

large, cool and dilute to 250 cc. and use aliquot portions of 50 cc. To this solution add from 5–10 g. of 20 mesh zinc. The tin will come out as metal. Pour off the green solutions when the precipitation of the tin is complete (this takes about ten minutes), and wash the cake of tin several times with hot water. Unite the filtrate and wash water and heat to 60°. Pass through the reductor in the order named, 50 cc. dilute HCl,¹ the solution containing the molybdenum, 150 cc. 2.5% (vol. conc. HCl), and finally 150 cc. hot distilled water. These pass into the flask of the reductor, which has been previously charged with 20 cc. 10% ferric ammonium sulfate and 20 cc. of the "titrating solution." This solution is next titrated with approximately 0.1 *N* potassium permanganate and the amount required calculated to MoO₃.

If it is desired to determine the amount of tungsten in a sodium tungstate solution, add to that solution a quantity of sodium chloride solution, and proceed as when molybdenum is present.

A fairly accurate separation of tungsten and molybdenum may be effected when they are present as ammonium salts, but the method is not to be highly recommended.

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[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD COLLEGE.]

THE MOLECULAR WEIGHT OF SODIUM CARBONATE AND THE ATOMIC WEIGHT OF CARBON REFERRED TO SILVER AND BROMINE.

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Investigations concerning radioactivity have increased rather than diminished the interest in atomic weights. The possibility indicated by recent research that variations in these figures may exist in radioactive elements² stimulates further research in all directions concerning these quantities; for such variations cannot be due to chance, but must have fundamental cause. To be sure, no valid evidence of variation in any value except that for lead has as yet been found; but whether or not the atomic weights vary in a few cases, they still probably remain the most fundamental figures which come within our scientific ken. Therefore, no amount of trouble is too great to secure complete and satisfactory knowledge of them.

¹ Containing 2.5% by volume of the strong acid.

² Richards and Lambert, *THIS JOURNAL*, **36**, 1329 (1914); also *Z. anorg. Chem.*, **88**, 429 (1914), and *Science* (June 5, 1914), p. 831. This conclusion has been supported also by Soddy (*Proc. Chem. Soc.*, **30**, 134 (1914)), by Maurice Curie (*Compt. rend.*, **158**, 1676 (1914)), and by Hönigschmid and Mlle. S. Horovitz (*Ibid.*, p. 1786); also *Z. Electrochem.*, **20**, 319 (1914).

It is well recognized by everyone conversant with this matter that as many different methods as possible for determining each atomic weight should be employed. F. W. Clarke has often emphasized this point. The difficulty in carrying out this recommendation is that so few substances lend themselves to accurate analysis. Crystalline precipitates always carry down some of the mother liquor from which they were prepared, and hence many usual analytical methods are not permissible, when great accuracy is required. For this reason, and so as to get consistent and comparable results with different metals, the analysis of the chlorides and bromides has been one of the chief methods employed at Harvard—because the spongy nature of the silver halides makes it possible to wash them with unusual thoroughness. But some means of verifying these results by comparison with an entirely different standard would be highly welcome. For this purpose a new process, involving cross-reference, has recently been carried out in the Wolcott Gibbs Memorial Laboratory; and the present paper describes this new method of attack.

The plan was simply this: the purest sodium carbonate was to be weighed with scrupulous care, dissolved in water, and exactly neutralized with hydrobromic acid. The amount of silver necessary to precipitate this hydrobromic acid was then to be determined by the usual process. In this way the chemical equivalence between the weights of sodium carbonate and silver could be simply determined, and the silver halide standard referred directly to an entirely new substance, namely, sodium carbonate. The accuracy of the process turned, of course, upon obvious criteria: first, the purity of the sodium carbonate and hydrobromic acid; secondly, the complete and exact neutralization without loss of material; and thirdly, the purity of the silver. The sodium carbonate, silver and silver bromide alone were weighed; but the hydrobromic acid obviously had to be prepared in a state free from every trace of other acids as well as from bases. As will be seen, the outcome was very satisfactory,

Preparation of Materials.

