THE ATOMIC WEIGHT OF MERCURY.

(SECOND PAPER.)

BY C. W. EASLEY.

Received July 30, 1910.

In a series of experiments on the atomic weight of mercury, described in a previous communication,[1] mercuric chloride of very great purity was prepared and its analysis tended to show that the accepted value of this constant was too low. This conclusion was reached as a result of work having to do with the ratio $HgCl_2 : 2AgCl$. Since the results differ from the accepted value by three-tenths of one per cent., it seemed best to establish their correctness in a general way before publication. This was done by determining the percentage of mercury in mercuric chloride but it was explicitly stated that the method of verification was involved and did not approach in accuracy the one by which the ratio $HgCl_2 : 2AgCl$ was determined and that the former was employed merely to indicate the general neighborhood in which the true value lay. The value obtained by this, less accurate, method differed from the first by less than one-tenth of one per cent. but the process was so questionable from the standpoint of the complete collection[2] of the mercury that the same ratio has been determined in another way by work in this laboratory. The results corroborate and agree very closely with the higher value previously published. To determine this ratio, the metal was deposited electrolytically from mercuric chloride of the same degree of purity as that employed in the previous work, the methods of preparation being identical. The value obtained, 200.63, is in almost exact agreement with the finding of the previous investigation, 200.62, calculated from the ratio $HgCl_2 : 2AgCl$, which was believed to give a result with very small error.

Historical and Critical Survey.

In order to find a possible source of error in the work of previous investigators, it may be best to append the work already published.

The table brings to light the fact that mercury itself constitutes one term of every ratio. The metal has been liberated from the several compounds by two methods: (1) by heating with calcium oxide or copper in a stream of an inert gas by means of which the mercury was swept out of the tube containing the reacting mixture, the vapor being condensed in a portion of the apparatus, used subsequently for weighing

---

[1] THIS JOURNAL, 31, 1207.

[2] That a small portion of the finely divided metal passed by the filter in the process of its separation from the filtrate containing the chlorine was known from the solvent action of the mercury salt on the silver chloride. This was described in the previous paper. In fact, only a few of the attempts to collect and determine the mercury were successful, owing to its tendency, under the conditions of the experiments, to be precipitated in such a finely divided state.

the deposit; (2) by depositing the metal on a platinum dish with the aid of the electric current. It is not unlikely that the first method is subject to loss of mercury through imperfect condensation, as it will be shown later that the vapor pressure of mercury at rather low temperatures, although small, is sufficient to be of considerable importance. This would seem to be the main point of weakness in all the previous work, as the preparation of the compounds in a fairly pure condition, with the exception of the oxide, appears to be a comparatively simple matter.[2] Whether any of the compounds escaped contact with the lime or copper, however, might be questioned. The process was certainly complete in the electrolytic method of Hardin but the details concerning such an important matter as the drying of the deposit are so meager that the results do not carry the weight that their agreement would otherwise warrant.

	Ratio.	Atomic weight.
Turner (*Phil. Trans.*, 1833, 531)	$HgO : Hg$	200.63
Erdmann and Marchand (*J. prakt. Chem.*, 31, 395)	$HgO : Hg$	200.20
Hardin (THIS JOURNAL, 18, 1003)	$HgO : Hg$	200.04
Erdmann and Marchand (*J. prakt. Chem.*, 31, 395)	$HgS : Hg$	200.52
Turner (*Phil. Trans.*, 1833, 531)	$HgCl_2 : Hg$	199.67
Millon (*Ann. chim. phys.*, 18, 345)	"	200.22
Svanberg (*J. prakt. Chem.*, 45, 472)	"	199.71
Hardin, (THIS JOURNAL, 18, 1903)	"	200.06
" " " " "	$HgBr_2 : Hg$	199.80
" " " " "	$Hg(CN)_2 : Hg$	199.84
" " " " "	$Hg : Ag$	199.92
Turner[1] (*Phil. Trans.*, 1833, 531)	$HgCl_2 : 2AgCl$	......

