

LXIX.—*The Determination of Atomic Weights by means of the Normal Sulphate.*

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IN certain groups of elements, for example, the cerium group (Ce, La, Di, Yt, Yb, Er, Sm, Sc), the magnesium-group (Cd, Be, Zn, Mg), the lead-group (Pb, Tl), two members of the tin-group (Zr, Th), and also for the non-metals sulphur and fluorine, the use of the sulphate in the determination of atomic weight constitutes either the only available method, or is at least the most trustworthy.

With some seventeen other elements, important determinations of atomic weight have been made by means of this salt, though they do not in these cases occupy so important a position as other methods which have been employed.

No further proof is needed of the necessity of making such estimations as accurate as possible, and much of the confusion which has arisen in certain of these groups may be traced to the difficulties which stand in the way of a precise measurement of the atomic weight, or what is the same thing, of the equivalent weight of the oxide. Two very considerable sources of error indeed preclude the possibility of comparing the results obtained by any two observers, or even by the same observer. The first is that there are undoubtedly differences in the character of the material used, differences which it is desirable to arrive at by definite gravimetric determinations; but in doing this we are confronted by the second obstacle which frustrates such an attempt, since there is without doubt a large variation due to the method by which such gravimetric determinations have to be made. Get rid of this manipulative error as far as possible, so that the results obtained shall be comparable, and then there will be a possibility of approaching the intricate problem of mixed oxides from this side with a fair chance of success. In the usual process by which an oxide is transformed into the normal sulphate, there are several sources which give rise to errors of unknown dimensions.

When 3 or 4 grams of a sulphate are heated for a long period at a temperature below dull redness, and then for a shorter period at dull redness, and these operations are repeated several times, there is the probability (and indeed in some cases, as we shall see, the certainty) that part of the salt is raised to the temperature of decomposition, whilst part again may not reach the temperature at which free sulphuric acid is expelled. We are thus confronted with two sources of error, of opposite sign, and of which we are ignorant of even the relative value.

Such differences vary with the time during which the experiment lasts, so that, granting even perfect manipulation, the results of two experiments would not be comparable, and unless the conditions were in all respects the same they could not be expected to agree with that approach to accuracy which is attainable by other methods. It is further manifest that dealing as we are with sources of error of opposite sign, constant weight is no sufficient guarantee of accuracy, but only an indication that a balance has been struck. This is one example of the circumstances which rob such determinations of their precision. It is true that the use of a double crucible diminishes the error from the causes mentioned, and also brings other errors, arising from the changes to which the crucible is liable, within the narrowest limits. Until, however, two factors are known, there is no certain ground for the presumption that a correct result has been obtained.

These factors are—

(a.) The temperature at which a sulphate gives up all the free sulphuric acid with which it may be mixed.

(b.) The temperature at which a normal sulphate begins to undergo decomposition.

Marignac (*Ann. Chim. Phys.* [6], **1**, 289) has, indeed, rejected the determination of the atomic weight of zinc by the conversion of oxide into sulphate because he was convinced that partial decomposition of the sulphate had taken place during the process of expelling free sulphuric acid. Baubigny (*Compt. rend.*, **97**, 854, *et seq.*), conscious of the same difficulty, attempted to overcome it by using a sulphur-bath for the operation. This, however, though it may answer in certain cases, does not in any sense satisfactorily meet the objections, for, in the first place, the temperature of decomposition of the sulphate may (and in some cases certainly does) fall below  $448^{\circ}$ , and the establishment of constant weight at one given temperature does not necessarily prove anything more than that at that particular temperature, after a certain lapse of time, a state of equilibrium is set up.

Baubigny (*loc. cit.*) heated copper sulphate for three hours in the sulphur-bath, and then found that no further alteration of weight was produced by heating for ten hours at the same temperature.

Similarly he heated zinc sulphate seven hours, and then found that for the next eight hours it remained constant. Before the method of determining the atomic weight from the normal sulphate can be considered satisfactory, therefore, the temperature limits already spoken of must be known. For instance, if it be found that a sulphate gives up free sulphuric acid at  $350^{\circ}$ , and begins to decompose at  $450^{\circ}$ , it will be sufficient in all determinations to heat at some temperature sufficiently removed from these limits (say  $400^{\circ}$ ) till the weight is constant. With these precautions, the determination would be received with as much confidence as determinations by other methods.