In an investigation of this kind the details of experimentation are of the utmost importance, therefore the necessary minutiae are given below.

Three different specimens of sodium carbonate were prepared: the first simply by many recrystallizations from water in platinum vessels; the second from recrystallized hydroxide made by the reaction of sodium bromide on silver oxide; and the third from sodium amalgam electrolytically produced from hydroxide resulting from the reaction of barium hydroxide on sodium sulfate. In making the first sample 3 kg. of "C. P." sodium carbonate were dissolved in pure water, filtered while cold through hardened filter paper, and at first recrystallized four times from pure water in porcelain dishes with centrifugal washing and draining.

The solution of the crystals was again filtered, as before, through washed filter paper, and recrystallized five times in platinum vessels, again with centrifugal draining and washing. The solution of this ninth crop of crystals was finally filtered through the platinum mat of a carefully prepared Gooch-Munroe crucible, and recrystallized, making ten crystallizations in all. The last crop of crystals, contained in a platinum dish, was dehydrated in a vacuum desiccator over fused sodium hydroxide, and was called Sample A.

As briefly suggested above, the second sample B was prepared in a very different way. Sodium hydroxide (previously twice recrystallized) was added in excess to twice recrystallized silver nitrate. The washed precipitate of oxide was treated with a solution of sodium bromide which had been five times recrystallized as hydrate. The resulting sodium hydroxide solution was then once recrystallized from concentrated solution by strong cooling, and was transformed into sodium carbonate by passing pure carbon dioxide into the solution through an inverted platinum funnel. The solution was filtered through a platinum mat, and the salt was thrice crystallized. All these operations were carried out in platinum, except the crystallization of sodium hydroxide, which was carried out in silver.

For the sake of especial care, the preparation of the third sample, C, involved yet different processes. Sodium sulfate was added in slight excess to barium hydroxide, each having been previously four times recrystallized. The solution was decanted from the precipitate through a platinum filter and the resulting sodium hydroxide crystallized by cooling. A solution of this sodium hydroxide was electrolyzed in an amalgamated iron dish. The solid amalgam, after thorough washing, was partly decomposed by water, and the solution was evaporated to crystallization. The pure caustic alkali was transformed into carbonate as in the case of Sample 2, and the salt thus obtained was thrice recrystallized. All operations, except the electrolysis in the iron dish, were carried out in platinum or silver.

The hydrobromic acid was prepared from an especially pure sample of potassium bromate, which we owed to the kindness of Edward Mallinckrodt, Jr., of St. Louis. Three kilograms of this material (which showed only a trace of chlorine and no iodine) were three times recrystallized in porcelain; even the first crystals gave no test for chloride. Portions of the very pure product were decomposed to bromide by heating in platinum, and the bromide was fused. Proper quantities of bromate, bromide and very pure redistilled diluted sulfuric acid were gently heated in a glass-stoppered distilling flask. The pure bromine which distilled off was twice redistilled from the similar potassium bromide, and passed with hydrogen over hot platinized asbestos. The hydrobromic acid thus

formed was dissolved in pure water, concentrated, and three times redistilled through a quartz condenser.

Three samples of silver were used. The first was made from pure silver nitrate by a well tested method.¹ The salt, five times recrystallized, was reduced with ammonium formate prepared from redistilled ammonia and formic acid. The metal was thoroughly washed, dried and fused in hydrogen on a boat of pure lime made from six times recrystallized calcium nitrate. The buttons were then etched with nitric acid, washed with ammonia and much water, and dried at 400° in a vacuum.

The second sample was prepared with twice as much care, but appeared to be no purer. Silver nitrate, ten times recrystallized, was reduced in a silver dish with ammonium formate made by passing ammonia from redistilled ammonium hydroxide contained in a platinum retort into formic acid, twice redistilled in quartz, contained in a gold flask. The silver powder was washed many times with purest water, then fused and dried as in Sample 1.

A third sample of silver, prepared by Dr. H. H. Willard in our research on lithium perchlorate, was used in an analyses Nos. 4 and 5.²

The quantitative identity of these three samples is evidence that all were as pure as possible.