The loss of mercury at low temperatures due to its vapor pressure, however slight, is not to be overlooked. At a given temperature, the loss would obviously depend upon the rate at which the vapor was swept through the condensing tube, or, in the case of drying deposits on platinum dishes, on the amount of convection currents in the immediate neighborhood. In the first case, it is entirely possible that the condensation of the mercury, its partial pressure in the mixture being small, from the stream of hot gas was not complete in spite of the fact that gold leaf was employed to collect the portions which might escape. The question involved in the later electrolytic work is the same but here we have to do with the metal spread over the surface of a dish which "was washed

---

[1] In this determination, no account whatsoever was taken of the solvent action of mercury salts on silver chloride so that the values have been excluded from the table as being subject to known error. The results were abnormally high.

[2] It was shown in the previous paper that the sublimation of the chloride from material containing water, such as recrystallized salt, is attended with the production of a slight amount of basic salt.

several times with boiling water and carefully dried." The temperature and method of drying are not stated.

It is well-nigh impossible to reproduce the exact conditions under which various observers have worked but some experiments were undertaken to show the effect of evaporation at moderately low temperatures on the weight of mercury. However, no attempts at exaggerating the ordinary drying methods were made. Instead of exposing a considerable surface of the metal such as a deposit on a dish, a globule of dry mercury having a surface of 1.5 sq. cm. was placed in a weighing bottle 3 sq. cm. in cross section and 5 cm. in height. The bottle was placed in an air oven and maintained for such periods of time and at such temperatures as are shown in the accompanying table. Under such conditions there are no air currents to any extent and no other liquid whose vaporization would tend to carry away the mercurial vapor with it.

Hours in oven.	Temperature of oven.	Total loss in grams.	Loss in grams per hour.
3	50°	0.0016	0.00053
4½	50	0.0024	0.00053
10	50	0.0033	0.00033
6	50	0.0027	0.00048
3½	50	0.0010	0.00029
19	50	0.0057	0.00030
8	60	0.0050	0.00063

The results are as concordant as one might expect and even under these conditions, where the evaporation is reduced to a minimum, the loss is considerable. Especially in the case of a mercury deposit on a platinum dish,[1] the effect is not to be neglected because of the relatively large error[2] due to the small amount of mercury which may be satisfactorily dealt with in this manner.

In the following work, in view of the errors which might arise from the volatility of the metal, it was decided to dry the mercury at ordinary temperatures, using acetone to remove the water as was done in the previous work. The error committed by this procedure is exceedingly small although under favorable conditions the evaporation of mercury may be measured at quite low temperatures. Thus, in a room, subject to draughts, at a temperature of 25°, a slight though decided loss was noticed on several occasions when a considerable surface of mercury was exposed for 24 hours.

---

[1] The manuals on electro-analysis do not agree on the temperature at which mercury should be free from water. One commonly used, however, recommends the drying on a moderately warm plate.

[2] Thus, with one gram of mercuric chloride, the average amount used by Hardin, each change of a tenth of a milligram of the metal in the neighborbood of the actual amount present affects the atomic weight in the first decimal place.

General Method.

In order to secure recognition of the higher value of the atomic weight of mercury by any method, the latter must be free from the objections urged against the process used in determining the same ratio as described in the preliminary paper.[1] The electrodeposition of mercury from the chloride under proper conditions realizes this condition to a marked degree. That the metal is completely freed from the chlorine by this process is well known and its complete collection is assured from the form of the apparatus. Again, electrolytic methods in general possess simplicity. In the work here described even greater simplicity, and therefore greater accuracy, has been attained from the manner in which the deposit is handled. A special vessel was devised in which the metal was deposited in globular form by means of a mercury cathode and without being removed was washed by decantation, freed from water by means of acetone and finally weighed. A test of the method is whether a globule of mercury can be subjected to the above-mentioned treatment without change of weight. Many experiments bearing on this point show that the changes in weight, a similar vessel receiving similar treatment, of course, serving as a counterpoise, are small, never being greater than a tenth of a milligram and generally no more than a few hundredths. Such changes may therefore be attributed to errors incident to weighing glass vessels of the size employed. By the electrolysis of known weights of mercuric chloride with precautions to be mentioned later, one has a method at once simple and accurate and possessing the very great advantage, other things being equal, that relatively large amounts of mercury may be deposited without increasing the error of measurement. Over twenty grams of mercuric chloride were electrolyzed in the tube with the same ease and accuracy as were the smaller amounts.

