the occlusion of hydrogen, whereas the reverse is the case. Occlusion is accompanied by expansion in all directions.[1]

Another explanation offered is that a shunt conduction through the electrolyte, by which the wire was surrounded, varied with the transfer resistance between wire and electrolyte, and that these variations were responsible for the changes of resistance observed. Such an explanation is clearly inapplicable to the experiments in which the supplementary gain of resistance was found to continue unaltered after the electrolyte had been withdrawn.[2] In the ordinary experiments, each wire was annealed to constant resistance in nitrogen, and its resistance was again taken after the introduction of the electrolyte, but before electrolysis was begun. In no instance could a change of resistance, due to the presence of the electrolyte, be detected with certainty. Hence the shunt conduction was itself negligible, and such second-order differences in this factor as may have resulted from changes of transfer resistance could hardly have exerted an appreciable effect. It should be borne in mind that our measurements of resistance were not made while the electrolytic current was flowing.

As regards Professor Newbery's further elucidation of his hydride explanation, it does not appear to us in any way to remove the necessity for attributing to these compounds the extraordinary conductivities discussed above.

We are, therefore, still of the opinion that the simplest explanation of the supplementary conductance is to be found in the assumption of a transient conducting form of hydrogen.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF ILLINOIS.]

THE ELECTROLYTIC DETERMINATION OF THE HALOGENS: AN INDIRECT METHOD.

BY J. H. REEDY.

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The determination of the halogens by their electrolytic deposition on silver anodes has been regarded by most investigators as impracticable, since the silver anode begins to dissolve, either during the last stages of the electrolysis, or immediately upon completion of the halide ion deposition. Results are low, owing either to precipitation of silver halides in the solution or to the migration of silver to the cathode. Various expedients to overcome this difficulty have not proved satisfactory, and gravi-

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[1] Poggendorff, *Phil. Mag.*, [4] 37, 474–5 (1869); Thoma, *Z. physik. Chem.*, 3, 71 (1889).

[2] THIS JOURNAL, 40, 1516 (1918).

metric and volumetric methods have remained the standard processes for these determinations.

In a previous paper[1] it was shown that in most solutions there is a retardation in the solution of silver anodes until an anodic potential of about 0.52 volt[2] is reached, when the current, which is analytically negligible below this value, rather abruptly shows a marked acceleration of action. With halide solutions, however, action begins at lower potentials, depending upon concentration. The relation between potential and concentration is shown in Fig. 1. This suggests that the deposition of the halogens might be accomplished by carrying out the electrolysis with an anode potential of 0.52 volt, or a very slight excess of this value. To this end the decomposition potential of a 0.5 molar sulfuric acid solution saturated with silver chloride was determined, using silver coated with silver chloride as an anode and bright platinum as the cathode.

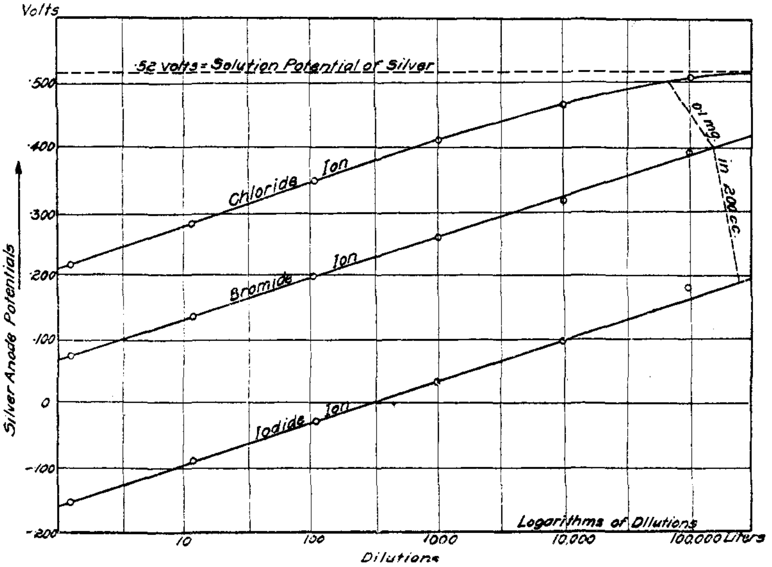

Fig. 1.—The change of potential of silver halide electrodes with dilution of ions.