In a research of this kind, involving exact neutralization, especial pains must be taken, not only with the solid substances concerned, but also especially with the water and gases which are employed. Water was thrice distilled, alkaline permanganate and a few drops of sulfuric acid being used in successive distillations, as usual. A thoroughly washed condenser of block tin was employed. Especial care was taken to exclude the products of combustion of the burners from the product. For much of the work, where carbon dioxide must be rigorously excluded, the water from the final distillation was condensed in such a way that it was collected cold in a stream of air wholly freed from carbon dioxide. The air used for this purpose, and in other cases where carbon dioxide must be excluded, was drawn direct from the vent supplying the filtered air to the laboratory before its entry into the room, and was washed and driven by a water blast through a long tube of copper oxide and through Emmerling towers containing, in succession, solution of copper sulfate, potassium permanganate dissolved in dilute very pure phosphoric acid, pure permanganate made alkaline by potassium hydroxide which had been fused to drive out volatile substance, and concentrated potassium hydroxide; then over solid, fused potassium hydroxide, and, finally, where it was

¹ Richards and Wells, Carnegie Inst. of Washington, Publication No. 28, 19 (1905); THIS JOURNAL, 27, 475 (1905); *Z. anorg. Chem.*, 46, 74 (1905).

² Richards and Willard, Carnegie Inst. of Washington, Publication No 125, 16 (1910), Sample A.

necessary to have especial purity and absence of moisture, over fused potassium hydroxide and resublimed phosphorus pentoxide, and over hot copper oxide, being filtered at last through a porous cup to retain dust particles.¹ The apparatus was, of course, constructed entirely of glass with fused or ground joints.

Carbon dioxide was generated in an Ostwald apparatus by the action of diluted, redistilled hydrochloric acid on selected pieces of pure marble. The gas was first passed through three towers containing sodium bicarbonate solution, and afterwards through three towers of boiled, concentrated sulfuric acid to which a trace of potassium dichromate had been added, and, finally, through a long U-tube of resublimed phosphorus pentoxide.

In one preliminary experiment nitrogen was used. This was prepared by the Wanklyn method of passing ammonia and air over heated copper. The apparatus for this purpose was kindly loaned us by Professor Baxter and Dr. C. J. Moore. Glass stopcocks were lubricated with a very small amount of a mixture of viscous paraffines containing a little pure melted rubber, as suggested by Ramsay. They were so arranged that either pure air or carbon dioxide could be passed, separately or mixed, through the familiar Harvard bottling apparatus;² and also when needed through vessels in which the solution of the sodium carbonate and the evaporation of the bromide were carried out.

Preparation of Sodium Carbonate for Analysis.

The almost anhydrous carbonate, after long drying in a desiccator over fused caustic alkali, was placed in a weighed platinum boat, covered with a piece of platinum foil, and heated gently in a quartz tube attached to the bottling apparatus. A removable mica sleeve wound with a thin ribbon of a commercial high-melting alloy furnished the necessary heat, with the help of a moderate electric current. After completing the dehydration, the platinum foil was removed and the boat and contents were heated for several hours at a gradually increasing temperature until the salt just fused, pure carbon dioxide being passed through the tube. As soon as fusion had taken place, the application of heat ceased and pure air was admitted, gradually decreasing the amount of carbon dioxide until, when the boat was cold, pure air was passing over it. The weight obtained this way was constant after successive trials, which was not the case when the salt was fused in nitrogen or air, a slight gain in weight being usually noted in the latter case. In the presence of air, at about 850°, fused sodium carbonate attacks platinum to a slight extent, especially if the salt is kept fused for a considerable time. Hoping to avoid this difficulty,

¹ Richards and Cox, *THIS JOURNAL*, 36, 819 (1914).

