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

THE MOLECULAR WEIGHT OF SODIUM SULFATE AND THE ATOMIC WEIGHT OF SULFUR.

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The preparation and neutralization of pure sodium carbonate, for which the way had been cleared by the work described in the foregoing paper, provides a standard of reference for many other precise determinations. The present paper discusses briefly a series of determinations of the ratio between sodium carbonate thus prepared and sodium sulfate made from it by exact neutralization with sulfuric acid. This comparison had already been attempted long ago by one of the authors.[1] The old determinations were, however, made only as a side issue in the course of an extensive study of the atomic weight of copper; they showed a rather large range of error, and were made with sodium carbonate which was then known to contain traces of silica;[2] moreover, our recent work on the fusion of sodium carbonate showed that this older specimen, merely dried at a dull red heat, must have contained traces of water also. Therefore, it seemed well worth while to repeat the experiments with modern precision.

The program here was simpler than that involved in the immediately preceding research on carbon. The fused sodium carbonate was carefully weighed, and treated in the platinum retort with a very slight excess of pure sulfuric acid; the solution was then freed from carbon dioxide and evaporated quantitatively in a quartz flask without boiling, but with the help of a current of air; and the remaining salt was fused and weighed.

Preparation of Materials.

Most of the materials were prepared just as before, the same three samples of sodium carbonate being employed. The sulfuric acid was made from the purest acid of commerce (which contained only minute traces of impurity) by three successive distillations in a non-tubulated glass retort over a ring burner. Only the middle portions of each distillate were used. Among other substances sought in this acid was selenium, which was tested for in a 20 cc. portion of the original substance by dilution with twice its volume of water, treatment with half its volume of concentrated hydrochloric acid after cooling and then boiling until the mixture occupied about 35 cc. No free chlorine was detected during this process, and the solution upon treatment with sulfur dioxide showed no red coloration. This test is supposed to show 0.003% of selenium; therefore, presumably, this element was absent. The quantitative outcome to be given later certainly indicates that no element with a greater atomic weight than sulfur was present, confirming the qualitative test.

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[1] *Proc. Am. Acad.*, **26**, 268 (1891); *Z. anorg. Chem.*, **1**, 180 (1892).

[2] *Ibid.*, 247 and 157, respectively.

The pure redistilled acid was diluted with pure water to a convenient standard concentration, suited to the capacity of the weighing buret and the amount of carbonate to be neutralized.

The preliminary standardization of the standard solution of acid was carried out as follows, much more simply than in the final experiments. This simple preliminary procedure is within the scope of the apparatus in any laboratory, and may be useful to those wishing to standardize an acid solution. A quantity of air-dehydrated, thrice recrystallized sodium carbonate was placed in a weighed platinum crucible. This was heated on a pipe stem triangle while dry carbon dioxide was passed in through a Rose crucible lid, the usual porcelain delivery tube having been replaced by a slightly longer, hard-glass tube. After having been kept at a temperature below fusion for some time, the salt was carefully fused and kept in a liquid condition for a few minutes. It was then cooled in a current of carbon dioxide and weighed again. The crucible and contents were placed in a weighed quantity of the standard solution of sulfuric acid known to be insufficient to neutralize all the carbonate, and the liquid was heated nearly to boiling after the addition of the mixed indicator. When the acid had been exhausted, the effervescence naturally ceased, and the solution of the carbonate proceeded very slowly; therefore, it could be easily determined when more acid was needed. Adding acid drop by drop, from time to time, the carbonate was finally dissolved and the solution remained neutral. The process may, of course, be conducted with even less trouble by adding at first a slight excess of acid and titrating back with hydroxide. By this crude method 1 g. of sodium carbonate was found to be equivalent to 41.032 g. of acid solution, while in the more carefully executed titration in the first regular analysis, 1 g. of pure sodium carbonate was found to be equivalent to 41.0280, or a difference of 1 part in 10,000. This is a degree of accuracy far exceeding that possible by the ordinary methods used for the volumetric neutralization of sodium carbonate, which gives rather questionable results in inexperienced hands.[1] The standard acid evidently contained 2.255% of H_2SO_4.

