# THE ATOMIC WEIGHT OF MERCURY.

[PRELIMINARY PAPER.[1]]

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This work was begun with the object of determining the atomic weight of mercury by finding the chlorine content of mercuric chloride, no one, save Turner[2] seventy-five years ago, having used this method. In fact, Hardin's work[3] is the only contribution to the general subject since 1848. The accepted value of the atomic weight of mercury is based altogether on determinations of the metal itself in several of its compounds. Hardin deposited the mercury in a platinum dish electrolytically but the very small amounts which can be so collected leaves much to be desired for an atomic weight determination; furthermore, the treatment of such deposits before weighing, subject as they are to loss from volatilization of mercury if the temperature is too high and, on the other hand, to retention of water, if the temperature is too low, may not have been submitted to sufficient scrutiny. Most other experimenters[4] have liberated the mercury from some compounds at temperatures above its boiling point and have attempted to collect the metal, a procedure of doubtful accuracy.[5] Determinations along different lines should, then, fill a gap and serve as a check on previous work.

Determinations of chlorine, in general, due to the already classic work of Stas and Richards, may be executed with a high degree of precision, so that this method has been used in atomic weight work whenever possible. When one seeks to apply the method to mercury, however, he is confronted with the fact that silver chloride[6] is very soluble in mercury salts and he must, therefore, apply a correction for this solubility, find some agent which inhibits the dissolving power, or remove the mercury entirely, leaving the chlorine in a form that may be precipitated as silver chloride. Any of these procedures is subject to objection, so that the atomic weight of mercury may not, perhaps, be as accurately determined from the ratio $HgCl_2 : 2AgCl$ as that of many other elements. In spite of objections, results so concordant have been obtained in the work presented in this paper that the values seem deserving of considerable weight. The atomic weight found is in the neighborhood of 200.6, three-tenths of a per cent. higher than the accepted value. A high result was expected but the new value was so different that publication of the results

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[1] Change of residence renders advisable the publication of the work at this time.

[2] *Phil. Trans.*, **1833,** 531–535.

[3] THIS JOURNAL, **18,** 1003 (1896).

[4] See Clarke, "Recalculation of the Atomic Weights;" Smithson. Coll., "Constants of Nature," 1897.

[5] See Brauner, Abegg's Handbuch.

[6] Wackenroder, *Ann.*, **41,** 317.

has been withheld until evidence from another direction could be obtained. Fortunately, extended work shows that the treatment accorded the salt to remove the mercury, for this was the plan finally adopted, leaves the latter in such a form that it may be readily determined. The accuracy of this procedure does not approach that of determining chlorine, partly because of the increase in number of operations and partly because of the elusive nature of mercury which makes its complete collection a very difficult task. This phase of the work, however, leads to a value near 200.5, less than one-tenth of a per cent. different from that given by the halogen determination, but still over two-tenths of a per cent. above the generally accepted value of 200.0. The value 200.5, apparently a minimum, lends strength to the belief that the higher result, 200.6, lies very close to the absolute value of the constant. The results are stated conservatively, however, as further study of the subject will be necessary to give confirmation to the higher value. Such work has already been started along the line of the electro-deposition of the metal.

*General Method.*—The solubility of silver chloride in mercuric nitrate is so great and the suspended particles settle so slowly that the plan of treating mercuric chloride directly with silver nitrate was discarded as subject to too great error. Since the efforts of Debray[1] and others to find some means of inhibiting the action of mercury salts had failed, little time was spent in this direction.

