reagent in question. The results are summed up in the following paragraphs in which the concentrations of zinc are given in milligrams per liter.

Freshly prepared ammonium sulphide is not a good testing reagent for zinc at room temperatures. Ten mg. sometimes produces no turbidity. The delicacy is improved somewhat by raising the temperature to 50–60°. The objection to polysulphide is the precipitation of sulphur.

Hydrogen sulphide is a very satisfactory reagent. In a neutral solution of zinc sulphate 1 mg. of zinc may be detected at 50–70°. The limit at the same temperature is about 4 mg. if 100 cc. 0.90 ammonia are added. At 10°, with 40 cc. of 0.90 ammonia present, 10 mg. of zinc will not produce any turbidity for several minutes. Hydrogen sulphide, with or without ammonia, is not a delicate test for zinc when large amounts of potassium oxalate are present.

Potassium ferrocyanide is very satisfactory at a temperature between 50 and 70°. The solution should be made acid with 10–15 cc. of sulphuric acid (1.84) and potassium ferrocyanide added until the concentration is about 25 grams per liter. Under these conditions 0.5 mg. of zinc will produce a turbidity even in the presence of large amounts of the salts of organic acids.

[CONTRIBUTION FROM THE MASS. INSTITUTE OF TECHNOLOGY, LABORATORY OF INORGANIC CHEMISTRY.]

ON THE CAUSES OF THE HIGH RESULTS IN THE ELECTROLYTIC DETERMINATION OF ZINC.

BY ELLWOOD B. SPEAR.

Received February 14, 1910.

It has been shown in the previous article that the electrolytic determination of zinc by several methods is attended by high results. The cause must then be due to the presence of some foreign substance in the deposit such as:

1. Enclosure of liquid.
2. Salt precipitated with the zinc.
3. Hydrogen adsorbed or deposited as hydride.
4. Metal deposited with the zinc.
5. Zinc oxide or hydroxide deposited with the zinc.

The first part of this article consists of a detailed consideration of the above-named possibilities and the conclusion is finally reached that the formation of zinc oxide, or hydroxide, is the real cause of the high results. The second part deals with theoretical considerations.

The method of preparation of the solutions to be electrolyzed and the experimental conditions during the electrolysis were, except where otherwise stated, the same as in the preceding article.

Enclosure of Liquid.—It is extremely improbable that a smooth deposit of zinc would enclose a liquid, yet the best deposits are too high. Heating the dried deposit to 200° should reduce the weight, if any liquid were present. This was done repeatedly with different deposits and an insignificant increase in weight was always noticed, due, doubtless, to a very slow oxidation of the zinc. Further, electrolytic zinc that had been deposited from a solution that contained only sodium and zinc sulphates was carefully washed with water, alcohol and ether successively, dried and weighed. This weight was found to be invariably too high, if all the zinc had been deposited from solution. These deposits were next dissolved in hydrochloric acid, evaporated almost to dryness and the residue dissolved in a few cc. of water. On adding barium chloride not a sign of turbidity resulted on long standing. If any of the liquid had been enclosed some turbidity must have been in evidence under the conditions of the experiment. The last argument would also apply if any salt had been precipitated with the zinc.

Hydrogen Adsorbed or Deposited with the Zinc.—That any appreciable quantity of hydrogen is not contained in the deposits was proven in the following manner: About 0.4 gram of zinc was deposited on a copper gauze electrode from a sodium acetate solution. The deposit was in every case from 0.7 to 2.0 per cent. too high, which would correspond to 3 to 8 mg., or 40 to 100 cc. of hydrogen gas. The gauze electrode with the zinc deposit was put into the ignition tube *A* (Fig. 1) and covered with mercury. Flask *B* was filled to the neck with water and connected with the water in *C* by a short tube. *B* served as a trap to catch any mercury that might distil over. *C* was a 100 cc. graduated tube and was connected with the water in *D*. The mercury was boiled in *A* for 20 minutes. When the apparatus had cooled the water rose in *C* to the same level at which it stood before the heating. If any hydrogen had been contained in the zinc deposit it would have been given off and caught in *C* when the zinc formed an amalgam with the mercury.

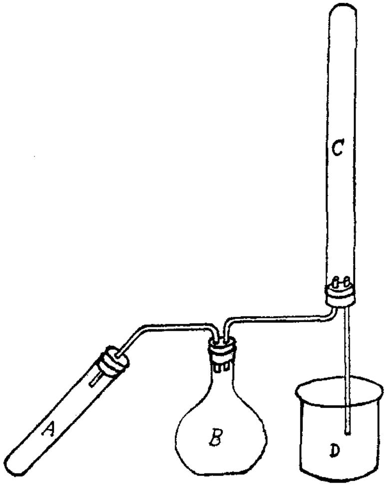

Fig. (1)

Metal Deposited with the Zinc.—If the high results were caused by the presence of a foreign metal, such as sodium, in the deposit, then there should be some relation between the magnitude of the error and the concentration of the sodium salts present during the electrolysis. This proved not to be the case, although the concentration was varied from zero to 200 grams per liter. Furthermore, two of these deposits were analyzed for sodium as follows: About one-half gram of the deposit was dissolved in hydrochloric acid and the zinc precipitated with ammonium carbonate. After acidifying with hydrochloric acid the filtrate was evaporated to dryness and the ammonium salts expelled. On once more precipitating the remaining zinc in a small volume with ammonium carbonate and expelling the ammonium salts the residue was not weighable. 10 to 20 mg. of sodium chloride must have remained if the high results are to be accounted for by the presence of sodium in the deposits.