² Richards, Faraday Lect., *J. Chem. Soc.*, 99, 1203 (1911). See Richards and Parker, *Proc. Acad. Arts and Sciences*, 13, 86 (1897).

we used a gold boat in preliminary work, but this steadily gained in weight even after 60 hrs. treatment with nitric acid and prolonged ignition in air. Returning to the platinum boat, we found that in a stream of pure carbon dioxide free from air it was possible, by very gradually increasing the temperature until the salt was just fused, to prevent any significant action on the platinum boat. Thirteen fusions decreased the weight of the boat only 0.27 mg., or 0.02 mg. during each fusion.

There is reason to believe that sodium carbonate thus fused in a stream of pure carbon dioxide is purer than sodium carbonate prepared in any other way. The cooled mass could have contained no excess of carbon dioxide, since the vapor pressure of this gas from the bicarbonate at the temperature employed is enormous; moreover, because the salt came to constant weight on successive fusions, there is no suspicion of abnormal loss of carbon dioxide. Because we have been able to find no record of anyone's having prepared the salt in this way before, these samples were perhaps the purest specimens of it which have ever been made. Our experience shows that sodium carbonate, as ordinarily prepared for quantitative work, is not perfectly dry. Material heated at dull redness for a short time, as usual in most laboratories, was found to lose on fusion sometimes as much as 0.05% of moisture; and even after two hours of such heating the loss was about 0.03%. Material heated for a long time just below the fusion point lost on fusion only about 0.003%. The losses during our experiments ranged between these limits. It is true that for ordinary work such errors are immaterial; but in the most accurate work they become highly important.

The Solution and Quantitative Neutralization of the Sodium Carbonate.

Having been carefully weighed in the weighing bottle containing dry air, into which it was transferred in the bottling apparatus, the sodium carbonate was now dissolved and neutralized in pure, dilute hydrobromic acid. This solution was provided in carefully weighed quantity almost exactly necessary to neutralize about 5 g. of sodium carbonate, the amount usually employed in a determination. Because the method of dealing with this standard acid solution was somewhat unusual, a brief description is fitting.

Specially designed weighing burets containing the desired quantity of acid solution (about 200 cc.) were employed to weigh it. A large amount of the solution had been prepared shortly beforehand, and preserved in a bottle of resistant glass, from which it could be removed by a paraffin-coated and -lined glass syphon. Air was admitted to the bottle after passing through a U-tube containing a solution of the same nature and concentration as that in the bottle. When the buret was to be filled, after thorough agitation of the solution (which was at room temperature) a portion was drawn off sufficient to wash the interior of the syphon—

the last of this being added to the U-tube, replacing the solution which had previously been in the tube. Small portions of the acid solution were now run into the dry weighing buret, which was closed and gently shaken until it was thoroughly rinsed and filled with the vapor of the solution. The buret was then filled, with the syphon-tip inserted far into its interior, to avoid evaporation. Subsequently, the buret was carefully wiped with a slightly damp, perfectly clean linen cloth, and thereafter touched only with platinum forceps or linen cloth. After standing with the upper cock nearly closed in the balance case for one hour, the weight was taken by substitution, using a precisely similar, partly filled companion buret as substituting tare. Before filling a buret, the bottle containing the acid solution had been placed for some hours near the balance so that long waiting was unnecessary.

The required amount of solution was next removed from the buret and placed in the bowl of a very large platinum retort, the graduations upon the buret allowing one to determine to within 0.1 g. when the required weight had been removed. The buret was then returned to the balance case and in not less than an hour its weight was determined as before. It was found that three such complete manipulations could be carried out in succession; each consisting of weighing after one hour in the balance case, removing buret to the titration-room, replacing and removing the tip from the buret outlet, and reweighing, without any change in weight exceeding a milligram. As a rule, of course, in actual analysis, only one such operation was carried out.

As will be detailed, the concentration of this solution was exactly determined by reference to silver—the solution being weighed out for this purpose in successive portions just as for the neutralization; but, in order to not interrupt the narrative, the discussion of the neutralization will be continued.