The Material.—For the sake of comparison with the work previously published, three samples of mercuric chloride were prepared with the same care and in precisely the same manner as in that work. For the details reference should be made to that paper. The corresponding samples are designated by the same numbers in both communications. The analyses of these samples are considered in a series by themselves for the reason that no suspicion whatever is attached to the purity of either the salt or the mercury obtained from it.

Not so much can be claimed for sample o which was originally intended for the preliminary work in order that some uniformity of results might be attained while the method was being tested out. To this end, the choicest appearing crystals from Kahlbaum's highest grade of mercuric chloride were sublimed in a current of dry air in the special tube described in the previous paper. A large fraction coming over first was

---

[1] THIS JOURNAL, 31, 1207.

discarded, but most of the remainder was collected. During the sublimation, the temperature was maintained in the neighborhood of 300°. An exceedingly small residue, for commercial material, remained, which had every appearance of being carbon. The salt was entirely soluble in water.

The results of the analyses of this sample were quite concordant, and a search was begun to discover the nature of the traces of impurities for it was evident that very pure salt was being dealt with. Slight amounts of arsenic only could be found in the original Kahlbaum salt and none whatever in the sublimed portion, so that it was decided to use the results of the analyses of this sample as evidence in this investigation. Naturally, less weight must be attached to the results from this sample, subjected to physical treatment only in its purification, than to the values from samples 1, 2, and 3, especially as the latter samples were the last to be analyzed and thus greater manipulative skill was possible at this stage of the work. That some impurity was present, however, was evidenced from the fact that the globule after drying had a peculiarly striated appearance here and there, although the surface was lustrous. Any metal deposited simultaneously must have been present in very small amounts and would probably have dissolved in the mercury. The deposition of platinum was not the cause for the same phenomenon did not occur with any of the other samples. Judging from the high results, if a foreign metal is present, it must have an atomic weight higher that that of mercury, which is quite improbable. The sample gives a result so little above that of the final series, however, that the difference might be accounted for by the retention of a minute quantity of water or even acetone by the peculiar surface which, in turn, might have been caused by the slightest amount of an impurity.[1]

Weighing.—A Sartorius balance was used and the consecutive weighings could be relied upon to one-fortieth of a milligram. In determining the weight of the salt, substitution was the method employed while, in the case of the mercury, the tube containing the metal was counterpoised with a similar tube and was subjected to the process of double weighing in order to correct for the inequalities in the length of the balance arms.

---

[1] That the presence of very small amounts of certain impurities interferes with the tendency of the separate particles to unite is well known. In washing the mercury obtained from this sample, the particles sometimes became detached and considerable more difficulty was experienced in reuniting them than in the case of the other samples. It is not impossible that a small amount of packing material, often found in chemicals, was destroyed during the sublimation and that some of the products distilled over so that the appearance of the mercury might be due to very small detached particles of the metal itself covered with a film of organic matter.

The gold-plated brass weights were calibrated and the proper corrections applied. The following vacuum corrections were made:

+0.000080 gram per gram of mercuric chloride.
—0.000055 gram per gram of mercury.