Zinc Oxide or Hydroxide Deposited with the Zinc.—An attempt was made to reduce the zinc oxide by heating the deposit in a current of hydrogen gas. Owing to the volatility of the zinc and also of the zinc oxide, this was found to be impracticable. Reasons for believing in the presence of the oxide, or hydroxide, in the deposit are given below:

Zinc deposits from sulphuric acid solutions, where impoverishment of zinc in the cathode portion is prevented, have highly reflecting metallic surfaces and are found to be pure zinc by the best gravimetric methods. This was proven in the following manner: One gram of zinc sulphate was dissolved in 50 cc. of water to which was added 1 cc. of sulphuric acid (1.20). A rotating platinum crucible was made the cathode, pure zinc the anode, and the zinc deposited with a current of one ampere. The deposit was washed with water, alcohol, and ether, respectively, dried and weighed. The zinc was then dissolved in a few cc. of hydrochloric acid and the crucible again weighed. The zinc was determined by the phosphate method.[1] The results were as follows:

Elec.	Zn taken.	Zn found.
1	0.1890	0.1891
2	0.1837	0.1841
3	1.1054	1.1040

Zinc deposits from neutral or dilute alkaline solutions have little or no metallic appearance. Those from acetate or oxalate solutions are dull gray. The upper portion of the deposit is often quite white, resembling zinc hydroxide. Deposits from strongly alkaline solutions are gray to black, depending upon the fineness of division of the metal; they are never smooth or metallic if the cathode portion becomes impoverished with regard to zinc. These finely divided, black deposits decompose water so rapidly, if sodium salts are present, that the bubbles of hydrogen gas can be seen rising from the surface of the metal. If they are wet with water and let dry in a desiccator they increase in weight and become quite white.

---

[1] Talbot, "Quantitative Analysis," p. 64. Dakin, *Ztschr. anal. Chem.*, 39, 273 (1900).

Pure zinc deposits obtained from sulphuric acid solutions increase in weight and become white and non-metallic on the outside if made cathode for some time in a nearly neutral or slightly alkaline solution. In very dilute sulphuric acid solution (10 cc. (1.20) per liter) the appearance and weight do not change. In strongly acid or alkaline solutions the zinc dissolves faster than it is reprecipitated by the current, and the weight of the electrode consequently decreases. This is shown by the following experiments:

Pure zinc deposits were obtained from sulphuric acid solution according to the method already given. They were then dried, weighed, made cathode in a neutral sodium acetate solution free from zinc and electrolyzed for 30 minutes with a current density of 2.5 amperes. The results are given below. Column 1 is the weight of the zinc obtained by the deposition from dilute sulphuric acid solution; column 2 gives the weight after 30 minutes:

1.	2.	
0.1833	0.1839	Deposits became non-metallic in appearance.
0.5202	0.5237	" " " "
0.2499	0.2508	" " " "
0.2787	0.2787	Very dilute acid. No change in appearance.
0.1810	0.1783	Acid stronger. No change in appearance

In order to prove that the oxidation of the zinc did not take place after the electrolysis while the electrode was being washed and dried, the following experiments were carried out: 0.2 to 0.4 gram of zinc was deposited from a sodium acetate solution according to the best methods that we have found. Copper gauze was employed as cathode and the deposits were all excellent. When the electrolysis was finished, without disconnecting the current or stopping the electrode, the solution was gradually replaced by water, alcohol and ether, respectively, and finally with ether that had been dried with sodium. The electrode, completely submerged in ether, was now put into a covered dish and the ether evaporated off in a current of hydrogen. In this way the deposit was never allowed to come in contact with the air until the zinc was quite dry. It would, therefore, be impossible for the oxidation of the zinc to take place after the electrolysis. The results of several analyses carried out in this manner are given below. Column 1 gives the weight of pure zinc taken and column 2 the weight of the deposit:

1.	2.
0.2106	0.2129
0.2439	0.2472
0.2513	0.2592
0.2671	0.2855
0.2843	0.2894
0.2713	0.2747
0.3014	0.3033
0.3177	0.3238

When solutions of sodium acetate are electrolyzed they become alkaline, owing to the formation of sodium hydroxide at the cathode and the oxidation of the acetate to carbon dioxide and subsequent escape of this gas at the anode. If the solution is not sufficiently concentrated with respect to sodium acetate the zinc will be precipitated out as hydroxide as soon as the solution becomes alkaline. If too much free acid is present all the zinc cannot be precipitated. If an excess of the acid is avoided, then the layer of liquid in the immediate neighborhood of the cathode becomes slightly alkaline, zinc hydroxide is formed in this layer and is precipitated with the zinc, possibly because it is enclosed or adsorbed.

