caused by the retention of water in the unfused sodium carbonate employed in the early work—and there can be little question that this substance must have really contained in 1891 at least as much water as we found it to contain in 1913, under similar circumstances.[1] The sodium sulfate had been fused, then as now. Hence the atomic weight of copper as found in 1891 by comparison with sodium carbonate must have been lower than the truth by perhaps 0.022. Correcting, we find the recalculated atomic weight of copper to be 63.554 (instead of 63.532[2]) a value much more nearly agreeing with that found from the direct comparison with silver, namely, 63.57.

This investigation, like the foregoing, was conducted under the favoring auspices of the Carnegie Institution of Washington.

Summary.

The quantitative conversion of pure fused sodium carbonate into pure sodium sulfate is described, the ratio of the equivalent weights of these substances being found to be 1.00000 : 1.340155. Assuming Na_2CO_3 = 105.995, as found in the preceding research (Ag = 107.880), the molecular weight of sodium sulfate becomes 142.050, and the atomic weight of sulfur becomes 32.060. This is in reasonable agreement with the earlier Harvard value, 32.069, and the mean of the two, 32.065, may perhaps be taken with some confidence as the most trustworthy value thus far recorded. This research, like that immediately preceding it, has been useful in confirming by cross-reference many varied methods and results, and in eliminating slight apparent inconsistencies in earlier results; and the out-come seems to strengthen our confidence in the processes upon which our present table of atomic weights is founded.

CAMBRIDGE, MASS.

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

A REVISION OF THE ATOMIC WEIGHT OF CADMIUM.

[THIRD PAPER.]

THE ELECTROLYTIC DETERMINATION OF CADMIUM IN CADMIUM CHLORIDE.

BY GREGORY PAUL BAXTER AND MINER LOUIS HARTMANN.

Received November 14, 1914.

In three recent papers dealing with the atomic weight of cadmium, Hulett and his collaborators at Princeton University have obtained concordant results, which indicate that the atomic weight of cadmium

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[1] See page 100 of preceding article.

[2] This recalculation is of the figures on the top of p. 271, *Proc. Am. Acad.*, **26** (1891). Na_2CO_3 is assumed as 105.995 above, instead of as 106.108, as it was twenty years ago.

is 112.3, a value one-tenth of a unit lower than that obtained in the Harvard Chemical Laboratory some years ago. Perdue and Hulett,[1] by the electrolytic determination in a mercury cathode of the cadmium in both the hydrated and anhydrous sulfate, and by the determination of the water in the hydrated sulfate, found the atomic weight of cadmium to be 112.30. Laird and Hulett[2] simultaneously deposited silver and cadmium electrolytically, the latter in a mercury cathode. From the relation of the weights of the two metals deposited, they compute the atomic weight of cadmium to be 112.31 (Ag = 107.88). Very recently Quinn and Hulett[3] have determined by electrolytic deposition in a mercury cathode the cadmium content of anhydrous cadmium chloride and bromide. The atomic weight of cadmium found in this way is 112.3 (Cl = 35.458, Br = 79.92). Thus the three investigations support one another in a striking way.

On the other hand, Baxter and Hines[4] analyzed anhydrous cadmium chloride, by comparison with pure metallic silver and by weighing the silver chloride formed, with the average result for the atomic weight of cadmium of 112.417, while a little later Baxter, Hines and Frevert[5] repeated this work on cadmium chloride with the result 112.418. The latter investigators also analyzed anhydrous cadmium bromide in a similar fashion, and obtained the identical value 112.417.

Such a serious discrepancy is very disturbing, since it points to some fundamental difficulty with either the electrolytic determination of metals in a mercury cathode or with the analysis of metallic halides by the "silver" method. In the determination of the cadmium in cadmium chloride, the discrepancy amounts to 0.0004 g. of metal in every gram of chloride, while one gram of cadmium chloride would yield 0.0010 g. less silver chloride if the atomic weight of cadmium has the higher rather than the lower value. Since in all the investigations referred to several grams of material were used in each experiment, the uncertainty is obviously far greater than any ordinary experimental error.

The "silver" method of analysis of metallic halides has already been subjected to prolonged and searching investigation, and has been found to yield results in very satisfactory agreement with those obtained by radically different methods.[6] Furthermore, in the investigations upon the cadmium halides in this laboratory, no especial difficulties were encountered. The silver halides were found to be free from occluded material, both by direct analysis and by the comparison of the quantity of silver used with

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[1] *J. Phys. Chem.*, **15**, 1579 (1911).

[2] *Trans. Am. Elec. Soc.*, **22**, 385 (1913).

[3] *J. Phys. Chem.*, **17**, 780 (1913).

[4] THIS JOURNAL, **27**, 222 (1905); *Z. anorg. Chem.*, **44**, 158.

[5] *Ibid.*, **28**, 770 (1906); **49**, 415.

[6] Cf. Richards and Archibald, *Proc. Amer. Acad.*, **38**, 443; Baxter, Thorvaldson and Cobb, THIS JOURNAL, **33**, 319 (1911); Baxter and Hoover, *Ibid.*, **34**, 1657 (1913).

the weight of silver halide produced in each experiment. Furthermore, there was no evidence of basicity in the salts which had been made anhydrous by fusion in an acid atmosphere, and the fact that both chloride and bromide yielded identical results made it improbable that either retained moisture during fusion. We decided, therefore, to repeat a portion of the work of the Princeton investigators, by determining electrolytically the cadmium content of the anhydrous chloride. Neither of the other methods used by Hulett and his collaborators seemed as promising as this one, for, as Richards[1] has already pointed out, hydrated crystals are likely to contain an excess of included or *dissolved* water, while it is not easy to obtain in a coulometer silver deposits in which the proportion of occlusions is known. Both of these difficulties would tend to *lower* the observed atomic weight of cadmium.