As already stated, the exactly weighed acid solution was placed for the neutralization of the sodium carbonate into the body of a large platinum retort, very kindly given by Professor J. M. Crafts; and the weighed boat with the fused carbonate was carefully lowered into the solution. The tightly fitting cover was then placed on the retort, with the condenser tube attached; and the whole was set aside for some hours, usually overnight. The condenser tube was packed with scraps of platinum foil to serve as baffles, and the lower end placed into a gold flask which served to collect any solution projected in minute drops during the evolution of gas. When the fused salt was completely dissolved, the retort with condenser attached was very gradually warmed during several hours until at last boiling commenced. The supply of heat was then decreased and the condenser tube and gold flask were removed and rinsed into the retort, which was now covered, placed in an electric oven or bath, and warmed

while very pure air was passed in through a hard glass tube bent to deliver the air just above the surface of the liquid. During the evaporation thus conducted, the temperature of the oven was maintained at a point slightly above 100° , actual ebullition being prevented by the cooling effect of rapid vaporization. When the volume of the solution had been reduced to about one-half, the heating was discontinued, and the retort was cooled in a current of pure air. Methyl red was added to the cool liquid as indicator, showing in general an alkaline reaction; this outcome had been arranged beforehand in weighing the acid, in order to prevent possible loss of bromine during the evaporation.

The next step was the completion of the titration, using a very dilute solution (approximately $0.01 N$) of hydrobromic acid, which had been prepared by diluting the more concentrated acid and standardized by titration against dilute carbonate-free sodium hydroxide and by precipitating with silver nitrate. This dilute standard solution was weighed in a smaller set of weighing burets, and added drop by drop to the solution in the retort. For this purpose, the platinum cover of the retort had been removed and a glass plate having two small openings put in its place; through one of these openings the tube admitting a rapid stream of pure air was passed, while the other served to admit the tip of the weighing buret. When a distinct acid reaction was attained, the buret was removed; and if the amount added was comparatively large the buret was weighed and emptied. If, however, the amount added was small, the buret was placed in the balance case and removed for a second addition after the carbonic acid formed by the previous addition had been expelled. As with the stronger solution, we found that it was possible, using care not to touch the buret with the hands and allowing but little change in the temperature of the room, to work with the buret for several hours without producing a significant change in the weight.

The expelling of the carbon dioxide produced by the addition of dilute acid was usually complete within one-half hour at a temperature just below boiling, with a rapid current of pure air passing over the solution. In no case was there a change in the depth of indicator color after the solution had been heated for one hour. Consequently, this was the usual time of heating the retort, after the addition of a portion of dilute acid. Experience taught that a certain depth of pink was required in order that the solution would be left neutral when the excess of carbonic acid had been expelled, and this helped materially to shorten the tedious process of reaching the end point by this method. In short, this method of adding successive small portions of very dilute hydrobromic acid was continued until an end point slightly on the acid side of exact neutrality was reached, which remained unchanged when cold, after at least an hour's heating, frequently with slight boiling during the last stage. It was thought

for a time in the preliminary work that the end point might be determined in a hot solution; but the action of the indicator is less reliable at the higher temperature under the conditions concerned; and the difficulty of manipulating the hot solution, especially because of the obstruction of clear vision by the drops condensed on the glass plate, caused us to cool the liquid in order to attain the accuracy demanded.

In two titrations an equivalent amount of *p*-nitrophenol was added to the methyl red. This mixture is very well adapted for the titration of all strong acids and bases, working from either acid or alkaline solution. With a concentration of ionized hydrogen of 10^{-8} , the mixture shows a distinct yellow color, at 10^{-7} the color is a very faint greenish yellow, almost colorless, while at 10^{-6} the pink of methyl red appears. In hot solution it is less reliable than methyl red alone, tending to make the solution appear too alkaline; but it resumes its normal reaction when cooled to room temperature. It cannot be depended upon in solutions containing more than 15 or 20% of dissolved substance, especially in sulfate solutions. The weight of the indicator substance required is very small; from 0.05 to 0.08 mg. of methyl red sufficing for 100 cc. solution;—and the amount transformed, when a distinct pink is noticed, is not more than one-half this, as determined by Noyes's method of superimposing solutions. Hence, considering the high molecular weight of the indicator, it is certain that no weighable amount of acid or base was required to combine with the indicator. Confirming this conclusion, it was found that one drop of 0.01 *N* solution of acid containing 0.03 mg. of bromine would change the reaction from distinct alkaline to distinct acid. For yellow or red indicators the eye is much more sensitive to a small change in color when the solution is placed in the bottom of a platinum vessel than when it is contained in glass or porcelain. The methyl red, of course, gives the final evidence as to the true neutral point, but for rapid work the mixture of indicators can be used to advantage, since it gives more warning of approach to the end point from either acid or basic side.