The search for a process of removing mercury from a solution of mercuric chloride proved a long and laborious task. Not only must the mercury be completely separated from the chlorine but the deposit of mercury or its compound must be of such form as may be easily filtered and washed so that no portion of the solution remains with the deposit. Furthermore, the chlorine must be left in a state to be converted by silver nitrate to silver chloride. Such requirements are hard to meet. Many metals remove mercury from solutions of its salts but a portion of the mercury is always found combined with chlorine in the form of insoluble mercurous chloride. This action is not surprising in view of the fact that mercury itself in contact with mercuric chloride forms calomel. In the case of cadmium in a weak acetic acid solution of mercuric chloride, the formation of mercurous chloride was very slight but no means of entirely preventing its formation was found. Among other agents tried were phosphorous acid, hypophosphorous acid, hydrazine, hydroxylamine, and hydrogen peroxide. The most promising results given by preliminary work were obtained with hydrogen peroxide in weak alkaline solution. Kolb[2] was the first to publish the fact that this reaction permits of the determination of mercury in its compounds although the various com-

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[1] *Compt. rend.*, 70, 849 (1870).

[2] *Chem.-Ztg.*, 25, 21.

pendiums have made note of the reducing action of hydrogen peroxide on mercuric oxide. The method was subjected to careful study in this laboratory to discover whether the chlorine from the mercuric chloride could be determined as silver chloride after the mercury itself had been filtered off. Careful search revealed the presence of chlorine as chlorine ions only. While this investigation was in progress, Kohn,[1] using the peroxide method, published some determinations of chlorine and bromine in mercuric chloride and bromide respectively, showing that the method is of analytical value. The application of the method with all details will be discussed in Part I and Part II where the determinations of mercury and chlorine respectively in mercuric chloride will be taken up.

## Part I.—The Determination of Mercury in Mercuric Chloride.

A known weight of mercuric chloride was dissolved in as small a quantity of water as possible in a flask of Bohemian glass. A tube, bent upon itself several times to form traps, was ground into the neck of the flask and prevented the escape of spray along with the disengaged oxygen. The peroxide was added through this tube, the successive additions, of course, washing back and renewing the charges in the traps. Approximately 0.3 gram sodium hydroxide above the calculated amount required to precipitate mercuric oxide was added. A three per cent. solution of hydrogen peroxide was next added, two or three cubic centimeters at a time, the yellow color of the oxide gradually attaining the grayish tinge of the free mercury. All traces of oxide finally disappear and the solution becomes clear save for particles of finely divided mercury. A few cubic centimeters of peroxide in excess were added and the flask was heated on the steam bath for ten minutes in order to cause the formation of a single globule. There was always a centigram or so (see table of results) of finely divided mercury, possibly entangled in silica, which, together with an amount never exceeding a milligram sometimes found in the solution, must be added to the weight of the globule to give the total weight of the mercury.

Preliminary work showed that a globule of pure dry mercury could be agitated with water and dried with acetone without appreciable change in weight. The accurate determination of the mercury in the globule, then, offered no difficulty. After separation from the solution, it was poured into a 50 cc. flask into the side of which was blown a bulb capable of containing the amount of mercury dealt with. The flask could thus be completely inverted and still retain the globule while practically every drop of solution or water could be drained off. Several washings with water were made and each was poured into a small filter to retain any possible traces of mercury. Five additions of pure redistilled acetone were then made and each in turn decanted. The last traces of acetone

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[1] *Z. anorg. Chem.*, **59**, 271 (1908).

in the flask were removed with a current of dry air, the flask being kept at 30°–35° for half an hour. The surface of the metal was clear and lustrous, no trace of foreign matter being apparent. The flask with its contents was then weighed, tared with a flask that had been similarly treated in every respect.