The results of this research have been satisfactory beyond our anticipation in the exactness with which they support the earlier Harvard work, for if one adds to the percentage of chloride found by Baxter, Hines and Frevert the percentage of cadmium found here, the sum is exactly one hundred per cent. within the limit of experimental error.

In the analysis of cadmium chloride and bromide, Quinn and Hulett converted weighed amounts of anhydrous salt to sulfate and deposited the cadmium electrolytically in a mercury cathode contained in an amalgamated platinum cup. Our method was simpler and safer, in that the cadmium chloride was not converted to sulfate, but was electrolyzed directly. The greater portion of the chlorine is freed as such at the anode, and, while a small amount of perchloric acid which is formed, remains, this is far less hindrance to the complete deposition of the metal than the relatively large amount of sulfuric acid which results from electrolysis of the sulfate. Even under these conditions small amounts of cadmium invariably remained undeposited, but these were readily collected and determined by evaporation and weighing as sulfate.

Furthermore, our cell was so constructed of glass that it contained the anode as well as the cathode, so that any attacking of the anode by the free chlorine merely resulted in the transfer of platinum from one part of the weighed apparatus to another; and the cell was so nearly closed that explosions of liquid during the drying of the amalgams could cause no loss of mercury.

Contrary to the experience of Quinn and Hulett, we observed no blackening of mercury or electrolyte during electrolysis. This, however, may have been caused by the platinum beaker used by them as cathode.

Purification of Cadmium Chloride.

Although it seemed unlikely that salts of foreign metals in the cadmium material were the cause of the difficulty, yet a large portion of our

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[1] THIS JOURNAL, **33**, 888 (1911).

energy was spent in the purification of the cadmium. Furthermore, the purity of the different preparations was very carefully followed by photographing the spark spectrum with metallic electrodes in a Féry quartz spectograph which covered the range 2100–6000$\mu\mu$. The most difficult impurity to eliminate from cadmium is lead, but we were able to show that no one of our preparations contained a quantity of lead large enough to affect the observed atomic weight of cadmium, and some of the material was wholly free from lead, so far as we could determine.

The spectographic method of detecting impurities is, of course, a sensitive one. In most cases, extremely small proportions of impurities appear unmistakably in the photograph. For instance, lead analyzed by Mr. F. L. Grover in this laboratory, and found to contain less than 0.004% of copper gave a spectrum in which the two strong copper lines were very prominent, while in the spectrum of one of our samples of crude cadmium, containing 0.2% of lead, the lead line of wave length 4058 was as prominent as many of the strong cadmium lines. None of our material could possibly have contained as much as one-tenth of this quantity, yet 0.02% of lead would raise the apparent atomic weight of cadmium by only 0.01 unit. The difficulty in analyzing material containing only spectroscopic traces of impurities has prevented our finding the limit of sensitiveness of the method in the case of cadmium and lead, but this subject in general is under investigation in this laboratory. We have assumed the complete or almost complete disappearance of the lines of impurities in the spectrum to be an indication that sufficient purity has been attained.

The first specimen of cadmium with which we started was found, spectographically, to contain about 0.1% lead, a trace of copper, considerable nickel, and traces of thallium, indium and calcium. No zinc lines could be seen in the spectrogram, and subsequent analysis in the wet way confirmed the surprising conclusion that zinc was not present. The purification of this material by electrolysis with a dissolving anode was first attempted. Various electrolytes were tried, the most satisfactory from the standpoint of a compact cadmium deposit being a slightly acid solution of the chloride. If the solution was neutral, basic salts were precipitated. During the electrolysis thallous chloride was gradually deposited on the bottom of the dish. The small crystals of metal which separated were frequently raked toward the platinum cathode by means of a glass rake in order to prevent short-circuiting, but occasionally were removed, and after thorough washing with water centrifugally drained. The crystals were then fused in a thoroughly leached "alundum" boat in a current of electrolytic hydrogen. Electrodes made from this metal gave a spectrum in which only lead and copper lines could be seen in addition to the cadmium spectrum, the lead lines of essentially the original intensity, the copper lines considerably reduced in intensity. Since a second electrolysis with an electrolyte made from the pure metal produced very little further diminution in the proportions of impurity, the electrolytic method of purification was then discontinued. The crystalline metal from the second electrolysis was washed, dried and fused as before.

Next, the buttons of metal were cleaned by etching with dilute hydrochloric acid and then were dissolved in hydrochloric acid containing a small amount of nitric acid in a quartz flask. Both acids were distilled through quartz condensers previous to use. As soon as the cadmium had dissolved, the solution was evaporated to small bulk four times with a large excess of hydrochloric acid, in order to remove nitric acid, and the salt was twice crystallized from the solution saturated with hydrochloric acid gas, as the acid chloride. The crystals were dried in a vacuum desiccator over caustic soda. This salt was found to contain a small proportion of ammonium chloride, formed presumably by the action of the metal on the nitric acid during solution, but since this ammonium chloride was volatilized during the subsequent fusion of the cadmium chloride, it could do no harm. This specimen of chloride is Sample A.

Since Sample A, after fusion in a current of hydrochloric acid, was found to contain a small amount of black residue, apparently carbon and silica, as will be shown later, the attempt was made to eliminate the difficulty by fusing the salt in a current of hydrochloric acid before crystallization. The mother liquors of Sample A, containing much hydrochloric acid, were used to dissolve more of the twice electrolyzed cadmium, with the help of a small amount of nitric acid, all in a quartz flask. The solution was evaporated to small bulk several times with a large excess of redistilled hydrochloric acid to eliminate the nitric acid. Nearly all the excess of hydrochloric acid was expelled by evaporation in quartz, and then evaporation to dryness in a platinum vessel followed. The dry salt was then fused in platinum boats in a current of hydrochloric acid gas, purified and dried by an apparatus described later, in a quartz tube. When the fused salt was dissolved, a considerable quantity of the black residue was found. This was removed by filtration on a platinum-sponge (Gooch-Munroe-Neubauer) crucible, in such a way that the solution came in contact only with platinum and quartz. The crystals obtained by evaporating the solution in a platinum dish and cooling were crystallized from solution in pure water a second time. This salt is designated Sample B. The yield was small because of the small temperature coefficient of solubility of the chloride.