The most obvious remedy that suggests itself would be to make the solution so strongly alkaline that the formation of zinc hydroxide would be impossible. This has been found to be impracticable because hydrogen is evolved so rapidly at the cathode that the character of the deposit is destroyed as soon as the solution becomes depleted with respect to zinc. Furthermore, strong alkaline solutions attack zinc deposits, especially those that are finely divided, so vigorously that it is almost impossible to completely precipitate the zinc. If the current density is increased, the solution foams because of the rapid evolution of hydrogen and a bad deposit results.

Theoretical Considerations.—A certain potential exists between a pure zinc electrode and a solution of zinc salts of given concentration. This potential depends upon the concentration of zinc ions, not upon the total amount of zinc in the solution and increases as the concentration of the zinc ions decreases. Therefore the applied electromotive force necessary to deposit zinc from a solution of its salts must be increased as the electrolysis proceeds. These facts are expressed mathematically by the following well-known equation:

$$\pi_{\mathrm{Zn} \rightarrow \mathrm{soln.}} = E_{\mathrm{Zn}} - (RT/2F)\ ln\ C_{\mathrm{Zn}^{++}} \qquad (1)$$

π is the fall of potential in volts between the electrode and the solution, E_{Zn} is a constant equal to π when the concentration of the zinc ions is unity, R is the gas constant, F one Faraday's equivalent, C the concentration of the zinc ions in gram mols. per liter.

A similar equation must apply to hydrogen at atmospheric pressure surrounding a reversible electrode and a solution containing hydrogen ions:

$$\pi_{\mathrm{H}_2 \rightarrow \mathrm{soln.}} = E_{\mathrm{H}_2} - (RT/2F)\ ln\ C^2_{\mathrm{H}^+}. \qquad (2)$$

If the hydrogen electrode is taken as zero, the potential between pure zinc and a normal solution of its ions is 0.77 volt.[1] The limiting concentration at which zinc can be quantitatively determined is about 10^{-5}. Assuming complete dissociation and putting these values in equation

---

[1] Wilsmore, *Z. physik. Chem.*, **35**, 308.

(1) we get as a result 0.91 volt. The potential of the hydrogen electrode aginst a neutral solution calculated by equation (2) is 0.41 volt. It would, therefore, be impossible to precipitate zinc electrolytically from a neutral solution were it not that the overvoltage of hydrogen on zinc electrodes is high. For actual working conditions, then, we must add to equation (2) another term, η, which is a variable and is dependent upon the nature of the electrode and upon the current density.

By decreasing the concentration of the hydrogen ion *i. e.*, by making the solution alkaline, it would be more and more difficult to evolve hydrogen at the electrode. Unfortunately, however, the concentration of the zinc ion is diminished to a far greater extent than that of the hydrogen ion by the addition of a base, and thus the conditions are still more unfavorable for the complete precipitation of the zinc. This is apparent from the following considerations:

The equilibrium equation for the dissociation of water is

$$(\mathrm{H})(\mathrm{OH}) = K_1 \text{ or } (\mathrm{H})^2 = K_1^2/(\mathrm{OH})^2. \qquad (3)$$

Zinc hydroxide is an amphoteric electrolyte and therefore dissociates both as an acid and as a base. For the dissociation as an acid we have the equation

$$(\mathrm{H}^+)^2(\mathrm{ZnO_2}^{--})/(\mathrm{Zn(OH)_2}) = K_2. \qquad (4)$$

As a base,

$$(\mathrm{Zn}^{++})(\mathrm{OH_2}^-)^2/(\mathrm{Zn(OH)_2}) = K_3. \qquad (5)$$

Substituting (3) in (4) we get

$$\mathrm{K}_1^2(\mathrm{ZnO_2}^{--})/(\mathrm{OH})^2(\mathrm{Zn(OH^-)_2}) = K_2. \qquad (6)$$

Dividing (5) by (6) and transposing we get

$$(\mathrm{Zn}^{++})(\mathrm{OH}^-)^4/(\mathrm{ZnO_2}) = K_3K_1^2/K_2 = K_4.$$

We see, then, that while the concentration of the hydrogen ion is inversely proportional to the concentration of the hydroxyl ion raised to the first power, that of the zinc ion is inversely proportional to the concentration of the hydroxyl ion raised to the 4th power. From these considerations, in connection with equations (1) and (2), it will be easily seen that it becomes relatively more and more difficult to precipitate zinc as we increase the concentration of the hydroxyl ion.

Summary.

In this article it has been experimentally shown that the high results obtained in the electrolytic determination of zinc are not caused by the enclosure of liquid, presence of a salt, hydrogen in the deposit, nor by the presence of another metal. The true cause is the deposition of zinc oxide or hydroxide with the zinc.

Theoretical considerations for the electrodeposition of zinc have been discussed and reasons for the rapid evolution of hydrogen in strong alkaline solutions have been given.