To obtain the requisite information, it was necessary to heat the salt containing excess of sulphuric acid at say  $350^{\circ}$  as long as any decrease in weight was observed, then to heat at successive temperatures, each about  $10^{\circ}$  higher, for several hours, weighing after each operation. In this way, a range of temperature was found within which no variation of weight occurred, and ultimately a point was attained at which further decrease of weight took place, indicating that the normal salt was beginning to part with its sulphuric acid. To carry this out, a form of apparatus was necessary by which it should be possible readily to keep the salt at definite and successively increasing temperatures for a considerable time. This consisted essentially of a heating tube (*Chem. News*, **54**, 302) mounted horizontally in a furnace heated by Bunsen burners, the tube inclosing an

air thermometer, and a narrower tube into which the substance to be experimented upon was introduced in a platinum boat. The air thermometer served not only to measure the temperature, but in combination with a column of mercury in a U-tube, also acted as a gas regulator. The lesser tube containing the platinum boat could be readily connected with a pump by which dry air could be aspirated through it in order that the salt should not be exposed in an atmosphere of the acid fumes. It was also easy by use of this accessory to pass the air so aspirated through a solution of barium chloride, and thus ascertain whether decomposition was taking place. With such an apparatus, the temperature could be estimated and easily kept within  $5^{\circ}$ . At the end of each period of heating, the platinum boat was withdrawn, cooled, and weighed, the same conditions being observed throughout the series of experiments. The salts examined were the sulphates of bismuth, sodium, lead, barium, zinc, magnesium, and didymium. The details of experiment will be given more fully in the case of the sulphate of bismuth, and only such facts quoted with regard to the remaining sulphates as may be of special interest; it being understood that the course of investigation was the same in all the cases. In each set of experiments, a determination of the atomic value has been calculated from the results. Though care was taken that the materials used were of sufficient purity for the purpose, the results are not intended to be regarded as having any pretension to the accuracy demanded in a careful estimation of atomic weight; they were intended rather to serve as a means of checking the work as it proceeded. The precautions taken and the amount of substance used in the experiments did not indeed admit of their being considered in any other light.

*The Normal Sulphate of Bismuth,  $\text{Bi}_2(\text{SO}_4)_3$ .*—On heating bismuth trioxide with pure concentrated sulphuric acid, a clear solution is obtained. When this is allowed to cool under such conditions that the sulphuric acid does not take up moisture from the air, a beautifully crystalline product separates.

The sulphuric acid was decanted and used to dissolve a fresh portion of the oxide. The sulphate so obtained was purified by repeated crystallisation from hot sulphuric acid. A portion of the sulphate was placed in a platinum boat and introduced into the heating tube, and as in this experiment the object was to ascertain the temperature limits spoken of above, it was advisable not to take too large a quantity for this experiment. The results were as follow :—

Bismuth sulphate heated at 340° weighed 0.7253 gram.				
"	"	3 hrs. longer at 345°	0.7223	gram.
"	"	3	"	345 0.7223 "
"	"	3	"	365 0.7222 "
"	"	5	"	386 0.7223 "
"	"	5	"	405 0.7224 "
"	"	9	"	435 0.7148 "

Thus the salt up to 405° remained quite constant within the error of experiment, but at 435° it lost 0.0076 gram in the course of nine hours. At 345°, therefore, normal sulphate of bismuth gives up the excess of free sulphuric acid, and between 405° and 435° decomposition of the salt commences.

When 0.5932 of the sulphate was ignited there remained 0.3891 oxide; this result gave as the atomic weight of bismuth 204.44, a value which was manifestly too low. Although no very accurate result could be anticipated from so small a quantity of the substance, the difference was greater than might be expected on this ground. It was found, in point of fact, that when the oxide was ignited in the blowpipe a loss occurred through volatilisation, and in the course of heating this amounted to several milligrams. On the other hand, if the substance was kept below the point of fusion, it retained sulphuric acid; thus 2.1755 grams of the sulphate exposed to the flame of a good Bunsen burner for 40 hours lost weight during the whole time, but even at the end of this time, when the variation was less than a milligram after three hours' heating, there remained still 0.0318 gram of  $\text{SO}_3$ . The sulphuric acid, indeed, was got rid of a little above the point of fusion, but loss of oxide through volatilisation ensued if the temperature was kept sufficiently high to ensure the complete decomposition of the sulphate. Deville has indeed noticed that zinc oxide dissociates and loses weight at high temperatures, and Cooke, in his determination of the atomic weight of antimony, records that silver is volatilised, even below its melting point.

The volatility of oxide of bismuth and the loss likely to accrue in consequence, has, as far as I know, not been noticed, and hence those determinations in which it has been overlooked cannot be received with confidence.

Löwe (*Zeit. anal. Chem.*, **22**, 495) for instance estimated the atomic weight by conversion of the metal into the oxide, fusing the oxide in a platinum vessel. Although, therefore, the direct conversion of sulphate into oxide is desirable from its simplicity, it cannot be used in such cases, and the relation of sulphate to oxide must be ascertained by precipitation.

A second and larger portion was now taken, and heated with the following results:—

After 8 hours	at 360° weighed	2.2189 grams.
„ 3 „ longer	„ 376 „	2.2186 „
„ 2 „ „	„ 405 „	2.2185 „
„ 4 „ „	„ 418 „	2.2165 „

The point of decomposition is in this case more nearly approximated, and falls therefore between 405° and 418°, and it was not considered necessary to attempt to fix it with any greater degree of precision. We may take it that sulphate of bismuth may be safely heated as high as 405°, beyond this there is risk of decomposition. A determination of sulphuric acid gave for 2.2155 grams of the sulphate 1.4615 grams of oxide, and the atomic weight of bismuth calculated from these results is 208.33. A third series of experiments was made under like conditions, the respective weights of sulphate and oxide being 1.5635 grams and 1.0267 grams, giving an atomic weight of 208.43.