An auxiliary solution, 100 times less concentrated, was next prepared by diluting a weighed amount of the main standard solution with a weighed amount of water. These solutions were kept in resistant glass bottles with paraffin-covered rubber stoppers and paraffin-coated syphon tubes. Air was admitted through large U-tubes filled with beads and with portions of solution removed from time to time from the bottles. That a dilute solution may be preserved without appreciable change in concentration, was shown by the results of the titration of hydrobromic acid against sodium carbonate described in the previous paper.

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[1] The uncertainty due to the indicator alone may amount to as much as 0.5% in the presence of carbonic acid. See A. A. Noyes, THIS JOURNAL, 32, 815 (1910).

The Neutralization and Determination.

The exact titration of accurately weighed amounts of the purest fused carbonate against sulfuric acid was carried out essentially as in the case of the hydrobromic acid. The end point chosen was slightly more on the acid side of exact neutrality, the hydrogen ion concentration being about 10^{-6}, because the excess of acid could be driven off during the subsequent ignition. The non-volatility of sulfuric acid from aqueous solution allowed more variation in the method of reaching the end point than in the earlier case. The quantity of the main sulfuric acid solution required to combine with the observed weight of sodium carbonate was weighed out, and the carbonate was dissolved in the acid in the platinum retort. In determinations 2, 3, and 6 the neutral point was reached by several further very small additions of very dilute acid, as in the earlier case. In Nos. 4 and 5 a slight excess of sulfuric acid was added in the first operation, and the solution was titrated back with standard sodium hydroxide solution from a weighing buret. In No. 1 a very slight excess of acid added was removed by repeated evaporation and ignition of the sodium sulfate to constant weight, followed by thorough fusion in a rapid current of air. These different methods of treatment, by substantially agreeing as to their results, established the fact that the carbon dioxide had been completely expelled from the solution when the end point was reached in the hydrobromic acid analysis described in the preceding paper.

After the solution of sodium sulfate had been rendered neutral or slightly acid, it was concentrated by passing pure air over the solution in the covered platinum retort until the volume indicated that the solution would be slightly more than saturated at room temperature. It was then transferred, while warm, to a small quartz flask in which it was to be evaporated and fused somewhat in the manner employed in a previous research upon silver nitrate.[1] In the present case, however, the flask had the tube for admitting the air fused into the top of the flask, and a side exit tube attached after the fashion of a gas washing bottle. Both tubes were provided with ground quartz stoppers. The flask had a capacity of about 100 cc. and was not too large to weigh accurately. The transference from the retort to this flask was naturally the most delicate part of the work. By placing a curved glass rod within the retort with the curve emerging tangent to the inner edge, but free from the outside portion of the rim, it was possible to pour the solution from the retort along the rod without danger of loss. A small funnel tube drawn out and bent slightly at its extremity guided the stream well down into the inlet tube of the quartz flask, and the transfer was facilitated by clamping the flask in an inclined position. The flask having been filled to within a short distance below the end of

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[1] Richards and Forbes, Carnegie Inst. Wash., Publication **69**, 51 (1907). THIS JOURNAL, **29**, 808 (1907).

the inlet tube, was placed in an electric heater, maintained at a temperature just insufficient to cause ebullition—pure air being passed in through a glass tube ground to fit the quartz inlet tube. The retort cover and condenser were then thoroughly rinsed, and the solution with several wash waters placed in the platinum retort and concentrated to small bulk; then the solution was added to the contents of the quartz flask. Generally, three such series of washings were carried out until it was certain that every weighable trace of salt had been transferred. After the sodium sulfate solution had been completely collected in the quartz flask and dried, the large electric oven (which had completely enclosed the flask) was exchanged for another consisting of a fire-clay tube wound for a higher temperature, and large enough to enclose only the bulb. With this heater a temperature just sufficient to fuse the edges of the mass of sulfate was maintained for several hours, after which the temperature was raised for a short time to the point necessary to fuse the salt (about 875°). A current of pure air was passed through the flask throughout all these steps. It was found that two hours' heating at the lower temperature (about 850°) produced constant weight, and that on fusion only a very small apparent loss in weight appeared, the average in five trial determinations being 0.01 mg. per gram of salt. This absence of a decrease in weight shows that very little water was retained within the porous, brittle solid at this high temperature. The final calculation was, of course, made on the basis of the weight of salt after fusion, and for the purpose of correcting this weight to the vacuum standard, the density of fused sodium sulfate (previously unknown) was determined as follows: 6.07615 and 8.43725 g. of salt (*in vacuo*) displaced 1.9519 and 2.7063 g. (*in vacuo*) of toluene, respectively, the toluene having a density of 0.8661 at 20°. The two determinations yielded as results 2.696 and 2.700 for the density, respectively—or in the mean, 2.698.

