

[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., CHEMICAL LABORATORY OF HARVARD COLLEGE.]

**A REVISION OF THE ATOMIC WEIGHT OF ZINC.
THE ELECTROLYTIC DETERMINATION OF ZINC IN ZINC BROMIDE.**

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The success met in the electrolytic estimation of cadmium in cadmium chloride and bromide led to the hope that a similar method might be successfully applied to other elements. In the case of the metallic halides it is thus possible to make a complete analysis, that is, the halogen may be determined by comparison with silver and the metal by electrolytic deposition. Where the sum of the two is essentially 100% the evidence obviously is of the strongest kind that constant error has affected neither method.

The close similarity of cadmium and zinc in properties made it likely that the methods as worked out for cadmium could be applied with little variation to the determination of zinc. Such proved to be the case. We found it possible in the first place to deposit zinc in a mercury cathode very nearly although not quite completely, and that the zinc amalgam could be satisfactorily washed with alcohol and dried without perceptible rusting. The amalgam thus produced does not oxidize at all rapidly, even on exposure to air. The general method of procedure was essentially that described in detail in the preceding paper upon the analysis of cadmium bromide. Weighed amounts of zinc bromide which had been dried by fusion were dissolved in a small amount of water in a glass electrolytic cell, and the metal was deposited as completely as possible in a mercury cathode, the bromine liberated at the anode being swept away by bubbling a slow current of hydrogen through the solution. The electrolyte was then completely freed from bromine and bromide by evaporation with nitric and sulfuric acids, and the residue was returned to the cell for further electrolysis. The amalgam finally was washed with alcohol and dried in a vacuum, while the electrolyte was evaporated and a slight residue of zinc sulfate was weighed. In other experiments the zinc bromide was completely converted to sulfate before electrolysis.

Purification of Materials.

Reagents were purified exactly as described in the previous paper.

Zinc Bromide.—Analysis 1 was made with zinc bromide prepared from commercial zinc by treatment with the purest bromine and purified by many crystallizations. For the other experiments material was purified with greater care as follows: Crude metal was freed from nonmetallic impurities by electrolytic transport from an anode of commercial metal through a concentrated solution of zinc bromide free from chloride to a platinum cathode, where the metal was deposited as a fine crystalline

mass. The crystals were leached as thoroughly as possible by digesting with cold, very pure water for some days, and then were dissolved by treatment with very pure bromine under dilute hydrobromic acid solution in a quartz flask. The solution was digested with an excess of zinc in order to remove more strongly electropositive metals, and after filtration through platinum sponge was evaporated to crystallization, and the product was three times more crystallized from very dilute hydrobromic acid solution in platinum vessels. A portion of the product was used for one analysis (Analysis 2). The remainder was fused in platinum boats in nitrogen charged with hydrobromic acid gas. The fused salt, which contained a very small amount of black material, probably carbon and silica as has been previously shown,¹ was dissolved in water and the solution was filtered through platinum sponge. The solution was then evaporated to crystallization, and the crystals were once recrystallized from very dilute hydrobromic acid solution. In all the crystallizations centrifugal drainage in platinum Gooch crucibles was used. The final product, when fused in an atmosphere containing hydrobromic acid gas, was free from all but the merest traces of black residue.

In order to follow the purity of the product, electrodes were made from the crude zinc, from the electrolytic product, and from the four and six times crystallized salt, and the spark spectra of the electrodes were photographed with a Féry quartz spectrograph. In order to prepare electrodes from the salt, a portion was dissolved in water and the metal was deposited as completely as possible from the solution, using platinum electrodes. The electrolytic deposit was thoroughly washed and dried, fused in an atmosphere of hydrogen in a hard glass tube, and made into electrodes by sucking the melted metal into hard glass capillaries. The crude material contained lead, cadmium and iron. The electrolytic metal was nearly free from iron, but contained the other impurities. The four times crystallized zinc bromide contained the merest traces of cadmium and lead, while in the spectrograms obtained with the final product only the strongest lines of cadmium were barely visible. We estimate the proportion of cadmium in the final product to be less than 0.001%.

To dry the salt for weighing it was first left in an exhausted desiccator over fused sodium hydroxide for some days. Then the crystals, which still contained the greater part of the water of crystallization, were heated gently in a weighed quartz boat in a current of either nitrogen or hydrogen, charged with hydrobromic acid gas by being passed through a fuming solution of the acid gas and dried by means of fused calcium bromide. During this process the boat was contained in a quartz tube which formed part of a "bottling apparatus." As soon as the crystal water had evapo-

¹ Baxter and Hartmann, *THIS JOURNAL*, 37, 121 (1915); Baxter and Grover, *Ibid.*, 37, 1040 (1915).

rated from the salt, the temperature was gradually raised until finally the salt was fused. After being allowed to solidify in the acid gas, the latter was replaced first with pure dry nitrogen and this in turn with pure, dry air. The boat was finally transferred to the weighing bottle in which it originally had been weighed, by means of the bottling apparatus.