After the sodium carbonate had been neutralized with hydrobromic acid, the sodium bromide solution resulting was quantitatively transferred to a glass-stoppered precipitating flask, and diluted; and the calculated quantity of silver, having been dissolved with great precaution in nitric acid, was added. The exact end point of the precipitation was determined in the usual nephelometric manner.

The above-described method of reaching the end point by gradual addition of very dilute hydrobromic acid was employed in five of the six determinations. In the third experiment (No. 11 in the second table below) a very slight excess of hydrobromic acid was added during the first operation. This excess was titrated very carefully with dilute, carbonate-free sodium hydroxide solution which had been standardized

against both dilute and concentrated hydrobromic acid solutions. The fact that in this experiment essentially the same quantity of hydrobromic acid was used as in the others, suggests that the danger of loss of bromine during evaporation from an acidifying liquid is very slight.

Besides thus finding the weight of silver needed to precipitate the ionized bromine balancing the ionized sodium from the sodium carbonate, we made separate determinations of the amount of silver needed to precipitate given weights of the same solution of hydrobromic acid, and also in four cases weighed the silver bromide which resulted. By giving the exact weights of silver and of bromine corresponding to a given weight of the hydrobromic acid solution, these determinations made it possible to compute (in a way entirely independent of the other determinations) the amount of silver and silver bromide corresponding to given weights of the solution used for neutralizing various portions of sodium carbonate—it being assumed, of course, that the neutralization was correctly performed. The agreement of these results with the others showed that, at least as far as the determination of the bromine was concerned, the earlier results were trustworthy. They showed, moreover, that no significant amount of hydrobromic acid was lost, on the average, during neutralization and evaporation, for the silver analyses were made in one case after evaporation and in the other case without any such treatment. Several of these analyses were made in the midst of the earlier series; indeed, the intention was to make them alternately.

The question having arisen as to the possible action of the dilute hydrobromic acid on the resistant bottle in which it was kept, experiments were instituted on purpose to test this point; for such action would have had a highly deleterious effect upon the result, introducing sodium bromide from a foreign source. The final distillation of the acid had occurred on March 20, 1913, and not long afterwards the solution was made up in its final form. All the analyses were concluded before the 10th of May, an interval of less than seven weeks. Six months after that, the acid having remained in the same bottle, two portions of 60 g. each were separately evaporated in a quartz dish, and the barely visible trace of residue was dissolved in water, transferred to a small platinum crucible, dried and weighed. In each case the residue weighed only 0.1 mg., and the solution in water was found in the nephelometer to contain an amount of soluble bromide equivalent to 0.04 mg. sodium bromide. The amount of sodium bromide formed from the flask during the first six weeks in question must, therefore, have amounted to less than 0.01 mg., a negligible quantity. It should be stated that this flask had previously been used for dilute hydrobromic acid for several years; probably a new bottle would not have yielded so satisfactory a result.

Incidentally, in order to reduce the results to the vacuum standard,

the specific gravity of sodium carbonate was determined by weighing it in a pycnometer, under toluene which had been found in two closely agreeing experiments to have a density at 20° of 0.8661 referred to water at 4°. Thus 9.7256 g. and 5.62691 g. of salt were found to displace 3.32581 g. and 1.92439 g. of toluene, respectively, at the same temperature. The two values for the density of the salt were, therefore, 2.5327 and 2.5325, respectively. This value is distinctly higher than the results of other experimenters. For example, Schroeder found values ranging between 2.43 and 2.51.¹ The difference is doubtless due to the more compact condition of our fused material, and the absence of air held within the pores of the substance.