The small amount of finely divided mercury was collected on a small filter, often a double one, several filtrations sometimes being necessary to retain all the residue. The filter with its retained matter was now placed in the flask originally used for the reduction of the mercuric chloride and treated with 3–5 cc. of nitric acid, the acid having previously been used to dissolve any traces of mercury left either in the weighing flask or in the acetone washings after evaporation of the acetone. The flask with the trap of the exit tube full of water was then placed on the steam bath and 2–3 grams of bromine were added to ensure the presence of mercury as mercuric salts only. After further heating, the solution was diluted to 300–400 cc. and boiled to eliminate the excess of bromine. In case the chlorine was not to be determined in the original filtrate, the latter was added to the solution containing the nitrate and bromide and the resulting solution was treated with hydrogen sulphide, thus completely precipitating all the mercury, except that already weighed, as mercuric sulphide. The advantage of this course is that the scattering remnants of mercury may be collected in a form which, due to the great volume of the sulphide, does not admit of appreciable loss. It is not possible to weigh this sulphide directly, owing to the presence of free sulphur. The removal of the latter is troublesome and attended with greater error than the electrolytic determination of the metal by suspending the sulphide in a very dilute solution of hydrochloric acid. This method, originated by Classen[1] and used at Almaden for determining mercury in cinnabar, seems crude at first sight but preliminary work showed that for a few centigrams of material, the amounts actually in question, the error is negligible. The sulphide was separated from the solution by means of a very small filter and the latter was placed in a platinum crucible and covered with water acidulated with two or three drops of hydrochloric acid. A cathode of gold foil was used and a beautiful sky-blue deposit of mercury resulted which was easily washed and dried by means of acetone. Very small currents were used so that the complete deposition sometimes required two days. Under the conditions, there was no gain in weight of the cathode due to solution of platinum.

*The Atomic Weight of Mercury from the Ratio $HgCl_2 : Hg$.*—The table[2]

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[1] "Ausgewählte Methoden der analytischen Chemie."

[2] The balance used in this work admitted of consecutive weighings within one-fortieth of a milligram, a sensitiveness more than sufficient for the work. The gold-plated weights were calibrated and the proper corrections applied. All objects were

below contains the results of all the work done after the method was completely in hand. Each sample of the mercuric chloride was prepared separately.

| No. of exp. | Sample of $HgCl_2$. | Wt. of $HgCl_2$. | Wt. of Hg in globule. | Wt. of Hg collected electrolytically. | Total wt. mercury. | Atomic wt. mercury.[1] |
|---|---|---|---|---|---|---|
| 1....... | 2 | 23.43239 | 17.25575 | 0.05251 | 17.30826 | 200.44 |
| 2....... | 2 | 12.59751 | 9.27980 | 0.02628 | 9.30608 | 200.52 |
| 3....... | 2 | 10.94042 | 8.06674 | 0.01460 | 8.08134 | 200.46 |
| 4....... | 3 | 11.73734 | 8.63720 | 0.03324 | 8.67044 | 200.50 |
| | | | | | | Mean, 200.48 |

## Part II.—The Determination of the Ratio $HgCl_2$ : $2AgCl$.

Mercuric chloride was treated in precisely the same manner as that described in Part I for the determination of mercury. Special care was exercised in the separation of the metal from the slightly alkaline solution by filtration to render certain that all the chlorine passed into the filtrate and that all the mercury was retained. To this end, the solution was never allowed above the lower third of the filter cone; even in washing, the upper part of the filter was kept empty in order that no particles of mercury might pass by into the filtrate. The whole filter was finally washed but the wash water was collected separately and, after standing, poured through a new filter into the stronger solution. This procedure involved no appreciable loss. The solution, now containing the whole of the chlorine, was acidified with nitric acid immediately after the filtration, the exact amount of acid required being calculated from the known excess of sodium hydroxide present, and was now ready for the precipitation of silver chloride. This was done by weighing out approximately 0.2 gram over the required amount of silver and converting it into silver nitrate by adding approximately 1 cc. of nitric acid for each gram of silver used. The solution, boiled free from nitrous fumes and diluted to about tenth normal, was added to the equally dilute solution containing the chlorine. This solution contains, in addition to sodium chloride, a small amount of sodium nitrate from the neutralization of the sodium hydroxide so that the precaution[2] of diluting to ensure the exclusion of foreign matter from the silver chloride was observed, the dilution probably being greater than necessary. After standing over night, the supernatant liquid was poured through a Neubauer crucible in a photographic room and the filtrate, which contained a very small amount of silver chloride

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suitably tared with similar ones and the weighings made by substitution. In order to reduce the weights to a vacuum standard, the following corrections were made:

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

[1] In these results the value used for chlorine was 35.46, THIS JOURNAL, **31**, 4.