From the mother liquors of the second crystallization metallic cadmium was obtained by electrolysis between platinum electrodes. Spark electrodes made from this metal by drawing the melted material into hard glass capillaries showed very faintly the lead line 4058, and the copper lines 3247 and 3273, but we estimate the proportions of these impurities to be certainly less than 0.005%. No platinum lines could be seen.

Sample C was purified first by fractional precipitation of the sulfide with scrubbed hydrogen sulfide gas, as previously done by Baxter and Hines. From a dilute solution of cadmium chloride two small fractions were precipitated and rejected, then nearly all the remainder of the cadmium was precipitated in three fractions. These fractions were thoroughly washed with water, then dissolved in hydrochloric acid and reprecipitated. The first two fractions were combined and dissolved in redistilled sulfuric acid containing enough nitric acid to produce solution, for the red modification of cadmium sulfide formed during the washing of the sulfide does not easily dissolve. The third fraction, the most soluble, was not investigated in this research, since it corresponds to Sample D. The solution of the first two fractions was evaporated in a platinum dish until fumes of sulfuric acid were given off, and allowed to cool. Nearly all the sulfate remained insoluble in the excess of acid. After centrifugal drainage the salt was recrystallized by solution in water and precipitation by the addition of redistilled sulfuric acid, a far more economical and rapid process than crystallization from water. From a water solution of the product, metallic cadmium was deposited electrolytically upon a platinum dish as a loosely coherent mass of crystals, which were leached with water as thoroughly as possible. The greater part of the deposit was dissolved in distilled hydrochloric acid in the platinum dish, and the solution was evaporated to dryness in a quartz dish. In order to precipitate any platinum which might have been dissolved during the solution of the cadmium, a neutral solution of the residue was warmed with a portion of the original electrolytic metal in a platinum dish for some time. After filtration through a Gooch-Munroe-Neubauer crucible, the solution was again evaporated to dryness in a platinum dish and the residue was fused in a current of hydrochloric acid gas, as subsequently described. The fused material was dissolved in water, filtered through platinum sponge, and twice crystallized in platinum. The mother liquor from the first crystallization was tested for sulfate with negative results, showing that if the electrolytic deposit occluded any of the sulfate electrolyte, this must have been removed during the fusion of the chloride in hydrochloric acid. This fusion also served to char any residual organic material and also to separate the greater part of the silicic acid. Metal made from the mother liquors of the final crystals, when examined spectroscopically, showed faint traces of lead, platinum, and copper.

Sample D consisted of material prepared in the earlier researches by Baxter and Hines. Cadmium sulfate which had been made from Sample III (the most soluble) of the sulfide fractionation in the earlier research, was electrolyzed, and the metal converted to chloride exactly as in the case of Sample C. Metal made from the mother liquor of the final cadmium chloride crystals, when tested spectroscopically, was found to contain the merest traces of copper and platinum. This evidence was very satisfactory in showing that the material used by Baxter, Hines and Frevert was pure.

Samples E and F were purified by crystallization of cadmium bromide. This salt has a much larger temperature coefficient of solubility than either chloride or sulfate, and was found to give a far more rapid and convenient method of purification than any other which we tested. Several hundred grams of crude cadmium containing about 0.2% of lead and traces of copper and thallium, were covered with dilute hydrobromic acid solution and then dissolved by the addition of commercially pure bromine. A slight excess of bromine was removed by boiling, and the solution was then heated with metallic cadmium for some time to precipitate the more strongly electropositive metals. The solution was evaporated, and the salt content subjected to fractional crystallization according to the diagram shown here. After the first three series of crystallizations the fractions were filtered through platinum sponge, and platinum vessels only were subsequently employed. Metal prepared from the crystals of Fraction 11, so far as could be found out from spectrograms, was free from impurity of any kind.

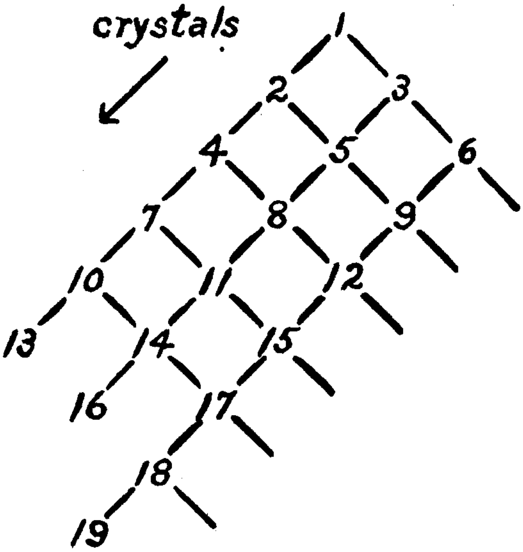

Fig. 1.

To prepare Sample E, Fraction 13 was converted to chloride by heating in a current of chlorine, as subsequently described. To prepare Sample F, Fractions 16 and 19 were combined, dissolved in hot water in a quartz flask, and a current of pure chlorine was passed in until all bromine had been expelled. The solution was then evaporated, the salt fused, dissolved, filtered and crystallized as with the other samples. Owing to an accident this material was lost after one analysis had been made.

In the crystallization of the cadmium chloride, owing to the high solubility of the salt, a large proportion of each sample remained in solution in the mother liquors. These were preserved in either quartz or platinum. To prepare Sample G these were combined, evaporated to crystallization, and the crystal product twice recrystallized. Owing to increased experience in crystallizing cadmium chloride, and to the large amount of available material, these crystallizations were more satisfactory than the earlier ones. This was shown by the fact that metal prepared from the mother liquor of the last crystallization was spectroscopically pure.

Purification of Other Materials.