The first of the tables below reports the weights of silver and silver bromide obtained from given weights of the standard hydrobromic acid solution. All the analyses are recorded, excepting two which met with accidents and could not be brought to completion.

TABLE I.—ANALYSES OF HYDROBROMIC ACID SOLUTION.

| No. of expt. | Sample of silver. | Wt. HBr sol. (in vac.). | Wt. Ag (in vac.). | Wt. AgBr (in vac.). | Wt. Ag per 100.000 g. solution. | Wt. AgBr per 100.000 g. solution. |
|--------------|-------------------|-------------------------|-------------------|---------------------|---------------------------------|-----------------------------------|
| 1..... | | 205.192 | | 17.05459 | ... | 8.3115 |
| 2..... | | 199.157 | | 16.55319 | ... | 8.3116 |
| 3..... | I | 212.457 | 10.14346 | 17.65772 | 4.7743 | 8.3112 |
| 4..... | II | 211.335 | 10.08975 | 17.56405 | 4.7742 | 8.3111 |
| 6..... | III | 201.663 | 9.62812 | | 4.7744 | ... |
| 8..... | II | 198.356 | 9.47115 | | 4.7748 | ... |
| Average..... | | | | | 4.77442 | 8.31135 |

Thus 100.000 g. of silver bromide are found (from the two averages) to correspond to 57.4446 g. of silver. Baxter² found 57.4453 g.—very nearly the same figure. If we assume Baxter's value (because determined in a simpler way) to be correct, our average, 4.77442 g. of silver, corresponds to 8.31125 g. of silver bromide, or very nearly the result 8.31135 found directly, as given above. The average between these averages, or 8.31130 g. of silver bromide, must represent very nearly the true amount of precipitated halide to be obtained from 100.000 g. of the hydrobromic acid solution. This weight of silver bromide corresponds to 3.5815 g. of hydrobromic acid gas—a figure which gives the percentage composition of the acid, enabling us to know the density of the solution and apply accurately the large correction to the vacuum standard in weighing.

Evidently the concentration of the hydrobromic acid remained essentially constant during the time concerned.

The second table, below, records the weights of hydrobromic acid solution taken for the neutralization of the several samples of sodium car-

¹ Landolt-Börnstein, p. 180 (1912).

² *Proc. Am. Acad.*, 42, 210 (1906).

bonate, the weights of these samples, the weights of the salt corresponding to 100.000 g. of acid solution, and finally the molecular weight of sodium carbonate and the atomic weight of carbon computed from these results (with the help of the weight of silver bromide corresponding to the hydrobromic acid as computed from Table I) if silver is 107.88, bromine 79.916, and sodium 22.995. Incidentally, the total weight of the dilute acid would have been capable of precipitating $1254.946 \times 0.083113 = 104.3023$ g. of silver bromide, hence we may write the proportion:— $104.3023 : 29.43501 = 2 \times 187.796 : 105.995 = \text{Na}_2\text{CO}_3$.

TABLE II.—MOLECULAR WEIGHT OF SODIUM CARBONATE, FIRST METHOD.

| No. of expt. | Wt. of HBr sol. (in vac.). | Wt. of Na_2CO_3 (in vac.). | Wt. of Na_2CO_3 per 100.000 g. solution. | Calc. mol. wt. Na_2CO_3 (if AgBr = 187.796). | Calc. at. wt. carbon (if Na = 22.995). |
|--------------|----------------------------|--|--|--|--|
| 9..... | 202.744 | 4.75555 | 2.34559 | 105.998 | 12.008 |
| 10..... | 204.673 | 4.80081 | 2.34560 | 105.999 | 12.009 |
| 11..... | 208.457 | 4.88936 | 2.34550 | 105.994 | 12.004 |
| 12..... | 240.119 | 5.63157 | 2.34533 | 105.987 | 11.997 |
| 13..... | 191.646 | 4.49516 | 2.34555 | 105.996 | 12.006 |
| 14..... | 207.307 | 4.86256 | 2.34559 | 105.998 | 12.008 |
| Sum, | 1254.946 | 29.43501 | Av., 2.34553 | 105.995 | 12.005 |