[2] Richards and Wells, THIS JOURNAL, **27**, 459–529 (1905).

due to the dissolving action of mercury salts present, was set aside for subsequent examination. The bulk of the silver chloride, still in the flask, was washed five times with water containing a slight excess of silver nitrate and the washings were rejected as no dissolved silver chloride was present. Seven or eight washings were made with water slightly acidulated with nitric acid. Estimation of the silver chloride in these washings was made by means of the nephelometer.[1] The precipitate was transferred to the crucible with the last wash water, dried at 145°-155° and weighed. The slight amount of water retained was determined by fusing the bulk of the dried silver chloride in a porcelain crucible. The above procedure, including the formation and treatment of the precipitate, follows very closely the one adopted by Richards and Wells[2] as the outcome of their detailed study of the properties of silver chloride.

The determination of the small amount of silver chloride in the filtrate after the removal of the precipitate of the silver salt was comparatively easy. The traces of mercury salts, if present, undoubtedly have a dissolving action on silver chloride but a portion of the latter may be present in a suspended state, due to the action of the extremely dilute solution of hydrogen peroxide on the finely divided platinum of the crucible. This may produce disintegration of any adjacent particles of silver chloride and cause them to pass into the filtrate. The amount actually found in the filtrate, less than half a milligram per liter on the average, forms a very small correction. A known fraction of the filtrate was treated with chlorine-free hydrogen sulphide, then rendered slightly ammoniacal with chlorine-free ammonia and a small amount of a solution of pure alum added. The filtered solution was perfectly clear when tested with the nephelometer. In order to determine its chlorine, comparison was made with a solution containing a known amount of chlorine which had received the same treatment as described above for the solution of unknown chlorine content. Thus gain or loss of chlorine due to manipulation or reagents would have little effect, since the standard had approximately the same chlorine value as the unknown solution. The solutions, filtered free from any insoluble material, were boiled the same length of time to liberate hydrogen sulphide and were made slightly alkaline with sodium hydroxide. The addition of small quantities of hydrogen peroxide oxidized any trace of sulphides to sulphuric acid. The solutions on being acidified were ready for examination in the nephelometer.

In experiments 3 and 4, a deviation from the course outlined above was made to discover if there might be a flaw in the estimate of silver chloride in the filtrate and, again, to have any advantage which results

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[1] Richards and Wells, *Am. Chem. J.*, **31**, 235-243 (1904).

[2] Richards and Wells, THIS JOURNAL, **27**, 459-529 (1905).

from determining the mercury and chlorine in the same sample of mercuric chloride. To carry this out, as soon as the mercury had been separated from the alkaline solution containing the chlorine, the solution was just acidified with nitric acid and pure hydrogen sulphide was introduced to remove any traces of mercury present. After filtration and removal of the hydrogen sulphide, the solution was treated with silver nitrate in excess and the silver chloride was washed, collected and weighed in the usual fashion. The removal of the hydrogen sulphide was accomplished by means of a stream of well-washed carbon dioxide, any spray being caught by having the exit tube of the glass-stoppered container dip into a small quantity of water which was subsequently added to the main portion. The traces of sulphide still remaining were oxidized to sulphuric acid by heating on the steam bath after the addition of small quantities of sodium hydroxide and hydrogen peroxide. The solution was then acidified with nitric acid, the required amount being calculated from the known quantity of hydroxide and was ready for the addition of silver nitrate. The mean of the results of these two experiments agrees with the mean of the other four, although the number of operations is greater and therefore the results are subject to greater error, as the deviations show.

