver is dissolved by sulfuric acid and hydrogen peroxide, with which statement we agree. We exposed the cathode described above to the action of a hot solution of 100 cc. of dil. sulfuric acid (1 : 10) and 25 cc. of 3% hydrogen peroxide solution for 5 minutes. The loss in weight was 0.1664 g.

The method now to be described for removing the copper from a silver cathode was developed in the course of an investigation of the behavior of trihalogen-methyl compounds with metals in the presence of aqueous ammonia, which is still in progress in this laboratory. In 1917 one of us⁴ published a preliminary statement to the effect that when a compound which contains the trichloro- or tribromo-methyl group is brought into contact with copper in the presence of strong aqueous ammonia, the copper is dissolved more or less rapidly, forming a solution of ammono-cupric chloride or bromide, while mono- or dihalogen-methyl compounds react very much less rapidly or not at all.

In 1919⁵ the further announcement was made that a similar effect is produced by using cuprous chloride instead of copper, but the reaction is much more rapid in this case than with copper, and it was suggested that this reaction could be used as a convenient and rapid qualitative test for the presence of compounds which contain the trichloro- or tribromo-methyl group.

¹ George McPhail Smith, "Quantitative Analysis," 1919, p. 95.

² Salkowski, *Chem. Z.*, **40**, 448 (1916).

³ Sand and Smalley, *Chem. News*, **103**, 14 (1911).

⁴ Doughty, *THIS JOURNAL*, **39**, 2685 (1917).

⁵ Doughty, *ibid.*, **41**, 1129 (1919).

During the past two years the present writers have studied the behavior of the chloro-acetic acids with copper and other metals, and the effect of aqueous ammonia in respect to this reaction. The result of this study will appear later. It is sufficient to say at this time that the reaction of ammonium trichloro-acetate in ammoniacal solution is by no means confined to copper. With cadmium the speed of the reaction is greater than with copper, and with zinc it is greater than with cadmium, while with nickel it is very slight and approaches zero very closely in the case of silver.

The reaction between copper and an ammoniacal solution of ammonium trichloro-acetate is exothermic to a surprising degree. When 19 g. of copper foil was added to a cooled solution of 32 g. of trichloro-acetic acid in 100 cc. of conc. aqueous ammonia (sp. gr. 0.90) contained in an Erlenmeyer flask, the copper was entirely dissolved in 6 minutes, and the temperature rose from 13° to approximately 105°, at which temperature the solution boiled.

On the other hand, there is almost no reaction between silver and the solution of ammoniacal ammonium trichloro-acetate. When a cooled solution of 16.3 g. of trichloro-acetic acid in 50 cc. of conc. aqueous ammonia was added to 32.4 g. of "molecular silver" (prepared by reducing silver bromide with glucose and sodium hydroxide), no effect was observed. After 24 hours 50 cc. of water was added and the flask, closed by a rubber stopper and Bunsen valve, was allowed to stand at laboratory temperature for 11 months, with frequent shaking during the first few weeks. The solution was then filtered from the silver and analyzed. The total amount of silver in solution was found to be 0.2096 g. Subsequent work makes it appear very probable that even this small amount was due to the presence of air in the flask rather than to the organic reagent.

From these experiments it appeared that it should be possible to use an ammoniacal solution of ammonium trichloro-acetate as a solvent, to remove a copper deposit from a silver cathode after determining copper electrolytically, and that by its use it might be practicable to substitute silver for platinum as the cathode material. The following experiments were performed to test the availability of the method.

a. The silver cathode previously mentioned was left for 18 hours in a stoppered bottle filled with a solution prepared by dissolving 16.64 g. of trichloro-acetic acid (1 mole) per liter of dil. aqueous ammonia, (3 volumes of conc. aqueous ammonia sp. gr. 0.90 to 5 of water). No loss in weight could be detected.

b. The silver cathode was replaced in the solution and a slow current of air was aspirated through the solution for 13 hours. The cathode then showed a loss of 0.0014 g.

c. The silver cathode was then placed in a solution containing one mol of ammonium chloride per liter of dil. aqueous ammonia (concentration as in previous experiment), and air was aspirated through the solution for 12 hours. The cathode lost 0.0008 g.