The average value for carbon is seen to be 12.005. Considering the circumstances, the agreement of the individual results is as good as could be expected. Before discussing the outcome, another series of more directly obtainable data (namely, the weights of silver actually needed for the precipitation of the exactly neutralized sodium bromide made from these specimens of sodium carbonate) will be recorded. In Table III these several weights of silver are entered in the fifth column (the quality of the silver being indicated by the numerals in the third, which correspond to the various samples already described). The next to the last column, again, contains the computed molecular weight of sodium carbonate, and the last column the atomic weight of carbon, calculated on the same basis as the values recorded in Table II.

TABLE III.—MOLECULAR WEIGHT OF SODIUM CARBONATE, SECOND METHOD. BY MORE DIRECT REFERENCE TO SILVER.

| No. of expt. | Sample of Na_2CO_3 . | Sample Ag. | Wt. of Na_2CO_3 (in vac.). | Wt. of Ag (in vac.). | Mol. wt. Na_2CO_3 if Ag = 107.88. | At. wt. carbon if Na = 22.995. |
|--------------|--------------------------------------|------------|--|----------------------|---|--------------------------------|
| 15..... | (A) | I | 4.75555 | 9.68023 | 105.995 | 12.005 |
| 16..... | (A) | II | 4.80081 | 9.77222 | 105.997 | 12.007 |
| 17..... | (B) | II | 4.88936 | 9.95301 | 105.991 | 12.001 |
| 18..... | (B) | III | 5.63157 | 11.46316 | 105.998 | 12.008 |
| 19..... | (C) | III | 4.49516 | 9.15003 | 105.997 | 12.007 |
| 20..... | (C) | II | 4.86256 | 9.89811 | 105.994 | 12.004 |
| Sum, | | | 29.43501 | 59.91676 | Av., 105.995 | 12.005 |

In brief, it appears that the atomic weight of carbon calculated from the weight of hydrobromic acid taken is exactly identical with that found from the directly determined weight of silver needed to precipitate the acid required for neutralizing the carbonate, each being 12.005 on the basis given, if silver equals 107.88. On the other hand, if $Ag = 107.871$ (a contingency not impossible), carbon becomes exactly 12.000. The probable error of the average of the entire series of twelve values, if each is given equal weight, is less than 0.001 in the atomic weight of carbon. This is less than 0.003% in the weight of the sodium carbonate, or less than 0.2 mg. in the actual weighing of this salt. The results then are about of the order of accuracy of much of the modern careful work on atomic weights.

The final limits for carbon, *viz.*, 12.000 to 12.005, according to the value for silver chosen, are near that found for carbon in other ways. The range is indeed, as small as the limit of accuracy of the usually accepted data concerning either carbon or silver. That in this entirely different way the old value for carbon should be verified is a highly comforting and reassuring circumstance. It inspires confidence in the accuracy of all the processes concerned, both in the new work on halogen compounds and the older work on carbon; because the single method may be always open to the suspicion that a small constant source of error may have been inadvertently overlooked, the value of such confirmatory evidence is great.

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Summary.

A new method of determining the molecular weight of sodium carbonate, and therefore, the atomic weight of carbon, is described, depending upon the neutralization of pure, fused, weighed sodium carbonate by hydrobromic acid, and the precipitation of the bromine both in the resulting sodium bromide and other portions of original solution by means of pure silver. It was found that 29.43501 g. of sodium carbonate were equivalent to 59.91676 g. of silver, and also to a weight of dilute hydrobromic acid which had been found in other tests to be capable of precipitating 104.3023 g. of silver bromide. From these results, if silver equals 107.88, sodium carbonate becomes 105.995 and carbon 12.005, and if silver equals 108.87 and sodium 22.993, carbon becomes 12.000. These limits in both cases are about the possible range of accuracy of the earlier determinations by various methods. Hence the present work, by connecting the various ratios in a new way, shows the consistency of a great variety of earlier work.