THE ATOMIC WEIGHT OF MERCURY FROM THE RATIO $HgCl_2 : 2AgCl$.

| No. of exp. | Sample of $HgCl_2$. | Weight of $HgCl_2$. | Weight of AgCl. | Atomic weight[1] of Hg. |
|---|---|---|---|---|
| 1 | 1 | 10.50276 | 11.08744 | 200.64 |
| 2 | 2 | 9.03634 | 9.54027 | 200.62 |
| 3 | 2 | 23.43239 | 24.73606 | 200.65 |
| 4 | 2 | 10.94042 | 11.55158 | 200.59 |
| 5 | 3 | 11.11409 | 11.73470 | 200.60 |
| 6 | 3 | 16.63910 | 17.56808 | 200.60 |
| | | | | Mean, 200.62 |

The above table contains all the experiments undertaken after the method was perfected with the exception of two which met with known accidents. The samples of mercuric chloride used in the several experiments were prepared separately, the figures showing that the preparations were probably free from accidental error. Owing to the high atomic weight of mercury, in order to form an amount of silver chloride sufficient to give leeway for any error due to its proper collection, one must use a considerable quantity of mercuric chloride. Fortunately, the method of preparing mercuric chloride here employed admits of pure material being made in large, just as readily as in small amounts, and the ease and accuracy with which the subsequent operations, barring

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[1] These results are calculated with the values Cl 35.46, Ag 107.88, THIS JOURNAL, 31, 4.

the washing and collection[1] of silver chloride, may be executed do not depend upon the amount of material used. Larger amounts of material, excessive for ordinary precipitations, were used in experiments 3 and 6 in the endeavor to find the effect of varying the concentration.

## Critical Estimate of the Results.

*The Ratio $HgCl_2 : Hg$.*—In determining the mercury in the average amount of mercuric chloride used, if we assume no error save in the collection of the metal itself, a gain or loss of each milligram changes the atomic weight of the element one unit in the first decimal place.[2] Had the weight found for the mercury been excessive, it must have been due to the presence of water, acetone, silica, iron from the sodium hydroxide, or platinum from the anode, any of which would of course give an apparently high value for the atomic weight. That the globule itself was free from these impurities, there is little doubt. If suspicion be attached to any of the processes, it would most likely fall upon the electrolytic recovery of the non-globular particles. Experiments with known amounts of mercuric chloride, made as nearly parallel as possible to the actual case, proved the method reliable and incidentally cast out any suspicion that the anode was attacked under the conditions of the electrolysis. That iron is present is hardly possible for the mercuric sulphide was precipitated in acid solution. When one considers that the collection of every trace of mercury is difficult, it would appear probable that the weights of mercury obtained were a minimum and that the atomic weight resulting was too low.

*The Ratio $HgCl_2 : 2AgCl$.*—In these determinations, every effort was made to find loopholes for loss of chlorine. Using 10 grams of mercuric chloride, every gain of 0.005 gram of silver chloride lowers the atomic weight one unit in the first decimal place. The drying and collection of silver chloride is so accurate a procedure and the agreement of the results is such that one must search elsewhere for error, the correction for which would give a lower value for the atomic weight of mercury. The presence of material not contributing chlorine in the mercuric chloride would give an apparently high atomic weight, but this supposition seems improbable from the manner of preparation. The question whether all the chlorine finally remains as chlorine ions was carefully examined especially as sodium hydroxide is said not to fully

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[1] The amount of silver chloride in Exp. 3 was too large for the crucible so that a portion of the precipitate was transferred to other crucibles and dried separately. The high value given by this experiment seems to indicate some loss of silver chloride in transference.

