The values for the ratio, V_0/U_0, and the transport number, $V_0/(U_0 + V_0)$, for the salts measured calculated from the specific velocities of the ions, are given in the following table :

Salt.	U_0.	V_0.	$\dfrac{V_0}{U_0}$.	$\dfrac{V_0}{U_0 + V_0}$.	
NH_4NO_3	0.00133	0.00176	1.32	0.570	0.487
KNO_3	0.00175	0.00176	1.00	0.501	0.483
$NaNO_3$	0.00131	0.00176	1.34	0.574	0.577
NaCl	0.00131	0.00180	1.37	0.581	0.596
$AgNO_3$	0.00111	0.00176	1.58	0.614	0.522

In column 6 the transport number of the anion in aqueous solution is given.

The work embodied in this paper was completed in the summer of 1902.

SUMMARY OF RESULTS.

A form of apparatus has been constructed by means of which the absolute velocities of certain ions in liquid ammonia have been determined.

The velocities of a number of univalent ions in liquid ammonia at —33° are from 2.4 to 2.8 times as great as they are in aqueous solutions at 18°, and are in agreement with the velocities calculated from conductivity measurements by the method of Kohlrausch.

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A RAPID AND CONVENIENT METHOD FOR THE QUANTITATIVE ELECTROLYTIC PRECIPITATION OF COPPER.

BY THEODORE W. RICHARDS AND HAROLD BISBEE.

IN ORDER to precipitate copper in a coherent film, suitable for careful washing and accurate weighing, it is necessary that during the electrolytic deposition there should always be enough ionized copper immediately at the surface of the cathode to carry the current from the solution to the electrode. If there is not copper enough present, hydrogen, or some other convenient cation, begins to carry the current, and the film becomes spongy or impure. This case may be discussed as a typical one.

What now are the conditions which determine whether or not enough copper is present to carry the current? Clearly, one of the conditions is the strength of the current to be carried. Corresponding to every solution, other conditions being fixed, is a maximum current which must not be exceeded. The rate of total precipitation is, of course, dependent upon this total current strength. Another is the area of the electrode on which the deposition is to be conducted, for only the copper in the immediate vicinity of the electrode can be deionized, and the greater the area the more copper is available, other conditions being equal. Therefore, the permissible rate of deposition and, consequently, the maximum current strength depends upon the area. Thus, it is the *current density,* or the strength of current for each unit of area, which determines whether or not a given cation is deposited in a pure state, other conditions being equal. Bunsen pointed out this fact many years ago.

Another essential condition which affects the permissible speed of precipitation is obviously the concentration of the solution of copper, for the more concentrated the solution the more copper will be present at the cathode ready for precipitation. Since ionization is an extremely rapid process, the whole of the copper present is probably available as a carrier, not merely that which is ionized. The "associated" portion ionizes at once as soon as the ionized portion is removed.

It is, of course, true that the single potential difference at the cathode, if measurable, would be an approximate index of the nature of the deposit, for this single potential difference rises in a mixture when the current density is increased above the "carrying power" of the most easily deposited ion. But, as is well known, the single potential difference would be at best only an approximate index, since with a single metal it varies over several tenths of a volt with varying concentration. As a matter of fact, the single potential difference at the cathode is not easily found, even arbitrarily, in actual analysis. The total difference of potential between the electrodes (or "Klemmspannung") is the sum of this quantity, the irregular fall of potential due to the usually unknown and changing resistance of the solution, and the anode potential, which, in turn, depends upon the mixture of anions present and the current density at the anode. Hence this total

difference of potential is a quantity which has no important significance unless all these circumstances are stated, and they usually are not stated in descriptions of analytical electrolytic methods. On the other hand, the current density is easily found, being simply the current strength in amperes divided by the area of cathode, usually expressed in square decimeters.

Thus, other conditions being equal, the possible speed of quantitative electrolytic precipitation increases directly as the area of the electrode and also approximately as the concentration in the electrolyte of the substance to be deposited.

Yet another circumstance must be taken into consideration in this connection, namely, the nature and concentration of other cations present. A current density which will yield a perfectly pure coherent deposit of copper when no impurities besides acid and zinc, for example, are present, will cause the copper to be seriously contaminated with another cation, such as arsenic, whose deposition-potential is nearer that of copper. Moreover, obviously, the greater the concentration of the foreign cation, the more danger is there of depositing it with the copper.