Water.—All the water was purified by double distillation, first from alkaline permanganate, then from very dilute sulfuric acid. Block-tin condensers were employed, no rubber or cork being used to connect the retort to the condenser. Frequently the water was received in platinum or quartz vessels, otherwise Jena flasks or non-sol bottles were used for storage.

Sulfuric Acid.—This substance was distilled from a non-tubulated glass retort into an air-cooled Jena glass receiver, with rejection of the extreme portions.

Alcohol.—Alcohol was distilled in glass, twice from lime and once from mercury. Fifty cubic centimeters upon evaporation in a quartz crucible left a residue which weighed 0.00016 g. before, 0.00006 g. after gentle ignition. In another experiment 200 cc. of water, 50 cc. of alcohol and 5 cc. of distilled hydrochloric acid were evaporated in a quartz dish, transferred to a platinum crucible and ignited gently with a drop of sulfuric acid. The crucible gained 0.00001 g.

Mercury.—Relatively pure mercury was three times distilled in vacuum.

Preparation of the Cadmium Chloride for Analysis.

The cadmium chloride was dried in preparation for weighing by fusion in a stream of dry hydrochloric acid gas. During this treatment the salt was contained, in the first three analyses, in a platinum boat, but usually in a quartz boat. The boat was placed in a quartz tube, which formed part of a "bottling apparatus,"[1] by means of which the boat could be transferred to the weighing bottle in which it was originally weighed without being exposed to moist air even for an instant.

The hydrochloric acid was generated by the action of the purest commercial concentrated sulfuric acid upon either fuming hydrochloric acid or sodium chloride, and the gas was dried by passing through five towers about 30 cm. long and 4 cm. in diameter, filled with glass beads moistened with concentrated sulfuric acid. Nitrogen was prepared by the Wanklyn method of passing air through concentrated ammonia solution and then over hot copper. The excess of ammonia was removed in two Allihn gas washing bottles containing dilute sulfuric acid, and the nitrogen was purified and dried by passing through towers containing silver nitrate solution, solid potassium hydroxide, concentrated sulfuric acid

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[1] Richards and Parker, *Proc. Amer. Acad.*, **32**, 59 (1896); *Z. anorg. Chem.*, **13**, 85.

and resublimed phosphorus pentoxide. Air was purified by reagents similar to those used in the purification of the nitrogen. The apparatus for generating and drying the hydrochloric acid was constructed wholly of glass, and the nitrogen and air purifying trains had rubber connections only at the beginning. Preliminary to fusion, the salt was heated gently by means of either an aluminum block furnace or an electric heating coil of "Nichrome" wire until the greater portion of the water had been expelled by efflorescence. The temperature then was raised until the salt was fused, and was maintained at this point for about fifteen minutes in order to insure the expulsion of a possible impurity of either ammonium salt or acids other than hydrochloric. After the salt had been allowed to cool, the hydrochloric acid gas was displaced first by a current of pure dry nitrogen, then by dry air. The boat was next transferred to the weighing bottle inside the "bottling apparatus," the weighing bottle was placed in a desiccator, and, after the desiccator had stood near the balance for at least an hour, the bottle and boat were weighed.

When salt treated as above is dissolved in water, a small amount of black material is left insoluble. Evidence was obtained in the course of this and other work which indicates that this material is largely carbon, but that it may contain silica. The source of the organic matter from which the carbon is produced by charring is not certain. Atmospheric dust and lint are undoubtedly responsible for a portion, the reagents and filters for the remainder. Preparing the hydrochloric acid gas from fused sodium chloride and concentrated sulfuric acid which had been heated with a small amount of permanganate until colorless, produced little or no diminution in the extent of the difficulty, which eliminates the gas in which the salt was fused as the cause. The source of the silica was probably the quartz dishes in which the concentrated solutions were heated.

The proportion of black material can be very much reduced by fusing the salt in hydrochloric acid, dissolving and filtering through a platinum sponge crucible preparatory to crystallization. This was done with all the preparations, except Samples A and E. A very considerable amount of black residue, obtained in purification of one of the samples, gave the evidence concerning the nature of the substance. This was filtered upon a Gooch-Munroe-Neubauer crucible, washed and dried. Upon gentle ignition, the carbon obviously burned, leaving a gray residue which was insoluble in a microcosmic salt bead. Mr. F. L. Grover in an investigation upon lead halides obtained similar evidence.

As has been stated, by suitable purification the proportion of black residue was made very low. In one experiment this was filtered upon a weighed Gooch-Munroe-Neubauer crucible and was found to weigh only 0.00002 g. Mr. Grover has found in lead chloride and bromide, similarly contaminated, in thirty-six experiments on an average 0.004% of black residue, but the lead salts were not fused prior to crystallization and were to be expected to contain, and apparently did contain, more of the impurity than any cadmium chloride sample, except Sample A which was not fused before crystallization. Evidently, the error produced by the residue at the most could not be large. But in the analysis the difficulty partially took care of itself, for a portion of the residue adhered to the amalgam and was weighed with it, while a portion was evaporated with the washings and upon ignition was burned. Under the circumstances no attempt has been made to correct for whatever slight error may have been introduced.

With Samples E and G, the residue was almost, if not quite, eliminated. Sample E was made from cadmium bromide by heating and eventually fusing in a current of pure dry chlorine containing a small amount of hydrochloric acid gas, the conversion being conducted in the quartz boat in which the salt was finally weighed. The salt was then fused in pure hydrochloric acid gas as described above. Some difficulty was experienced by persistent retention of chlorine gas by the salt even when re-fused in pure hydrochloric acid gas, and, therefore, fusion in the latter atmosphere was prolonged considerably to ensure complete elimination of the chlorine.

Sample G of cadmium chloride also was fused for some time in chlorine before fusion in hydrochloric acid, and no residue could be seen in either the fused salt or its solution.