[2] Hardin, THIS JOURNAL, 18, 81003 (1896), used an average amount of 1 gram of chloride making each unit in the first decimal place of the atomic weight vary with each tenth milligram of mercury finally collected, leaving a very small leeway for any error of drying and collection.

precipitate mercury from solutions of its salts. Diligent search in the filtrate after the removal of the chlorine ions as silver chloride failed, however, to reveal chlorine in any form except in the slight amount of silver chloride which was dissolved by the traces of mercury salts present. In addition to this evidence, the different concentrations at which the analyses were made form confirmation on this point. In experiments 5 and 6, the last to be carried out and therefore probably deserving of the greatest weight, any effect due to the incomplete precipitation of mercuric chloride by sodium hydroxide or any other constant error should be apparent, for while the amount of solution was the same in each, in experiment 5 approximately 11 grams of mercuric chloride were reduced while nearly 17 grams of the salt were used in experiment 6. Thus a constant error in each experiment would form a smaller percentage error in No. 6. The results, however, are the same.

The purity of the mercuric chloride would seem to be very great. Material contributing less chlorine than mercuric chloride or material entirely inert would, of course, give an apparently high atomic weight for mercury. The usual impurities of mercuric chloride would hardly justify the assumption, however, that metals of such high atomic weight as to give less chlorine are present. Silica and water, the more usual impurities, are certainly absent from the manner of preparation, only dry material being used in the synthesis of the mercuric chloride and the sublimation, of course, precluding the presence of silica. The most probable impurities would be chlorides of metals of lower atomic weight, the presence of which would give an apparently low value for the atomic weight of mercury. This supposition,[1] however, is hardly tenable in the light of the results. Chlorine in the reagents would again give an apparently low atomic weight.

There is a correction, owing to the dissolving action of sodium hydroxide on the glass flask, which was not applied, partly because of the difficulty of its accurate determination and partly because its small value hardly warranted the effort in the limited time at the disposal of the author. If any silica is present, however, the value given for the atomic weight of mercury as a result of this work is too low. That the error is negligible seems highly probable if we consider that the flask was of Bohemian glass, that the concentration of the 200–250 cc. of solution never reached twentieth normal with respect to sodium hydroxide and that the solution was filtered before precipitation with silver nitrate. Thus any insoluble silica should be separated from the solution and any soluble silica should not be harmful as the solution was acidified before being treated with silver nitrate.

*Preparation of Mercuric Chloride.*—Sublimation of mercuric chloride, recrystal-

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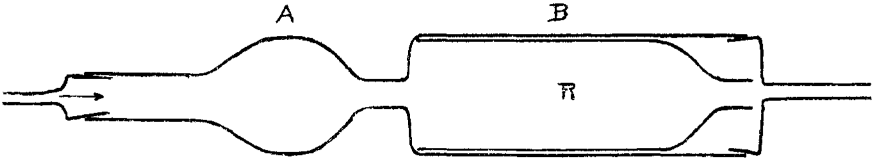
[1] See " Purification of Material."

lized, offers at first sight an easy means of separation from most foreign matter likely to be present. Preliminary work, however, in this direction was disappointing, as a sample of the sublimed material was never obtained entirely free from basic salts, even in a stream of hydrochloric acid. Brown colored material floated in the molten mercuric chloride and remained as a residue of the sublimate. This experience showed that water must be eliminated and it was at once decided to prepare the salt from its elements, both of which are capable of being obtained in a high state of purity. A product was thus obtained which was perfectly colorless when molten and which was completely soluble in water. No trace of a residue was ever observed even though as much as 25 grams of mercury were converted to chloride and sublimed at a temperature of 300°.