The weighing of vessels of quartz or glass as large as the flasks and burets used in this work is accompanied always by some difficulty; but if the vessels are provided with precisely similar counterpoises and if each piece of apparatus is kept in a separate desiccator and each weighed under precisely the same conditions after the same time, good results may be obtained. In this work, of course, the weights were carefully standardized, the counterpoises were made of volume and weight like those of the objects to be weighed, the weighing room was carefully guarded as to constancy of temperature, corrections for changes of pressure were applied when needed, and the customary details necessary for accuracy were faithfully heeded. The keeping of the small tube of radioactive material in the balance case greatly helps in the discharge of electrical charges—always so troublesome with large nonconducting vessels. The ideal laboratory conditions possible in the new laboratory, built especially for this kind of work, greatly facilitated the convenience of the task and accuracy of the outcome. The results of the comparison of sodium carbonate with sodium sulfate are given in Table I. In the first column is given the number of the experiment; in the second, the sample of sodium carbonate; in the third, the weight of sodium carbonate *in vacuo;* in the fourth, the weight of sodium sulfate; in the fifth, the weight of this latter salt corresponding to one gram of sodium carbonate; and in the last column, the atomic weight of sulfur—assuming that the molecular weight of sodium carbonate is 105.995, sodium being 22.995 and carbon 12.005, as found in the preceding investigation. The maximum deviation from the mean is less than 0.003% of the molecular weight of the sodium sulfate, and the "probable error" of the average value is less than 0.001.

TABLE I.—THE RATIO BETWEEN SODIUM CARBONATE AND SODIUM SULFATE.

No. of Expt.	Sample of Na_2CO_3.	Wt. fused Na_2CO_3 (*in vac.*). Grams.	Wt. fused Na_2SO_4 (*in vac.*). Grams.	Wt. of Na_2SO_4 from 1.000,00 g. Na_2CO_3.	At. wt. sulfur.
1	A	5.25191	7.03829	1.34014	32.058
2	B	4.50977	6.04382	1.34016	32.060
3	B	5.04233	6.75737	1.34013	32.057
4	B	3.67340	4.92304	1.34019	32.063
5	C	4.18724	5.61151	1.34015	32.059
6	C	4.55100	6.09916	1.34018	32.062
	Sum,	27.21565	36.47319	Av., 1.340155	32.060

Thus it is clear that 1.00000 part of sodium carbonate is equivalent to 1.340155 parts of sulfate; hence, if silver is taken as 107.88 and sodium carbonate as 105.995, Na_2SO_4 = 142.050 and sulfur is found to be 32.060. This figure is only a little below the value 32.069 found at Harvard eight years ago by a more direct method—the conversion of silver sulfate into the chloride.[1] The substantial agreement of the results affords good evidence that the roundabout comparison adopted in the present research is trustworthy in each of its varied steps, and incidentally confirms the value for carbon given by the foregoing research. Evidently we cannot be far wrong in assuming that the correct value for the atomic weight of sulfur is the mean between the two results—that is to say, 32.065. If silver is taken as 107.871 (instead of 107.88) this value becomes 32.056.

The comparison of the ratio of sodium carbonate to sodium sulfate with the old results of 1891 is not without interest. The average of all the old results[2] made the ratio 1.0000 : 1.3399, while the average of the last three most trustworthy results made it 1.0000 : 1.3400 (instead of the new value 1.340155). The respective errors of the older averages were thus 0.022 and 0.011%. Errors of this sort are precisely of the order

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[1] Richards and Grinnell Jones, *Pub. Carnegie Inst. Washington,* **69**, 69 (1907); THIS JOURNAL, **28**, 826 (1907).

[2] *Loc. cit.*

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

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

Summary.

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

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A REVISION OF THE ATOMIC WEIGHT OF CADMIUM.

[THIRD PAPER.]

THE ELECTROLYTIC DETERMINATION OF CADMIUM IN CADMIUM CHLORIDE.

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

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[1] See page 100 of preceding article.

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