The chlorine gas in which the salt was fused was generated from manganese dioxide and concentrated hydrochloric acid, and was scrubbed with wet glass wool, charged with hydrochloric acid gas in four towers containing beads moistened with concentrated acid, and dried in four towers of beads wet with concentrated sulfuric acid. The apparatus was constructed wholly of glass.

In the first three analyses a platinum boat was used to contain the salt. In the first analysis it lost 0.00013 g., in the second, 0.00009 g. This is in accord with other experience in the Harvard Laboratory in the fusion of chlorides in platinum boats in a current of hydrochloric acid gas. It is seldom that the loss in weight of the boat is even as large as the above if the acid gas is free from air. On the other hand, if the hydrochloric acid contains air, the platinum may be very seriously attacked. Since this is not at all in accord with the experience of Quinn and Hulett, who report a loss as high as 2.9 mg. in one experiment, one cannot avoid the suspicion that their fusion atmosphere was not free from air. Because of convenience in manipulation rather than for any other reason, in the later analyses quartz boats were used. One of these in nine fusions lost 0.00013 g., while the weighing bottle, which was rinsed in each experiment, and the boat together lost 0.00033 g. Such constancy is all that could be desired. The average weight of the weighing bottle and boat before and after the fusion of the salt was used in the calculations.

The Electrolytic Cell.

In our earlier experiments upon the electrolytic method we attempted to deposit the cadmium and chlorine simultaneously, the former in a mercury cathode, the latter substance upon a silver anode. We met the same difficulty which other experimenters seem to have found in trying to deposit relatively large amounts of halogen in this way, in loosening of the silver halide deposit from the electrode, owing apparently to local complete conversion of the silver to halide.

The problem of disposing of the chlorine otherwise might have been solved as was done by Quinn and Hulett, by converting the chloride to sulfate before electrolysis. Such a step is entirely unnecessary, however, for a platinum electrode of moderate surface is imperceptibly attacked by the evolution of large amounts of chlorine upon it. For instance,

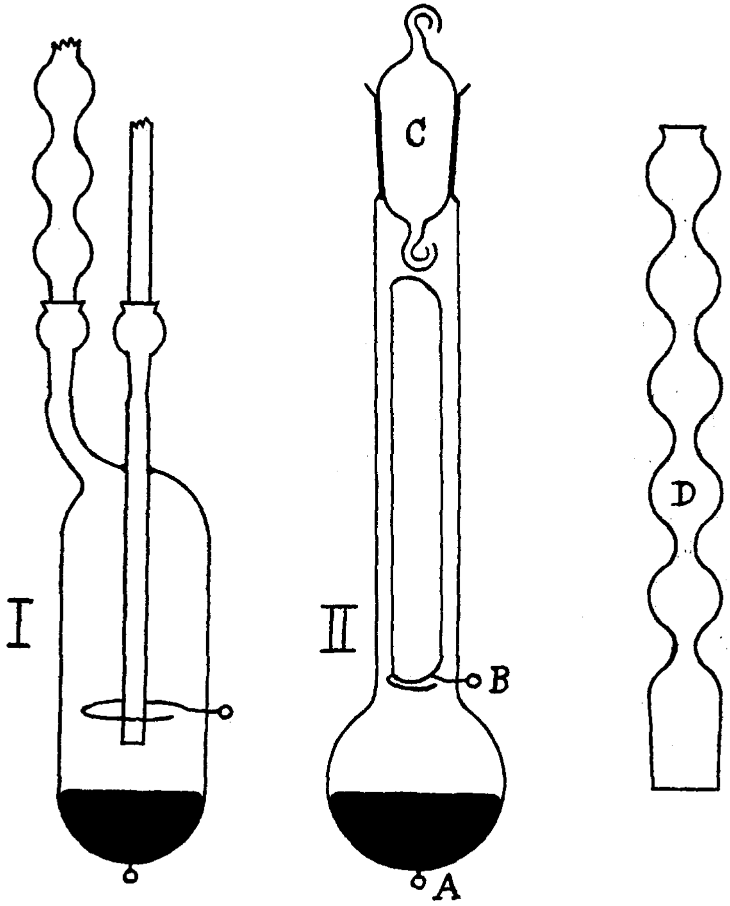

Fig. 2.

Easley[1] in the electrolysis of 125 g. of mercuric chloride found a platinum wire which served as anode to have lost in weight only 0.00015 g. One experiment of our own confirmed this constancy, for a weighed platinum wire anode lost no weight whatever in the electrolysis of several grams of cadmium chloride. Nevertheless, in order to make sure that no difficulty should be met from this source, a cell was constructed of glass with both cathode and anode permanently sealed in place. Thus any metal dissolved by chlorine liberated at the anode would almost immediately be deposited upon the cathode.

In the cell of Form I, in which the first two analyses were carried out, the salt after fusion was dissolved, and the solution was quantitatively transferred to the cell. The closed form was chosen at first in order to facilitate washing the amalgam and to prevent loss of mercury or amalgam by spurting while being dried at reduced pressure. In the later analyses the Form II was employed. The tube of this cell was large enough so that the boat, usually quartz, could be introduced bodily. During electrolysis it was supported upon the anode B, and at the end of the electrolysis it was removed before the amalgam was washed and dried.

The column of bulbs, D, ground into the neck served to catch spray formed during electrolysis. The stopper C was used to prevent loss of mercury by spurting during drying under low pressure, and always was weighed with the cell.

This cell was found particularly satisfactory in every way, and will be used for the exact analysis of other metallic halides in this laboratory.

Method of Analysis.

The cell was carefully washed and provided with a charge of thrice redistilled mercury, which had previously served as cathode during the electrolysis of dilute sulfuric acid for many hours, and was then several times rinsed, at first with water, then with alcohol. The outside also was cleaned with water and alcohol and wiped with a clean lintless cloth. In order to dry the cell and contents it was placed in a tubular desiccator containing fused potassium hydroxide and the pressure was reduced by a mechanical pump to a few millimeters. When the alcohol had evaporated, the cell was transferred to a second vacuum desiccator, containing fresh potassium hydroxide, for two hours. Finally it was placed with its counterpoise in still a third exhausted desiccator with solid potash where it was allowed to stand several hours before being weighed.