The apparatus in which the salt was prepared consisted of a wide tube constricted to form a compartment A for the mercury. In order to collect and transfer the salt uncontaminated, a receiving tube R fitted snugly in the portion B and served to catch the larger portion of material as it sublimed over. This receiver was drawn out at one end to act as a funnel in transferring the sublimate to the weighing bottle. The large volume occupied by the sublimate made it necessary to have a large receiving device and the non-hygroscopic[1] character of the salt admitted the use of this particular form. The joints were all of ground glass and in no part of the system with which this preparation tube was connected did the chlorine come in contact with rubber connections, the apparatus for preparing and drying chlorine being constructed of glass only. Chlorine in large excess was passed through the apparatus after the air had been swept out by a current of nitrogen. The mercury was kept at 300° by having compartment A in a constant-temperature oven. The metal became coated with fused chloride, perfectly colorless, which gradually sublimed into the receiver R. When the sublimation was complete, the chlorine was displaced by nitrogen and compartment B was heated to and maintained near 250°, a point beyond that of incipient sublimation, for ten or fifteen minutes. This precaution was taken to insure the removal of every trace of chlorine. The salt was finally allowed to cool in the stream of nitrogen to room temperature after which the transfer to the weighing bottle was made. Mercuric chloride thus prepared consists of a mass of long needle-like crystals.



*Mercury.*—Three preparations of the salt were made each finally involving the reduction, in a wet way, to the metal, a reaction which has proved sufficient in itself to give mercury of considerable purity. In the mercuric chloride of the laboratory, arsenic was the chief heavy metal present and this fact precluded the purification by sublimation before removal of the arsenic.

*Sample 1.*—A concentrated solution of mercurous nitrate on standing in the laboratory several years over mercury, had deposited some crystals which were perhaps purer than the supernatant solution. The crystals, washed and dried, were dissolved by the aid of dilute redistilled nitric acid and subjected to the action of redistilled hydrochloric acid, after much dilution. The mercurous chloride was thoroughly washed and treated with redistilled ammonia. After decantation and further

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[1] That the salt is non-hygroscopic was proven by preparing material in a glass tube and exposing it to air for the first time on the balance pan.

washing with ammonia a 3 per cent. solution of redistilled hydrogen peroxide was added, thus reducing the black precipitate to metallic mercury. The globule was thoroughly shaken with a solution of pure hydrochloric acid, washed with water and dried, the temperature being raised to the boiling point. The surface of the globule was free from foreign matter and lustrous.

*Sample 2.*—Kahlbaum's purest preparation was recrystallized and the crystals thoroughly washed and drained. Into a dilute boiling solution of these crystals, pure sulphur dioxide was introduced, thus precipitating mercurous chloride which was thoroughly washed and then digested with nitric acid. After washing, pure ammonia was added and the excess was removed by decantation. Further addition of sulphur dioxide then reduced a portion of the mercury salts to the element. This was washed thoroughly with water, dried and raised to the boiling point.

*Sample 3.*—Kahlbaum's preparation again formed the starting point and was recrystallized as in Sample 2. After washing and draining, 150 grams of the crystals were dissolved in 3 liters of water and strongly acidified with hydrochloric acid. Hydrogen sulphide was then added until a large precipitate formed. After standing, the clear solution was decanted and hydrogen sulphide was again added, this time to saturation. The precipitate was washed with water and then with ammonia to remove any residual arsenic sulphide, after which the precipitate was washed till free from ammonia. The mercuric sulphide was dissolved in aqua regia and the excess of acid removed by evaporation on the steam bath. Aside from a few easily removed particles of sulphur, the product was entirely soluble in water. The solution having been made alkaline with ammonia, the addition of hydrogen peroxide formed metallic mercury, which was treated as in Sample 2.

*Chlorine.*—The constant-boiling mixture of water and hydrochloric acid was treated with a small quantity of permanganate and boiled to remove traces of bromine and iodine. This solution of acid was dropped on potassium permanganate, Kahlbaum's best preparation, which had been recrystallized, some of it twice. A flask, with dropping funnel sealed in the neck, served for the purpose, the issuing gas passing through a wash bottle of water and then through eight towers.[1] The actual construction resembled that given by Richards and Baxter.[2] No ground joints were used, however, and the gas passed out at the top of the tower which was filled with beads drenched with concentrated sulphuric acid.