This value was found to be 0.59 volt, which corresponds exactly with the "solution potential" of silver (0.52 volt) plus the overvoltage of hydrogen upon bright platinum (0.07 volt). As long as this limiting voltage of 0.59 is not exceeded, the electrolysis of halide solutions with silver anodes was found to proceed with the formation of an adherent layer of silver halide on the anode and without precipitation in the solution. With the completion of the deposition of the halide ions, silver

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[1] *Am. J. Sci.*, 40, 400 (1915).

[2] Referred to the normal hydrogen electrode as 0.0 volt.

ions appeared in the solution with no break in the continuity of the current and with a scarcely noticeable rise in potential.

In order to maintain the conductivity of the electrolytic solution, especially at low concentrations of the halogen ions, some "inert" electrolyte must be present. Since there is a tendency towards increasing alkalinity in all electrolytic solutions where hydrogen is liberated at the cathode and the anion discharged is not hydroxyl, neutral solutions are not favorable media for this operation. The reaction potential of hydroxyl ions on silver anodes is only slightly above that of chloride ions, and with the increase in concentration of the former the potential is reached where hydroxyl ions will be discharged more readily than chlorine ions. Under such circumstances the deposition of the halogen can never reach completion. For this reason, in the experiments reported below, the halides were electrolyzed in the presence of 0.5 molar sulfuric acid.

It thus appears that the unsatisfactory technique of the usual methods for the electrolytic determination of the halogens may be much simplified and the process made more or less automatic by carrying out the analysis under a constant potential of 0.59 volt, and determining the halogen by loss of weight upon electrolytic reduction of the halide deposit to metallic silver. This indirect method is necessary since varying amounts of silver dissolve at the end of the electrolysis.

The apparatus is shown diagrammatically in Fig. 2. A lead accumulator, L, of fairly large capacity was used as a source of current, since this form of battery maintains an approximately constant potential on a closed circuit. The cathode was of bright sheet platinum, and the anode consisted of a frame of heavy silver wire covered with a cylindrical surface of fine silver gauze, the whole being coated with silver electrolytically, and afterwards heated in an electric oven to make the deposit firm and adherent. The volume of the electrolyte used was 200 cc. The voltage was read from a voltmeter, V, connected as shown in the figure, so that any current passing through it would not be indicated by the milliammeter M. By means of the sliding resistance R the potential was set at 0.59 volt. Upon closing the circuit a rather large current passed at first, but with the aid of efficient stirring diminished very rapidly and became negligible at the end of 15 minutes. The potential was then raised to 0.60

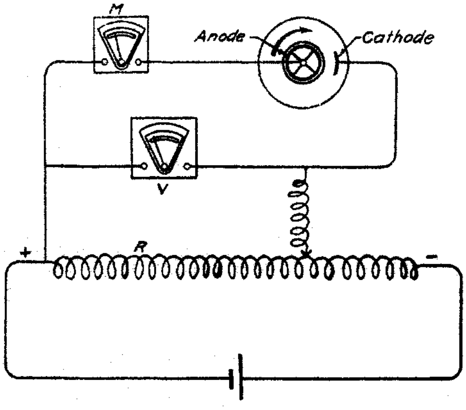

Fig. 2.—Diagram of apparatus.

volt and the current psssed 5 minutes more. The silver electrode, with its halogen deposit, after weighing, was made the cathode in a dilute solution of sodium hydroxide, which was electrolyzed until hydrogen was formed freely upon the surface of the silver. The silver halide was thus reduced to black silver, which was not very adherent and had to be handled carefully to avoid loss. After thorough washing, the electrode was heated to about 500° in an electric furnace until the deposit was white and thoroughly sintered together. The loss in weight on reduction represents the weight of the halogen. In most cases more or less silver dissolves from the anode towards the end of the electrolysis, remaining in solution as silver sulfate or plating out on the cathode as metallic silver. Representative results are given in Table I.

