Vol. XXVI. [July, 1904.] No. 7.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY

A REVISION OF THE ATOMIC WEIGHT OF BERYLLIUM.

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Received May 12, 1904.

The first determinations of the equivalent of beryllium were made by Berzelius in 1815,[1] and consisted of a single analysis each of an undoubtedly impure hydrous sulphate and chloride, both of which were probably also basic in character. The results are, therefore, of no interest in a discussion of the atomic weight of this element.

In 1842 Awdejew[2] carried out an extended investigation on the sulphates of beryllium and was the first to recognize the neutrality of the hydrous sulphate which Berzelius had considered an acid salt. He also prepared the sublimed chloride by the action of chlorine upon a heated mixture of beryllium oxide and sugar charcoal, and made three analyses of the product which did not show close agreement. They gave an atomic weight approximating 9.8, the high results being unquestionably due to the action of water on the sublimed chloride, as Awdejew

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[1] Schweigger *Journal*, **15**, 296.

[2] *Ann. der Phys. Pogg.*, **56**, 106; Clarke's "Constants of Nature," p. 132.

dried his gas by simply passing it over calcium chloride. His work on the sulphate was of much greater value. Four results are given varying from 9.18 to 9.49. The ratio of BeO to $BaSO_4$ was determined by precipitating the sulphuric acid with barium chloride, removing the excess of barium and then precipitating the beryllium as hydroxide by ammonia. Apparently no attempt was made to weigh the sulphate itself.

Weeren,[1] in 1854, published four determinations obtained from the hydrous sulphate by a method quite similar to that used by Awdejew, except that he precipitated his beryllium hydroxide by ammonium sulphide instead of ammonia, finding it to be somewhat soluble in the latter. His results varied from 9.18 to 9.42.

The following year Debray[2] published his investigation on beryllium and its compounds, and estimated the equivalent by means of the double oxalate of ammonium and beryllium. He determined the oxide by calcination after conversion into the nitrate and also estimated the carbon in separate samples by an organic combustion. His three results are far from agreeing closely, but the ratio between the two means of $BeO : 4CO_2$ gave $Be = 9.34$.

In 1869 Klatzo[3] obtained results varying from 9.13 to 9.40 by means of five analyses upon the hydrous sulphate, using the same method as Awdejew.

Nilson and Pettersen[4] were the next to take up the subject, in 1880. They had, for several years, been engaged upon investigations of the rare earths and had actively taken part in the controversy upon the equivalency of beryllium, which lasted so many years. In fact, they were the first chemists to definitely settle the matter by a determination of the vapor-density of beryllium chloride and, quite contrary to their previously held opinion, to establish its bivalency. In this atomic weight work they first attempted to use the sublimed chloride, but abandoned the trial upon finding calcium in their product and their glass tube apparently attacked. They then resorted to the crystallized sulphate as all previous investigators, except Debray, had done, but used an entirely different method, weighing the sulphate

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[1] *Ann. der Phys. Pogg.*, **92**, 124.

[2] *Ann chim. phys.*, [3], **44**, 37; Clarke's "Constants of Nature," p. 133.

[3] *J. prakt. Chem.*, **106**, 235.

[4] *Ber. d. chem. Ges.*, **13**, 1451.

itself after pulverizing the crystals and pressing between filter-paper, then igniting in platinum and weighing the oxide produced. Their sulphate too was probably purer than any previously made, having been produced from the sublimed chloride. Their four results agreed very closely, 9.09 to 9.114.

Krüss and Moraht[1] published their well-known investigation in 1891, their results also being obtained upon the hydrous sulphate, which they dried over phosphorus pentoxide before weighing. Their sulphate was derived from three different sources and was very carefully purified. They also used very much larger amounts of the sulphate for each ignition than any other investigator had done, which compelled them, however, to blast their specially constructed platinum crucible for unusually long periods of time. They made fourteen closely agreeing analyses, their results varying between 9.02 and 9.088.