When the weight of the salt had been determined, the boat was placed in the weighed electrolytic cell¹ containing about 100 g. of mercury, and the salt was dissolved in water which had been used to rinse the weighing bottle. Electrolysis was then begun with a current strength somewhat less than one ampere, and was continued for about sixteen hours. During the electrolysis a slow current of very pure hydrogen was caused to bubble through the solution, in order to remove the bromine liberated at the anode. At this point the bulk of the zinc had been deposited in the mercury, and the greater part of the bromine had been expelled. The electrolyte was now removed to a clean flask by suction, and the amalgam and cell were rinsed a few times with very pure water. The electrolyte was evaporated together with a small amount of nitric and sulfuric acids in a quartz dish. The residue of zinc sulfate, together with the excess of sulfuric acid, was dissolved in water and returned to the cell, and electrolysis was continued for some hours longer. Then the cell was again washed with chilled water which had been saturated with pure hydrogen, with especial pains not to break the electrolytic circuit until all of the electrolyte had been displaced. After the water had been removed as completely as possible, the cell and the amalgam were rinsed two or three times with very pure alcohol. The cell was then stoppered and the alcohol was evaporated in a small tubular desiccator containing fused sodium hydroxide, a Geryk oil pump being used to exhaust the desiccator. The pressure at first was not reduced below a few millimeters, since the rapid evaporation of the alcohol tended to blow the stopper out of the cell, but as soon as the alcohol had disappeared, the pressure was lowered as far as possible. After standing some time in this desiccator, the cell and its counterpoise were placed in a second larger desiccator, also containing fused sodium hydroxide, and were left in a high vacuum for some hours before being weighed. In the meantime the electrolyte, together with the aqueous and alcoholic washings, was evaporated in the quartz dish previously used in the same experiment, and when the liquid had been reduced to a volume of a few cubic centimeters, it was transferred to a weighed platinum crucible, and the evaporation continued at gradually increasing temperatures until the sulfuric acid had been expelled, and nothing but the residue of zinc sulfate remained. The crucible with its contents was then weighed.

¹ Form II, Baxter and Hartmann, *THIS JOURNAL*, 37, 123 (1915).

Since in the previous work with cadmium bromide it was found that the initial weight of cadmium thus obtained is usually too large, owing probably to the formation of a small amount of mercurous bromide upon the amalgam, the electrolysis was now repeated by dissolving the zinc sulfate residue in the platinum crucible in a small amount of sulfuric acid, returning the solution to the cell, and electrolyzing for several hours. The process of washing was repeated in exactly the same way as before, the amalgam was dried and weighed, and the electrolyte was evaporated, and the residue of zinc sulfate again determined. In most cases a loss in weight of a few tenths of a milligram occurred during the first electrolysis. If this was so, the process was repeated until the total weight of zinc, as obtained from the gain in weight of the cell and the zinc sulfate residue, became constant within less than a tenth of a milligram. The results as presented in the table are computed on the basis of the final weight.

Because the process of repeated electrolysis was a laborious and time-consuming one, in several analyses the zinc bromide was converted to sulfate before electrolysis. In order to do this the boat with the fused zinc bromide was placed in a quartz dish, and the salt was dissolved in the purest water. The boat was removed with careful rinsing, the rinsings being added to the original solution. Then concentrated sulfuric acid in excess of the amount necessary to convert the bromide to sulfate was added, as well as nitric acid, and the solution was gently heated on an electric stove, in order to liberate and vaporize the bromine. The temperature, however, was kept low enough so that boiling did not actually occur. After the solution had been evaporated until the volatile matter had been expelled and the zinc sulfate had separated from the residual concentrated sulfuric acid solution, the whole was dissolved in water and evaporation repeated, in order to decompose bromide which might have been included in the solid residue during the first evaporation. The second residue was again dissolved in the minimum amount of water, and the solution was quantitatively transferred to the weighed electrolytic cell. Electrolysis was now carried out as usual. The amalgam was washed and dried, and the residue of zinc sulfate in the electrolyte was determined. This residue, while never large, was always appreciable. Although in every case the zinc sulfate residue was dissolved in sulfuric acid, returned to the cell, and electrolysis repeated, the total weight of zinc obtained was never reduced by the process. The experiments in which this modification of the procedure was employed are indicated in the table. It can be seen that the results of these experiments do not differ from those in which the bromide was electrolyzed directly.

The weights were standardized by the substitution method described by Richards. All weighings of the cell and of the weighing bottle con-

taining the zinc bromide were made by substitution for counterpoises of the same material and of the same shape and size. A vacuum correction of $+0.000140$ g. is applied for every gram of zinc bromide. This is computed from the densities 4.219 for zinc bromide¹ and 8.3 for the brass weights. A vacuum correction of $+0.000003$ g. is applied for each gram of dissolved zinc. This is computed from the density of saturated zinc amalgam at 25° as found by Crenshaw,² 13.343. This amalgam contains 2.220 g. of zinc in 100 g. of mercury.