When the Cell I was used, the salt contained in the boat was dissolved in the minimum amount of water and the solution was introduced through the central tube. The boat was rinsed and the more concentrated rinsings added to the solution. The more dilute rinsings of the boat, as well as of

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[1] THIS JOURNAL, **32**, 1123 (1910).

the weighing bottle which originally contained the boat, were evaporated to small bulk in quartz or platinum and added to the main solution. During the electrolysis a slow current of the purest hydrogen was bubbled through the central tube.

When Cell II was used, the quartz boat containing the fused salt was transferred from the weighing bottle to the cell, and the salt was dissolved in the rinsings of the weighing bottle. The column of bulbs was inserted and last of all a small trap at the top of the column of bulbs.

The electrolysis was then started, at first with a current strength of a few tenths of an ampere. Later, when the greater portion of the cadmium was deposited, the current was increased until for the last two hours a potential of about 16 volts was maintained between the electrodes, the current strength being about one ampere. In all, about seven hours were consumed in each experiment. Gases evolved, at the anode at first, later at both electrodes, stirred the solution sufficiently well without other assistance. Toward the end of the electrolysis the column of bulbs was several times rinsed into the cell. In order to prevent heating of the cell, it was kept immersed nearly to the neck in clean, cold water during all of the electrolysis, and during the latter part, when the voltage was high, ice water was used.

At the end of the electrolysis, although practically all the metal was deposited and little chlorine was evolved upon the anode, yet a very considerable residual conductivity persisted with the evolution of hydrogen and oxygen. This was puzzling at first, but the cause was soon found to be the formation of a small amount of perchloric acid during the electrolysis.

When the deposition of the cadmium was essentially complete, *i. e.*, at the end of about seven hours, the cell was rinsed thoroughly with the purest water which had been saturated with the purest electrolytic hydrogen. The rinsing was accomplished by siphoning the liquid from the bottom of the cell into a clean flask and adding water at the top. Needless to say, the voltage between the electrodes was kept at a maximum during this preliminary washing. As soon as the cell was apparently clean, as indicated by a zero reading on the ammeter, it was disconnected from the battery circuit and further rinsed with water, the amalgam being agitated gently to dislodge any liquid which might have been imprisoned between the amalgam and the glass. Then the cell was rinsed with three 5 cc. portions of alcohol. The stopper was now inserted, the outside of the cell was cleansed with water and alcohol and dried with a clean cloth and the cell was placed in a vacuum desiccator. The drying of the amalgam was effected exactly as in the case of the mercury. In almost every experiment the amalgam was bright in appearance.

The aqueous and alcoholic rinsings were combined and evaporated in a quartz dish over an electric stove. When in small bulk they were transferred to a weighed platinum crucible and after the addition of a drop of redistilled sulfuric acid, they were evaporated to dryness. The residue was ignited to very dull redness and weighed. By precipitation with hydrogen sulfide and colorimetric comparison with standards, this residue was shown to consist chiefly of cadmium sulfate, but it may have contained traces of alkalis and silica extracted from the glass cell. Since, however, the weight of the residue was seldom as much as a milligram, and frequently much less, the assumption that the residue was cadmium sulfate in applying a correction could not have introduced any considerable error. In fact, the agreement of the experiments where the residue was unusually large with those where the residue was small emphasizes the legitimacy of such a correction.

The fact that we were never able to secure complete deposition of the cadmium is interesting in connection with the statement by Quinn and Hulett that no cadmium could be detected in the residual electrolyte of their experiments. They tested for cadmium by means of hydrogen sulfide and say "we evaporated all our electrolytes to one cubic centimeter and tested each in this manner, so there was little chance for any cadmium to escape deposition without being detected." With a four-gram sample of cadmium chloride such as they used, this "one cubic centimeter" would consist mainly of pure sulfuric acid. It is obvious that, unless this sulfuric acid were previously expelled, even large amounts of cadmium might have escaped detection in the residual electrolyte. In order to find out whether complete deposition of the cadmium really can be secured, Mr. M. R. Grose, with a cell like those used in our analyses, electrolyzed about four grams of once recrystallized cadmium sulfate, the current strength at the end being about one ampere, as in Quinn and Hulett's experiments. The electrolyte was carefully removed and evaporated, finally at a temperature sufficiently high to vaporize the sulfuric acid. The residue weighed only 0.7 mg., and while it contained cadmium, was obviously not wholly cadmium sulfate. The experiment was repeated with salt very carefully prepared from the pure bromide and the residue, which in this experiment weighed 0.5 mg., was found to contain about 0.2 mg. of cadmium sulfate. While it is thus unlikely that the error from incomplete deposition of the cadmium was large enough to explain the discrepancy in question, yet it is unfortunate that Quinn and Hulett did not evaporate their electrolytes to dryness in order to make certain that they contained neither cadmium nor any other substance. This is especially so since their cadmium chloride, which was prepared merely by dissolving purified metal, which had been distilled in hard glass, in hydrochloric acid in a Jena flask and evaporating to dryness in a platinum dish, was not subsequently crystallized. It must be said, however, that Quinn and Hulett, starting with weighed amounts of cadmium, were able to recover essentially all the metal by an electrolytic process similar to the analytical procedure.

In order to find out whether the cadmium amalgam, upon exposure to air, oxidizes continuously, about 75 g. of amalgam were placed in an open platinum crucible and allowed to stand upon the balance pan with occasional weighing. The results were as follows:

Weight after 1/2 hr	104.09162 g.
Weight after 1 1/2 hrs	104.09158 g.
Weight after 2 1/2 hrs	104.09160 g.
Weight after agitation	104.09159 g.