The Cathode.—In view of the difficulties attending washing and drying deposits on platinum dishes, it was decided very early in the course of the work to make use of a mercury cathode, an idea due to Wolcott Gibbs[1] in 1883 and used by him and others in depositing various metals in the form of amalgams. The main drawback to the more general adoption of such a method has been the difficulty of handling the deposit, an objection which has been overcome in this work. In the present case, such a cathode seems ideal in that it avoids an interface of any considerable area with another conducting surface, with the consequent questionable procedure of washing and drying under such circumstances. Again, one is not limited to the deposition of very small amounts of metal, which amounts cannot be exceeded in using platinum dishes, owing to the tendency of the mercury to collect in drops at the bottom of the dish; nor does the question of current density arise to change the nature of the deposit.

To discover whether or not hydrogen was retained by the mercury, a dilute solution of hydrochloric acid in one case and of sulphuric acid in another was electrolyzed and the effect on the weight of the cathode was determined. In one of the experiments only was there an increase in weight, so that the change in this exceptional case was considered accidental. Had this effect been caused by hydrogen, the atomic weight of mercury would have been changed only one unit in the second decimal place.

For the electrode, five to ten grams of mercury, prepared by the reduction of pure mercuric chloride, was placed in the electrolyzing tube in contact with the platinum wire. The mercury was first washed with water, treated with acetone and dried with air, as will be described later. At the conclusion of some of the experiments, a portion of the deposited metal was retained to serve as a cathode, thereby effecting a saving in the preparation of pure mercury. The globule constituting the cathode always possessed a clean, lustrous surface.

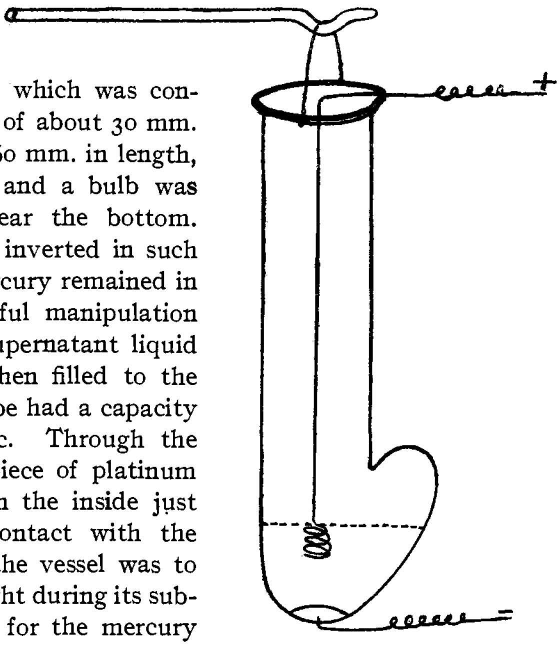
The Anode.—As concentrated solutions of mercuric chloride were to be electrolyzed with the consequent production of strong chlorine solutions, considerable time was spent in search for suitable anode material, for it was expected that platinum would be strongly attacked. Carbon in several of its forms was tried but it was not to be relied upon, either because of its absorptive properties or because of the tendency of portions to become detached. Again, such electrodes are difficult to treat

---

[1] *Am. Chem. J.*, 13, 571.

in such a manner that constant weight is maintained and thus one has no check on this important point. In describing a method of overcoming the solvent effect of chlorine on a rotating platinum anode, Smith[1] recommends the use of a layer of toluene or xylene on the solution just above the anode. This was tested, although in this work the anode was stationary, with the result, as afterward found, that more of the platinum was dissolved by this treatment than without the absorptive layer. It was therefore decided to use the platinum, as is ordinarily done, find its loss of weight, determine the amount in the solution after the electrolysis and thus calculate by difference the amount deposited with the mercury. Contrary to expectations, the loss of platinum by solution was exceedingly small and practically all of the dissolved portion was deposited with the mercury, none being found in solution at the conclusion of an experiment. The anode at the beginning of the experiments described later weighed 1.54895 grams and at their conclusion 1.54880; or, during the course of eleven experiments in which over 125 grams of mercuric chloride had been electrolyzed, the anode lost 0.00015 gram.