The sulphate retains its crystalline character even after heating, and does not very readily take up moisture from the air, indeed 1.5566 gram exposed for a quarter of an hour increased only half a milligram in weight. All the weighings were made, however, with the platinum boat enclosed within a tube, so as to avoid any error arising from this cause, and correction was made for displacement of air, with allowance for variation of temperature and pressure.

*Zinc Sulphate.*—The zinc sulphate used was prepared by dissolving the purest obtainable zinc in pure dilute sulphuric acid, leaving about one-third undissolved. The solution was concentrated and allowed to crystallise, and then recrystallised. The investigations on this salt were carried out in precisely the same manner as in the previous case. With 2.253 grams of the salt successively heated at 359°, 394°, and 410° for 22 hours, the extreme variations did not exceed half a milligram. When the temperature was allowed to rise to 427°, there was a loss amounting to 0.0018 in the course of four hours, and with a further rise of temperature the loss was of course greater. The salt which had undergone partial decomposition was now treated with excess of sulphuric acid, and again exposed for several hours to a temperature of 360°. It was found to have returned almost exactly (difference two-tenths of a milligram) to its original weight, and behaved on further heating exactly as the normal salt had done. The relation of sulphate to oxide was determined by igniting it over the blowpipe till the weight was constant. By this method, 1.2795 gram of the sulphate yielded 0.6443 gram of the oxide, corresponding to an atomic weight of 65.05. A determination was also made on a second

portion by precipitation with barium chloride, the value obtained for the atomic weight being in this case 64.96. Marignac's objection to the determination of the atomic weight of zinc from the normal sulphate, using the ordinary method, is therefore a perfectly valid one, and applies equally to bismuth, for there can be no doubt that the temperature  $410^{\circ}$ , at which approximately decomposition sets in with these salts, is exceeded under the conditions which are usually observed in such estimations. On the other hand, the use of a sulphur bath as suggested by Baubigny, is not admissible in these cases. It is indeed quite possible that if the heating takes place in a vessel to which air has not free access, the decomposition will not proceed so readily, but then it is essential that such a condition should be avoided, and the sulphuric acid removed from the atmosphere surrounding the salt.

*Magnesium Sulphate.*—In this case, the normal sulphate gave up all free sulphuric acid at  $360^{\circ}$ , and though heated for long periods at successive temperatures up to  $450^{\circ}$ , no sensible alteration of weight occurred. The relation of sulphate to oxide was determined by igniting the sulphate, and the result checked by precipitation with barium chloride. The last portion of the sulphuric acid is retained with great tenacity, and even on long ignition and when the weight remained constant a trace of sulphuric acid was still present, and this accounts no doubt for the value obtained, 24.84, for the atomic weight, being somewhat high. The determination of this relation by simple ignition cannot therefore be safely recommended.

The sulphates of lead and barium were also examined, and were found to give the normal sulphate on heating at  $360^{\circ}$ , whilst decomposition of the sulphate did not take place even at  $500^{\circ}$ . The immediate object of the experiments being to ascertain whether a sufficient range of temperature exists during which the salt is stable, it was considered amply sufficient to extend observations to  $500^{\circ}$ .

*Didymium Sulphate.*—In an investigation of this nature, it was certainly of interest to examine the behaviour of one of the group of cerium metals. The material used for the preparation of the didymium salt had been prepared by myself from cerite. It had been carefully freed from cerium, erbium, yttrium, and lanthanum, but contained a small quantity of samarium, no attempt having been made to separate this body. The sulphate was made into a paste with sulphuric acid, and heated at  $360^{\circ}$ . In the cases previously cited, the sulphate under these circumstances soon became constant in weight, and remained so, but with the didymium sulphate this was only approximately the case. An approach to a constant weight was manifest, but variations amounting to a milligram or more occurred, and with each successive increase of temperature the loss was accelerated. No range of tem-

perature could be found within which the salt remained perfectly constant. Thinking this might be due to the presence of a little oxalate, the salt was treated a second time with excess of sulphuric acid strongly heated, and then again introduced with excess of sulphuric acid into the heating apparatus. The same phenomena were, however, repeated. In this case, therefore, it seems that some modification must be made in the method if it is to give trustworthy results, and differences in the determinations of the atomic weight of didymium hitherto made are probably not entirely attributable to the variable character of the oxides employed, but due also to the readiness with which decomposition of the sulphate takes place. Whether the other earths of this group show similar variations remains to be seen. Possibly if the heating is done under reduced pressure, a range of temperature may be obtained even in this case. Of this, however, I am not able to speak at present.

In determinations of the atomic weight of the elements named at the outset of this paper, it is believed that precision may be introduced by the use of the precautions suggested, and under such conditions the accuracy attainable should be of a much higher degree than has hitherto been the case. It only remains to be mentioned that in the calculations that have been made in the course of the paper, the atomic weight of oxygen has been taken as 15.96, and that of sulphur as 31.984.

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