Although the amalgam seemed to be constant in weight, the possibility still existed that a superficial film of oxide formed at the outset might have an appreciable weight. This point was investigated in the following manner:

Several grams of pure cadmium were fused on an alundum boat in a current of the purest hydrogen. The resulting button was perfectly bright and clean. After standing in a desiccator for some hours it was weighed. The counterpoise of one of the cells was provided with about 80 g. of mercury and weighed by substitution for a similar vessel. The button was then introduced and after the cadmium had been allowed to amalgamate with the mercury, the system was weighed. The amalgam was of the same lustrous appearance as those obtained in the analyses.

	Grams.
Weight of vessel + mercury = counterpoise	+1.69317
Weight of cadmium	3.25227
Sum	4.94544
Weight of system after 7 hrs. = counterpoise	+4.94555
Weight of system after 31 hrs. = counterpoise	+4.94547

If oxidation of the cadmium really occurs, the change in weight is evidently so slight as to be beyond the limit of error of weighing. The lustrous appearance of the amalgams obtained in the electrolyses is further evidence that little oxidation took place.

One experiment was carried out to test the constancy in the weight of the mercury during the washing and drying operations. The cell was prepared for weighing as usual, and weighed. Then it was washed with water and alcohol, dried in vacuum and reweighed. A loss in weight of 0.00007 g. was found.

Further evidence upon this point was obtained by electrolyzing a dilute hydrochloric acid solution in the cell, and after the customary rinsing and drying, determining the change in weight. Furthermore, the rinsings of the cell were evaporated with sulfuric acid in a weighed platinum crucible which was then reweighed. The results follow: The numbers in the column headed "possible error" are obtained as the algebraic sum of the "change in weight of cell" and "weight of residue" multiplied by 0.54, the proportion of cadmium in cadmium sulfate.

Change in weight of cell. Gram.	Weight of residue. Gram.	Possible error. Gram.
—0.00001	0.00017	+0.00008
—0.00013	0.00012	—0.00007
—0.00004	0.00017	+0.00005

Some of the residue may have been extracted from the column of bulbs used to catch the spray formed in the electrolysis which was not originally weighed with the cell. At all events, since the weight of the residue is divided by two before being applied as a correction, the uncertainty is obviously less than a tenth of a milligram.

For several reasons, error from evaporation of mercury is not to be feared. In the first place, at 20° the vapor pressure of mercury is 0.0013 mm., and the weight of a liter, therefore, 0.000014 g. The desiccators used for the preliminary exhaustion had volumes somewhat less than a liter, the one used for the final exhaustion a volume of about two liters. But since the pressure was not reduced much below a millimeter, practically only the interior of the cells became saturated with mercury vapor. Furthermore, evaporation from the amalgams would be less than from pure mercury. Finally, since the counterpoise was exhausted with the cell at the close, evaporation from it would at least partially compensate for evaporation from the cell. On account of the low vapor pressure of mercury at room temperature, however, the difficulty could not in any case have been serious. Since only about two liters of hydrogen were evolved at the cathode in each experiment, not more than 0.00003 g. could have been lost in this way even if the gas was saturated with mercury.

The weights were standardized to hundredths of a milligram by the substitution method described by Richards.[1] All weighings were made upon a No. 10 Troemner balance. With the heavier objects, such as the weighing bottle, and the cell containing mercury or amalgam, the balance beam was left down some minutes before making observations in order to allow the slight bending of the beam to occur. A small amount of crude radium bromide was kept in the balance case to prevent the objects weighed from retaining electrostatic charges. The weighing bottle and cell were always compared with counterpoises of very nearly the same shape, size and volume in order to avoid variations from changes in atmospheric conditions.

A vacuum correction of +0.000152 g. per gram of cadmium chloride was applied, the densities of the weights and the salt being assumed to be 8.3 and 4.047, respectively. The vacuum correction of cadmium dissolved in mercury was computed as follows:

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[1] THIS JOURNAL, **22**, 144 (1900).

Temperature.	Density of mercury.	Concentration of amalgam.	Density of amalgam.	Vacuum correction per g. of dissolved cadmium.
20°	13.545	2.97	13.370[1]	—0.000017
25°	13.534	3.00	13.354[2]	—0.000016
25°	13.534	5.00	13.230[2]	—0.000015

An average vacuum correction of —0.000016 g. was, therefore, applied for every apparent gram of dissolved cadmium.

In a very few analyses the amalgam became so concentrated that a small amount of solid amalgam separated, but not in amount large enough to produce uncertainty in the vacuum correction.

Analyses 1 and 2 in the table of results were made with Cell I, and a platinum boat was employed. In Analysis 3 a cell similar to Cell II was used, but of considerably larger size. A platinum boat was used and introduced into the cell, where it was in contact with the anode during electrolysis, and was finally weighed with the cell. Allowance was then made for the weight of the boat at the outset. In all subsequent analyses a

THE ATOMIC WEIGHT OF CADMIUM.

Cl = 35.457.

Number of analysis.	Sample of $CdCl_2$.	Weight of $CdCl_2$ in vacuum. Grams.	Weight of Cd in vacuum. Grams.	Weight of $CdSO_4$ residue. Gram.	Corrected weight of Cd in vacuum. Grams.	Ratio Cd : Cl_2.	Atomic weight of Cd.
			Preliminary Series.				
1..........	A	6.08570	3.73151	0.00055	3.73181	1.58538	112.426
2..........	A	4.20489	2.57844	0.00036	2.57863	1.58562	112.443
3..........	A	5.36203	3.28771	0.00085	3.28817	1.58553	112.436
4..........	B	7.50512	4.60206	0.00028	4.60221	1.58538	112.426
5..........	B	6.71591	4.11814	0.00046	4.11839	1.58551	112.435
6..........	B	5.91556	3.62727	0.00067	3.62763	1.58555	112.438
7..........	C	5.49323	3.36782	0.00042	3.36805	1.58483	112.387
8..........	B	3.14416	1.92767	0.00044	1.92791	1.58513	112.408
9..........	C	7.58705	4.65143	0.00056	4.65173	1.58474	112.381
10..........	B	2.26738	1.38990	0.00030	1.39006	1.58444	112.359
11..........	B	5.93501	3.63936	0.00048	3.63962	1.58562	112.443
12..........	F	6.04122	3.70445	0.00084	3.70490	1.58578	112.454
13..........	D	4.07400	2.49779	0.00077	2.49821	1.58537	112.425
			Final Series.				
14..........	E	9.00004	5.51844	0.00064	5.51879	1.58529	112.419
15..........	G	6.56891	4.02776	0.00061	4.02808	1.58534	112.423
16..........	G	7.12956	4.37074	0.00186	4.37174	1.58522	112.414
17..........	E	8.57291	5.25636	0.00080	5.25679	1.58522	112.415
18..........	G	7.76294	4.75854	0.00291	4.76011	1.58521	112.413
Total.........		109.3659			67.0628	1.58530	112.420
Average..						1.58529	112.419
Average, rejecting Analyses 10 and 12..............						1.58535	112.421
Average of Analyses 14 to 18......................						1.58526	112.417