The platinum wire, weighing 1.5 grams and having a length of 35 cm., was wound at one end into a spiral, the latter being maintained at approximately 2 cm. from the cathode. The other end of the wire was connected with the battery terminal by means of a clip.



The Electrolyzing Tube.—The figure illustrates the essential features of this vessel, which was constructed of glass tubing of about 30 mm. diameter. The tube, 160 mm. in length, was closed at one end and a bulb was blown into its side near the bottom. The tube could thus be inverted in such a manner that the mercury remained in the bulb and by careful manipulation practically all of the supernatant liquid could be removed. When filled to the top of the bulb, the tube had a capacity of approximately 50 cc. Through the bottom was sealed a piece of platinum wire which projected on the inside just far enough to make contact with the mercury cathode. As the vessel was to remain unaltered in weight during its subsequent treatment, save for the mercury

---

[1] *Electroanalysis.*

deposited, all portions of the surface were carefully smoothed in the flame. To this same end, the platinum wire was connected with the battery terminal by means of a clip which precluded any abrasion of the surface of the platinum. For convenience during the processes of electrolysis and weighing, a platinum wire was wound about the neck of the tube to serve as a loop for suspension. During the former process, the tube hung on a glass rod; in weighing, the hooks on the balance arms were utilized as supports. It has already been stated that a counterpoise, similar in every respect to the electrolyzing tube, was used throughout the work. Consecutive weighings proved the adequacy of this procedure.

The Procedure.—A known amount of mercuric chloride[1] was placed on the cathode in the electrolyzing tube with sufficient water to make a total volume of 25 or 30 cc., the sides of the tube having been carefully washed down. A few drops of a dilute solution of redistilled hydrochloric acid were added to make the solution approximately one-fortieth normal. This was necessary to increase the conductivity of the solution at the outset and this particular compound was chosen in order not to introduce ions other than those which would be present later. The water added was not sufficient to entirely dissolve the salt so that the latter was dissolved, except in so far as its solubility was affected by the presence of substances formed during the course of the process, only as the solution became depleted by the electrolysis. With the strength of current used, the action had ordinarily proceeded for 8 or 10 hours before the disappearance of the solid phase. At the end of a similar period, the action was complete, as shown by the preliminary work, but traces of mercury compounds were probably adhering to the sides of the tube and to the funnel placed in the mouth of the tube to prevent loss in the form of spray. An addition of approximately 20 cc. of water was made in washing the funnel and walls of the tube and the current was allowed to pass several hours longer, after which no trace of mercury could be detected in the solution. Sometimes the whole process consumed 48 hours, varying altogether with the amount of salt to be electrolyzed and whether or not it was convenient to perform the subsequent operations. Copious fumes of chlorine escaped during the action and as is usual in the electrolysis of mercuric chloride, insoluble particles said to be the mercurous compound gradually accumulated at the anode only to fall off and finally disappear. To prevent any of these particles from becoming permanently lodged between the glass surface and the cathode, the globule was agitated by a gentle whirling motion of the tube. This was not attempted, however, until the electrolysis was practically complete for fear of entangling solution and from that time on the process was repeated at in-

---

[1] The non-hygroscopic character of the salt was proven in the previous work.

tervals to insure completeness. At no time was the agitation violent enough to sever the connection between the mercury and platinum. Sometimes the mercury exhibited a tendency to assume a form perhaps "deadened" and the separate particles had no tendency to unite with the main globule. Gentle tapping, however, generally sufficed to cause the formation of one globule.[1] It is not unlikely that the disengagement of hydrogen from the cathode was the cause of the separation of these small particles.