TABLE I.—DETERMINATION OF HALOGENS.

Wt. of electrode + halogen. G.	Wt. of reduced electrode. G.	Difference. G.	Error. G.	Wt. of silver dissolved. G.
Chlorine. Calc. wt. 0.0177 g.				
21.1048	21.0873	0.0175	−0.0002	0.0007
23.2998	23.2823	0.0175	−0.0002	0.0050
23.2987	23.2804	0.0183	+0.0006	0.0019
23.2929	23.2736	0.0183	+0.0006	0.0068
23.1783	23.1608	0.0175	−0.0002	0.0002
23.1443	23.1272	0.0171	−0.0006	....
23.1432	23.1260	0.0172	−0.0005	0.0012
Bromine. Calc. wt. 0.0396 g.				
21.1542	21.1145	0.0397	+0.0001	0.0011
21.1538	21.1144	0.0394	−0.0002	0.0071
21.1540	21.1144	0.0396	......	......
21.1389	21.0993	0.0396	......	0.0151
21.1366	21.0968	0.0398	+0.0002	0.0025
23.2888	23.2492	0.0396	......	......
Iodine. Calc. wt. 0.0629 g.				
21.1777	21.1156	0.0621	+0.0001	......
21.1585	21.0966	0.0619	−0.0001	0.0002
23.3350	23.2729	0.0621	+0.0001	0.0006
23.3327	23.2708	0.0619	−0.0001	0.0021
23.3309	23.2691	0.0618	−0.0002	0.0017
23.3312	23.2628	0.0628	+0.0008	0.0063

From this it appears that, even in the case of chlorine, where the potential required for the complete deposition lies very close to the solution potential of silver, the silver does not begin to dissolve until the precipitation of the halide is practically complete. It was found that, by carefully observing the limiting value, the formation of silver precipitates in the solution could be avoided. In a few cases, however, after the characteristic opalescence of the colloidal silver halide precipitate had appeared, it was found that by lowering the potential below 0.59 volt the solution could be cleared up again. But in cases where appreciable amounts of the silver halide had appeared in the solution, it was coagulated by the stirring, and in such form it dissolves too slowly for electrolytic decomposition to be practicable.

In spite of the unusual technique of the method, this procedure has been found to compare favorably with other gravimetric methods, both as to accuracy and speed. However, it must be confessed that this work was undertaken not so much for the purpose of developing a new method as for the confirmation of certain inferences drawn from the results of my study of electrode potentials.

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PASSIVITY OF COBALT.

BY HORACE G. BYERS AND CURTIS W. THING.

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Introduction.

In a paper by one of us[1] a report is given on a series of experiments on the passivity of cobalt and the following statement is made: "In solutions of the halogen salts, sulfates, nitrates, chlorates, nitrites, dihydrogen phosphate, citric acid, acetic acid, sulfuric acid, and nitric acid, cobalt as an anode goes quantitatively into solution. In the free acids, also, the metal dissolves by direct action of the acid so that the anode loss is greater than the copper equivalent. In caustic potash, neutral sodium carbonate, and potassium bichromate, cobalt fails to go into solution even to a minimal degree. When the plates which have been used in caustic potash are placed as anodes in solutions in which they dissolve, the initial high potential fall indicative of passivity is observed, provided the circuit is closed by immersion of the cobalt anode." It is stated in the contribution of Hollis[2] that cobalt, nickel and iron are passive in fuming nitric acid below a certain critical temperature which he fixes for iron at 100°, for nickel at 80° and for cobalt at 10°. In view of this contradictory behavior of cobalt and the difference between its behavior and that of iron and nickel it seemed worth while to make a further study of the topic. The experimental work detailed below is divided into 3 parts: (1) a study of the anodic behavior of cobalt in various solutions with change in concentration using small current density, (2) a study of the relation between the current density and the voltage drop across a platinum-cobalt cell using various solutions, and a comparison with similar cells using iron and nickel, and (3) a study of the anodic potentials of cobalt, iron and nickel.

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[1] THIS JOURNAL, 30, 1728 (1908).

[2] *Trans. Camb. Phil. Soc.*, 12, 462 (1904).