Finally, since only the substance in the immediate vicinity of the electrode can be deposited, and the diffusion of new substance into this vicinity is a slow process, it is clear that thorough agitation of the solution will greatly increase the permissible speed of precipitation by supplying fresh ionized copper to take the place of that deposited far faster than diffusion can supply it. This has been pointed out by Foerster and Seidel,[1] by Richards, Collins and Heimrod,[2] and others. Gooch and Medway,[3] and Exner,[4] working under E. F. Smith, have shown how greatly the maximum current density is raised, if artificial means is employed to stir the liquid.

In summing up the conditions which determine the speed of precipitation of a given cation in a pure state, the following are seen to be the essential ones: The area of the cathode, the concentration of the solution, the nature of the other cations present and their concentration, and the rate of circulation of the electrolyte.

[1] *Ztschr. anorg. Chem.*, **14,** 106 (1897).
[2] *Proc. Am. Acad.*, **35,** 131 (1899).
[3] Gooch and Medway: *Am. J. Sci.* (4), **15,** 320 (1903).
[4] Exner: This Journal, **25,** 896 (1903).

The method described in the present paper was planned so as to gain the greatest possible advantage from the adjustment of the first two of these conditions, the others being fixed by the conditions of the experiment. The solutions analyzed contained no metal besides copper which was more easily deposited than hydrogen, therefore hydrogen formed the convenient and well-known safety-valve, preventing the precipitation of other metals after the copper had been all deposited; and an admixture of hydrogen alone was to be feared. Diffusion and automatic convection, caused by gas bubbles, were alone depended upon to cause circulation, on account of the complexity introduced by mechanical stirring.

The essential adjustment of the variable conditions consisted in decreasing, as much as possible, the volume of the solution, and increasing, as much as possible, the surface of deposition. By spreading the concentrated solution in a thin film between two platinum electrodes, the result was easily attained. The most convenient form of apparatus consisted of a pair of concentric platinum crucibles or dishes, the annular space between them serving to contain the film of electrolyte. The vessels were prevented from touching one another by a suitably shaped construction of fine glass rod, looking like a miniature inverted tripod. For ordinary analytical processes where only the fraction of a gram of metal is precipitated, crucibles are large enough.

The actual space between the crucibles in our trials measured 5 milliliters,[1] and the liquid to be analyzed was measured from a standard solution with a carefully made Ostwald pipette[2] of this volume. To prevent loss by spattering, a milliliter of the best kerosene was added to the surface of the electrolyte.[3] The outer crucible (the cathode) was connected in the usual way; the inner anode crucible was prevented from floating by being filled with pure water, and was connected to the battery by simply touching its interior with a platinum wire. The immersed area of the cathode was about 33 sq. cm.

[1] The word *milliliter* is used here instead of its cumbrous counterpart *cubic centimeter* because the standard of volume has recently, by international co-operation, been decided as the liter and not the cubic decimeter. The difference between the two is indeed slight, but since both precision and brevity are in favor of the word milliliter, it seems advisable. See this Journal, **26**, 413 (1904).

[2] Ostwald-Luther : *Phys. chem. Mess.*, p. 135 (1902).

[3] This device was probably first used by Allerton Cushman in some experiments upon electrolyzing nickel in this laboratory in 1898.

In our experiments a solution of cupric sulphate of about molar strength was used as the standard solution. The solution was slightly acidified to prevent the formation of cuprous oxide at first. If the area of the cathode had been 100 sq. cm., this would have permitted a current strength of 2 amperes,[1] but the cathode being only a third of this area, a current strength of 0.7 ampere should not be exceeded. As the copper is removed, the solution soon becomes so dilute that unless the current density is diminished, hydrogen will begin to appear, and the copper will be spongy. The area remaining unchanged, the current density is easily lessened by diminishing the current strength. It was found most convenient to arrange a current strength somewhat smaller than the maximum at the start so that a third of the copper present was precipitated in ten minutes, and then to diminish the current strength to two-thirds of its former value, thus proceeding gradually, adjusting the current strength to the concentration, until so much of the copper was precipitated that all danger of forming spongy copper was past. If, in a first analysis the amount of copper is not approximately known, the second, at least, may be carried out rapidly in this way. In order to illustrate this procedure, the following table may be given, showing the calculated amounts for each period.