To free the tube of conducting material at the end of the electrolysis, a funnel, with its stem almost reaching to the surface of the mercury, was placed in the tube and without breaking the electric connections at least 500 cc. of pure water were poured into the tube, the overflow being caught in a large porcelain dish where any particles of escaping mercury could be detected. During the washing process, the tube was rotated as previously described so that no chlorine would be retained between the cathode and glass and thus remain in contact with the mercury after the breaking of the circuit. After removing the funnel, the water in the tube was decanted, the mercury with perhaps a drop or so of water remaining in the tube, owing to the bulb arrangement. Five washings were made with redistilled acetone, each being decanted in turn. The tube was next immersed to its neck in a bath of acetone to free the outer surface of water and was finally hung on a glass rod to dry. The counterpoise was subjected to exactly the same treatment. The two tubes hung side by side and were gently agitated from time to time to prevent the possibility of the retention of any acetone between the globule and glass. Meanwhile, a current of air of the same intensity was passed over each globule so that in a short time the vapor of acetone was effectually removed and the tubes were full of air ready for their transfer to the bal-

THE RESULTS.

PRELIMINARY EXPERIMENTS.

No. of expt.	Sample of $HgCl_2$.	Weight of $HgCl_2$ in vacuum.	Weight of Hg in vacuum.	Atomic weight[2] of mercury.
1	0	10.05743	7.43123	200.68
2	0	8.41289	6.21687	200.71
3[3]	0	10.99056	8.11897	200.52
4	0	10.28282	7.59681	200.58
5	0	19.57120	14.46032	200.65
			Mean,	200.63

---

[1] In the preliminary experiments where less pure mercuric chloride was being dealt with, more difficulty was encountered.

[2] Calculated on the assumption that chlorine has the value, 35.46, THIS JOURNAL, 32, 4.

[3] In expt. 3, a portion of the mercury became detached and during the washing was poured into the catch dish. It is possible that the low value obtained in this case may be explained by the incomplete recovery of the separated particles.

ance arms. As soon as constant temperature was attained, the weighing was made by the method described before. Repetition of the drying process insured its completeness.

The current was supplied by three storage cells and was reduced by means of a suitable resistance to one- or two-tenths of an ampere. The action proceeded quietly, no spray being noticeable and no rise of temperature above 30° took place.

FINAL EXPERIMENTS.

No. of expt.	Sample of $HgCl_2$.	Weight of $HgCl_2$ in vacuum.	Weight of Hg in vacuum.	Per cent. Hg in $HgCl_2$.	Atomic weight[1] of mercury.
1	2	8.14695	6.01909	73.882	200.61
2	1	11.03881	8.15592	73.884	200.64
3	1	13.48192	9.96129	73.886	200.66
4	3	11.08026	8.18610	73.880	200.60
5	3	11.31231	8.35819	73.886	200.66
6	3	21.44026	15.84060	73.882	200.62
				73.883	200.63

It now remains to consider the results in this and in the previous paper:

Series.	Atomic weight.
1. The ratio $HgCl_2$: Hg (from the previous paper)	200.48
2. " " $HgCl_2$: 2AgCl (from the previous paper)	200.62
3. " " $HgCl_2$: Hg (prelim. expts., this paper)	200.63
4. " " $HgCl_2$: Hg (final " " ")	200.63

Giving each series equal weight, the mean value of the atomic weight of mercury becomes 200.59. It is reasonable, however, in seeking an optimum result to reject any series known to be faulty either on account of the nature of the material dealt with or in method. For the last reason, Series 1 is dropped and for the first, Series 3 is thrown out. Considerable weight is attached to the mean value, 200.63, of the two remaining series for (1) the mercuric chloride analyzed was the same in each, and, from the manner of preparation, it must have been practically free from foreign material and (2) the complete analysis, by methods which seem above question and which are radically different, shows that the sum of the mercury and chlorine contents gives essentially the real value. Thus,

Per cent. Mercury:	
From the fact that 56.52119 g. of mercury resulted from 76.50051 g. of mercuric chloride (Series 4)	73.883
Per cent. Chlorine:	
On the basis that 86.21813 g. of silver were obtained from 81.66510 g. of mercuric chloride (Series 2)	26.118
The sum	100.001

THE UNIVERSITY OF MAINE.

---

[1] In the calculations, the atomic weight of chlorine has been taken as 35.46, THIS JOURNAL, 32, 4.