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[1] Richards and Forbes, Carnegie Inst., Publication No. **56,** 13 (1906).

[2] Hulett and De Lury, THIS JOURNAL, **30,** 1810 (1908).

quartz boat and the final type of cell were employed. In two analyses by mistake the voltage was considerably reduced just previous to the washing, and it was suspected that both cadmium and mercury dissolved by the free chlorine were still contained in the electrolyte. This conjecture was borne out by unusually large residues when the electrolyte was evaporated. Since mercury salts would have been lost by vaporization during the heating of the residue, the final result would be too low. This was apparently the case, the two results being 112.38 and 112.39. Because of the uncertainty and because a third analysis with the same sample of material (Sample D) was subsequently made, the two analyses affected by the accident are not included in the table. In the first analysis in which cadmium chloride which had been fused in chlorine was used, the chlorine was not completely expelled from the salt, as was indicated by a residual brown color. This analysis also yielded a slightly lower result than the average 112.39, and is omitted from the table. All other analyses are included.

It makes little difference how the results are treated. The final verdict is that the atomic weight of cadmium is essentially 112.42 (Cl = 35.457; Ag = 107.880), an outcome in exact agreement with the earlier work of Baxter, Hines and Frevert.

While the difference between the extremes is nearly 0.1 unit in the atomic weight of cadmium, yet, if the highest result and the lowest result are disregarded the extreme difference is nearly halved. Furthermore, the last five results, obtained with unquestionably the best material and after ample experience had been gained with the method, differ among themselves by only 0.010 unit. All things considered, the average of these last five determinations, 112.417, seems to us to represent most nearly the real verdict of the research.

It is worth noting that the *lowest* result in the table, 112.359, obtained with the smallest amount of chloride used in any of the experiments, is identical with the *highest* result obtained by Quinn and Hulett, 112.36. Furthermore, even without the correction for residue in the electrolyte, the average atomic weight of cadmium from our experiments is 112.39.

The average ratio of cadmium to chlorine obtained in Analyses 14 to 18, 1.58526, corresponds to the percentage 61.319 of cadmium in cadmium chloride, while Baxter, Hines and Frevert found the percentage of chlorine in the salt to be 38.681. The sum of the two is 100.000. So close an agreement is partly fortuitous, for a discrepancy of 0.001% would be extremely difficult to detect by any analytical method yet devised.

Summary.

1. Crystallization of cadmium bromide is found to be a very efficient and rapid method of purifying cadmium material.

2. A modified form of electrolytic cell utilizing a mercury cathode for the direct electrolysis of chloride solutions is described.

3. The percentage of cadmium in anhydrous cadmium chloride is found to be 61.319, while Quinn and Hulett found only 61.298%. The former percentage corresponds to an atomic weight of cadmium of 112.417 (Cl = 35.457), a value which is in perfect agreement with the earlier one found by Baxter, Hines and Frevert, 112.418. If chlorine is taken at 35.458, the atomic weight of cadmium becomes 112.421.

The analysis of cadmium bromide by a similar method is now under way in this laboratory, and the results closely confirm the higher value for the atomic weight of cadmium. The method will also be applied to the analysis of other metallic halides.

We are greatly indebted to both the Carnegie Institution of Washington and the Elizabeth Thompson Science Fund for very generous assistance which has enabled us to obtain apparatus best suited for the work.

Cambridge, Mass.

THE ELECTROLYSIS OF SOLUTIONS OF THE RARE EARTHS.

By L. M. Dennis and B. J. Lemon.

Received November 18, 1914.

Historical.

But little attention appears to have been paid to the possibility of separating the rare earths by electrolysis of aqueous solutions of their salts. Edgar F. Smith[1] stated that "didymium is not precipitated, either as nitrate or acetate, although a partial precipitation takes place at the positive pole." Brauner[2] electrolyzed a solution of didymium acetate using platinum electrodes. There formed on the negative pole a pale red crystalline crust which contained didymium and acetic acid. Solutions of the nitrate and of the sulfate of didymium gave similar products. Brauner's object in these experiments was to ascertain whether a superoxide would appear on the positive pole. No such formation was noted, and he did not pursue the subject further. In a brief article entitled "Electrolysis of Solutions of the Rare Earths,"[3] Krüss makes the following statement: "A solution of a chloride of a rare earth behaves upon electrolysis like a solution of an hydroxide in dilute hydrochloric acid; chlorine and hydrogen are set free at the electrodes, the solution loses more and more hydrochloric acid, and as the amount of the solvent diminishes, the hydroxide of the earth is precipitated in increasing amount. In this manner the rare earths can be removed from chloride solutions of mixtures of the earths, the amounts thus precipitated depending upon the

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[1] *Ber.*, **13**, 751 (1880).

[2] *Monatsh.*, **3**, 1 (1882).

[3] *Z. anorg. Chem.*, **3**, 60 (1893).