Periods (each 10 minutes).	Current for 10-minute periods (ampere).	Calculated weight. Weight of copper precipitated.
1	0.60	0.118
2	0.41	0.081
3	0.27	0.063
4	0.19	0.037
5	0.12	0.024
6	0.08	0.016
Residue still remaining in solution, and precipitated in 15 minutes by current of 0.06 ampere		0.0126
Total copper found		0.3416

The deposit was beautifully bright and lustrous, and was washed and dried with the greatest ease. The complete electrolysis demanded only one and one-quarter hours.

For a convenient table, designed for such calculations, see Küster, Log. Rechentafel, p. 45 (1904).

Four successive analyses thus conducted gave the following weights of copper: 0.3416, 0.3418, 0.3415, 0.3416; average, 0.3416.

[1] Richard, Collins and Heimrod : *Proc. Am. Acad.*, **35**, 148 (1899).

The shortest time was an hour and a quarter for the total. The same volume of standard solution, analyzed in dilute solution of 25 milliliters, gave 0.3418 as an average of two analyses; but five hours were needed to free the electrolyte from copper as effectually as had been possible with the concentrated solution in a quarter of the time. It is easily seen that the time of analysis is approximately proportional to the volume of electrolyte, other conditions being equal.

The chief difficulty in this method lies in the trouble of adjusting the current strength every ten minutes. For this reason it seemed to us worth while to test an automatic device for the purpose. We found that this was very simply arranged by using a storage cell at 1.9 volts as the source of electromotive force. The effective electromotive force is, of course, the difference between this value and that of the copper-oxygen couple; and because this difference diminishes with the diminishing concentration of the copper solution, the current strength and hence the current density will also diminish.[1] The diminution in the given instance does not exactly correspond to the values required by theory, but, practically, it is found to serve every purpose. The actual current strengths at successive periods, measured by an amperemeter of very low resistance placed in the circuit, were as follows: At the beginning, 0.50 ampere; after ten minutes, 0.32 ampere; after twenty minutes, 0.28 ampere; after an hour, 0.11 ampere; after an hour and a half, 0.03 ampere. This minimum current was maintained without change until the close of the electrolysis in three hours. In this way three successive trials of the apparatus yielded each 0.3416 gram of lustrous copper. In no case was enough copper found in the residual electrolyte to give a visible precipitate with ferrocyanide, even in a special case where this electrolyte was ten times normal in concentration of acid. A much stronger solution or the presence of nitric acid would probably cause estimable traces of copper to remain in solution, however.

Although the more recent work of Gooch and Medway, and of Smith and Exner, diminish the importance of this method as a

[1] This device has since been used by Denso (*Ztschr. Electrochem.*, **9**, 463 (1903)) and probably others also have thought of it. In our arrangement it is particularly effective, because the resistance of the electrolytic cell is very small. Our experiments were made in 1901.

means of gaining time in electrolysis, it is, nevertheless, possible that some analysts who wish to avoid the trouble involved in effecting mechanical circulation may find the method convenient. At least it is of interest theoretically, in that it demonstrates the gain which may be made by adjusting two of the essential conditions in the most favorable way.

In conclusion, the contents of the paper may be summarized as follows:

The consideration of the conditions necessary for speed in quantitative electrolytic precipitation shows that among the essential ones are the concentration of the solution and the area of the electrode. In the method described, these conditions are made as favorable as possible by concentrating the electrolyte and placing it between two large surfaces in a thin film, such as the annular space between two crucibles separated by a tripod-like device of thin glass rod. Copper was the metal used to test this apparatus. As the concentration of the electrolyte diminishes during the electrolysis, the current strength is diminished, either in steps by the operator, or automatically by employing a single storage cell without resistance. The time required for complete precipitation is inversely proportional to the concentration of the solution, if the cathode surface is unchanged.

THE ELECTROLYTIC PREPARATION OF CHLOROFORM FROM ACETONE.

By J. E. TEEPLE.

IN A recent article[1] a method was given by which almost the theoretical yield of iodoform could be obtained by the electrolysis of a potassium iodide solution in the presence of acetone. No diaphragm was necessary, the essential feature being the gradual addition of a substance such as hydrochloric acid, hydriodic acid, or still better, iodine, to neutralize the excess of potassium hydroxide as fast as it formed. The temperature was kept below 25°, the electrolyte was thoroughly stirred, a high current density used at the cathode and a comparatively low current density at the anode. In short, the aim was to keep the conditions always favorable for the production of a maximum amount of hypoiodite.

1 This Journal, 26, 170 (1904).