The ammoniacal solution of ammonium trichloro-acetate used in the preceding experiments hydrolyzes very slowly, and is entirely serviceable after standing for one year, during which no separation of chloroform can be seen. Concentrated aqueous ammonia acts on trichloro-acetic acid, as stated in various text-books, converting it, very slowly, at ordinary temperatures, into chloroform and ammonium carbonate.

As a result of the experiments described above, the following procedure is recommended for making analyses by use of a silver cathode.

Procedure. 1. *Cleaning the Cathode.*—Should the silver cathode be tarnished by hydrogen sulfide, it is placed in contact with pure tin foil in a boiling 10% solution of sodium hydroxide until perfectly bright. It is then washed with dil. hydrochloric acid, then with dil. aqueous ammonia and finally with distilled water. It is then rinsed with alcohol and the alcohol is ignited and allowed to burn off. After cooling in a desiccator the cathode is ready for use.

2. *The Analytical Procedure.*—The usual procedure for deposition of copper from nitric acid solution is followed exactly as when a platinum cathode is used, except that the current must be turned on before immersing the silver cathode, to avoid action of the nitric acid on the silver.

3. *Removing the Copper.*—After the final weighing the silver cathode is placed in a wide-mouthed stoppered bottle filled with a 10% solution of trichloro-acetic acid in aqueous ammonia (one part concentrated aqueous ammonia sp. gr. 0.90 and one part water). The copper is removed in about 10 minutes, the time depending on the amount of copper and the surface of the cathode. The cathode is then washed and dried as in (1) and kept in a desiccator or tightly stoppered bottle until needed.

The cathodes used in this laboratory were made of fine sterling silver gauze reinforced with silver wire, after the usual pattern of the platinum gauze cathode. These cathodes did actually lose weight appreciably, due to the action of the solvent on the copper contained in the alloy. The loss became smaller as they were used for successive analyses. It could doubtless be obviated entirely by plating the cathode with pure silver. These silver cathodes have been used side by side with platinum cathodes during the past year and have proved equally satisfactory in the hands of students.¹

Two g. of trichloro-acetic acid is required for the removal of one g. of

¹ These cathodes were made under the direction of Professor Arthur J. Hopkins and were used by students in his course in quantitative analysis.

copper. The reaction is apparently a quantitative one, involving 3 atoms of copper, cadmium or zinc, and 2 molecules of trichloro-acetic acid.

As a matter of economy or convenience, chloroform or carbon tetrachloride may be used instead of trichloro-acetic acid, but if this is done the ammoniacal solution should consist of one part of conc. aqueous ammonia and one part of alcohol (denatured will do) in order to increase the solubility of the organic trihalide. The latter may be added in any quantity, though it is well not to add more than will dissolve. If carbon tetrachloride is used it must be free from sulfur compounds, which it is very liable to contain, and which will stain the silver. The action of these reagents on copper is considerably slower than that of the ammonium trichloro-acetate solution.

Summary.

Copper can be rapidly and quantitatively removed from a silver cathode by means of an ammoniacal solution of a compound containing a trichloro-methyl or tribromo-methyl group. An ammoniacal solution of ammonium trichloro-acetate is recommended for this purpose, but a solution of chloroform or carbon tetrachloride in ammoniacal aqueous alcohol can also be used.

AMHERST, MASS.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 131.]

SOME NEW METHODS FOR THE DETERMINATION OF THE VAPOR PRESSURE OF SALT-HYDRATES.

BY ROBERT E. WILSON.

Received January 12, 1921.

I. Introduction.

The vapor pressures of salt-hydrates have been studied by a large number of investigators. Indeed, as the bibliography presented in the next section indicates, few physico-chemical phenomena have aroused a livelier or more sustained interest.

Both practical and theoretical considerations have united to arouse this interest. Much of the earlier work was done for the express purpose of substantiating van't Hoff's equation and other thermodynamic laws for the case of salt-hydrates. Others have worked with a view to determining the free energy of the compounds. Furthermore, a knowledge of the exact conditions under which salts are efflorescent, stable, or deliquescent, the preparation and preservation of pure hydrates of a given composition, the selection of desiccating agents, and the construction of phase-rule diagrams are important practical considerations which also depend on an accurate knowledge of the vapor pressure of hydrates.