## The Reagents.

*Hydrogen Peroxide.*—Merck's 30 per cent. solution was redistilled in an apparatus constructed wholly of glass, the first fraction being rejected. The second and richer fraction was diluted to form a 3 per cent. solution. Portions of this were tested for chlorides in the nephelometer after removal of the peroxide, which was accomplished in some cases by heating in platinum dishes, in others by the action of platinum sponge. The amounts found were practically the same in the several trials, the average showing 0.0002 gram of silver chloride per liter of peroxide, when treated with silver nitrate. As 10 grams of mercuric chloride require only 50 cc. of the peroxide, it is evident that the chlorine introduced from this source is entirely negligible.

*Sodium Hydroxide.*—This was prepared from metallic sodium which had been in possession of the laboratory for many years and which was surprisingly free from chlorine. Nernst's method for the preparation of sodium amalgam had been used but the advantage gained was not commensurate with the effort expended so that the

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[1] These towers were constructed with traps first employed, I believe, by Richards and Parker, *Proc. Am. Acad.*, **32**, 53–73 (1896).

[2] *Proc. Am. Acad.*, **33**, 113–128 (1897).

commercial sodium was employed in all the work. Some of this sodium was redistilled under reduced pressure in hard glass tubes but the resulting product proved no purer and was sometimes even less pure, due to the action of sodium on the glass. The unchanged commercial material, then, proved the most satisfactory. The sticks were carefully trimmed and 3 or 4 grams were melted under pure toluene. The lustrous surface of the globule was washed with pure benzene and immediately converted into sodium hydroxide in an atmosphere charged with water vapor, but free from carbon dioxide. Examination of the hydroxide, when neutralized with nitric acid and treated with silver nitrate, showed that the amount of chlorine varied but little in the several samples, a maximum quantity when converted into silver chloride amounting to only 0.0002 gram of silver chloride per 4 grams of sodium hydroxide. In some samples absolutely no chlorine was found. In addition to chlorine, the sodium contained a very slight trace of iron which, however, does not detract from the value of the reagent.

*Silver.*—Two samples of silver were prepared according to methods of Stas,[1] one from recrystallized silver nitrate by means of formic acid in ammoniacal solution, the other from thoroughly washed precipitated silver chloride by means of invert sugar in the presence of pure sodium hydroxide. The finely divided material thus obtained was fused on charcoal, cleaned, boiled with dilute sulphuric acid and then with water.

*Water.*—The water was twice distilled, the last time from a solution containing a small amount of sulphuric acid and potassium permanganate. A block-tin tube was used as a condenser.

*Nitric Acid.*—A chemically pure preparation was redistilled, using a quartz condenser, and the middle fraction, entirely free from chlorine, was retained.

*Ammonia.*—This was obtained by heating the chemically pure material of commerce and passing the gas into pure water. No chlorine was found present.

*Nitrogen.*—The ordinary laboratory method of passing a mixture of moist ammonia and air over heated copper gauze was employed. The excess of ammonia was absorbed by water and dilute sulphuric acid, the nitrogen then being passed through wash bottles containing a solution of lead oxide in sodium hydroxide to absorb any sulphides originating from rubber connections. The gas then passed into the drying towers constructed wholly of glass tubes, containing beads moistened with concentrated sulphuric acid.

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## NOTE.

*A New Thermoregulator for Use with Gas.*—The large coefficient of expansion of air renders it especially suitable for use in thermoregulators but, as far as we are aware, no regulator in which it is used has been described.

The diagram shown herewith represents such a regulator as applied in practice.[2] The bend of the U-tube *E* and *F* is filled with mercury as shown. Gas enters at *B*. The cylindrical bulb *A* is placed in the incubator or oven, which is to be kept at constant temperature, while the stopcock *D* is left partly open. As the temperature increases the air in

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[1] *Oeuvres*, **3**, 13.

[2] Dr. W. A. Noyes informs me that he has used an apparatus identical in principle with the above for several years but has never described it.