THE ATOMIC WEIGHT OF ZINC.

Zn:Br₂.

Br = 79.916.

| Number of analysis. | Wt. of ZnBr ₂ in vacuum. Grams. | Wt. of Zn from amalgam residue in vacuum. Grams. | Wt. of residue from electrolyte. Gram. | Total wt. of Zn in vacuum. Grams. | Ratio Zn : Br ₂ . | Atomic weight of zinc. |
|-----------------------|--|--|--|--|------------------------------|------------------------|
| 1..... | 6.88781 | 1.99857 | 0.00148 | 1.99917 | 0.408942 | 65.362 |
| 2..... | 6.79973 | 1.97241 | 0.00206 | 1.97324 | 0.408835 | 65.345 |
| 3..... | 7.67096 | 2.22673 | 0.00096 | 2.22712 | 0.409108 | 65.389 |
| 4..... | 8.02839 | 2.33109 | 0.00031 | 2.33122 | 0.409189 | 65.402 |
| 5 ³ | 7.18458 | 2.08428 | 0.00219 | 2.08517 | 0.408904 | 65.356 |
| 6 ³ | 7.55005 | 2.19143 | 0.00094 | 2.19181 | 0.409054 | 65.380 |
| 7 ³ | 7.71332 | 2.23883 | 0.00134 | 2.23937 | 0.409096 | 65.387 |
| 8..... | 7.11551 | 2.06545 | 0.00134 | 2.06599 | 0.409146 | 65.395 |
| 9..... | 7.44099 | 2.16000 | 0.00115 | 2.16047 | 0.409140 | 65.393 |
| 10 ¹ | 7.18828 | 2.08701 | 0.00065 | 2.08727 | 0.409188 | 65.401 |
| | | | | Average, | 0.409060 | 65.381 |
| Total..... | 73.57962 | ... | ... | 21.36083 | 0.409063 | 65.381 |
| | | | | Average, omitting Analyses 1 and 2 | 0.409103 | 65.388 |

Since Analyses 1 and 2 were made with zinc bromide of a less degree of purity than the others, we feel that the average of Analyses 3 to 10, 65.388, represents most nearly the real outcome of the work.

Richards and Rogers,⁴ by comparing zinc bromide with silver and weighing the silver bromide formed, found the atomic weight of zinc to be 65.376 (Ag = 107.880; Br = 79.916). In other words, they found zinc bromide to contain 70.971% of bromine, while in the present research the percentage of zinc is found to be 29.033. The sum is 100.004%.

The individual results are fairly consistent among themselves, and while the agreement of the average value with that of Richards and Rogers is not absolute, it certainly affords a very satisfactory confirmation of the earlier value. Since the investigation was interrupted at this point, it seems worth while to present the preliminary results. The subject is being pursued further in this laboratory.

¹ Richards and Rogers, *Proc. Amer. Acad.*, 31, 163 (1895).

² *J. Phys. Chem.*, 14, 158 (1910).

³ Changed to sulfate before electrolysis.

⁴ *Proc. Amer. Acad.*, 31, 158 (1895).

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GADOLINIUM SODIUM SULFATE.

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This investigation seemed to be of peculiar interest, since, according to some observers, gadolinium sodium sulfate was insoluble in sodium sulfate solution, while at least one other has suggested that its solubility might be used for a means of separation. Of course, the solubility of gadolinium sulfate in sodium sulfate solution might first increase and later decrease. This is true in the case of yttrium, and would explain the different observations that have been published. However, the following work shows that, when sufficient sodium sulfate was added so as to leave a slight excess, only about 0.6 g. of gadolinium sulfate was contained in a liter.

Pure hydrated gadolinium sulfate was prepared as follows: Gadolinium material was first separated from europium and less soluble earths by crystallizing the double magnesium nitrates in the presence of bismuth magnesium nitrate. The more soluble portions were then converted to the bromates and fractionated until the least soluble portions gave a pure white oxide. This bromate was converted into the oxalate and the latter treated with concentrated sulfuric acid and heated until all fumes ceased to be evolved. The anhydrous sulfate was next dissolved in water, and carefully crystallized over the steam bath. The crystals were removed, dried and finely powdered.

Bottles containing various amounts of gadolinium sulfate and sodium sulfate were made up, and about 50 cc. of water added to each. They were then rotated in a thermostat at 25° for several months. After they had settled, the liquid phase was analyzed in the following manner: Two samples were drawn from each bottle and transferred to tared weighing bottles. The first was diluted, heated to boiling, and treated with a warm solution of ammonium sebacate. The precipitate was washed free from sodium, ignited and weighed as the oxide Gd_2O_3 . The results were calculated as $Gd_2(SO_4)_3$ and as the equivalent of sulfur trioxide. The second sample was diluted, heated to boiling, acidified with hydrochloric acid and the total SO_3 precipitated as barium sulfate with barium chloride. This gave the total SO_3 , and by subtracting from this the SO_3 in combination with the gadolinium, the amount in the sodium sulfate