All results upon the atomic weight of beryllium obtained up to the present time are, therefore, based upon analysis of the hydrous sulphate $BeSO_4.4H_2O$, with the single exception of Debray, who used the double oxalate $Be(NH_4)_2(C_2O_4)_2$, and may be summarized as follows:

	Ratio determined.	Mean O = 16.
Awdejew	$BeO : BaSO_4$	9.34
Weeren	$BeO : BaSO_4$	9.27
Klatzo	$BeO : BaSO_4$	9.28
Debray	$BeO : 4CO_2$	9.34
Nilson and Petterson	$BeSO_4.4H_2O : BeO$	9.104
Krüss and Moraht	$BeSO_4.4H_2O : BeO$	9.05

BALANCE AND WEIGHTS.

The balance used in the analyses which follow was a new No. 1 Staudinger, which was bought especially for this work. The adjustment was so arranged that a difference in weight of 1 mg. caused a deflection of twenty divisions on the scale, which could easily be read to 0.2 of a division by means of the microscope attachment. The balance was placed in a second case enclosed on all sides and large enough to permit of convenient manipulation when the front was lifted. This case was attached directly to a brick wall 2 feet thick, with a shallow air space between the case and wall and without any floor connection, so that

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[1] *Ann. Chem.* (Liebig), **262**, 38.

it was not subject to any ordinary jar. It was situated in an evenly heated room. All weighings were made by the method of substitution against a tare consisting of a light thin glass weighing-bottle, containing a platinum crucible and cone of the same size and shape as those used in the analysis. This tare was treated in all respects the same as the weighing-bottles against which it was balanced, and both, on removal from the desiccator, were wiped with a soft cotton cloth and allowed to stand in the inner balance case. This case was kept as dry as might be by means of sulphuric acid.

The weights were of brass, platinum-plated and were compared individually and against a standard weight by the Kaiserl. Normal-Aichungs Kommission. I also compared them against each other and my comparisons agreeing closely with those certified to by the commission, their figures were accepted as correct. All weighings were corrected to a vacuum standard.

I. PRELIMINARY INVESTIGATIONS.

The Preparation of Material.—The beryllium compounds used in this investigation were derived from two sources, the first being beryl from Grafton, N. H., and the second Kahlbaum's "Berylliumhydrat."

Beryl is most readily and quickly attacked by fusion with sodium hydroxide, but no container could be procured which was not also acted upon to such an extent as to render it useless. Nickel crucibles on the market are too small to be of use except for analytical purposes, as the fused mass foams badly. The method of Lebeau,[1] who proposes the high heat of an electric furnace to volatilize a portion of the silica of the beryl and render the residue easily decomposable by acids, has distinct advantages to those possessed of the necessary facilities. Beryl itself is not affected by any acid, even hydrofluoric, and this fact renders a separation from orthoclase and quartz, which most of the large New Hampshire beryls contain, an easy matter.

After a careful study of the many other methods for the decomposition of beryl the following procedure was adopted as the most convenient in my laboratory. The powdered beryl was fused in a Battersea crucible with a mixture of sodium and potassium carbonates and the fused mass turned out to cool on a

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[1] *Compt. Rend.*, **121**, 641.

smooth iron plate. The melt was pulverized and washed with water, which removed soluble sodium and potassium salts, notable amounts of silica and some beryllium, but the loss was more than compensated for by the greater ease of the subsequent operations. The moist residue was just barely covered with water and concentrated sulphuric acid added in excess, by which procedure it became at once a dense jelly-like mass, which was easily broken up, dried and heated on a sand-bath to render silica insoluble. The fine, nearly white and dry powder so produced was washed with hot water, potassium sulphate added to the solution and the major part of the aluminum crystallized out as alum. The mother-liquor was oxidized with potassium chlorate and sodium carbonate carefully added in small portions at a time with intermediate boiling until the filtered solution was colorless. Most of the remaining iron and aluminum are thus precipitated before the beryllium, as Hart[1] has pointed out, and the selective action is undoubtedly due to the power which beryllium sulphate has of dissolving considerable amounts of its own carbonate. To the filtered solution sodium carbonate was added with care to avoid any great excess, as the precipitated basic beryllium carbonate is notably soluble in sodium carbonate solution, and the precipitate washed to remove sodium salts. It was then dissolved in excess of sulphuric acid and the $BeSO_4.4H_2O$ crystallized out on evaporation. After a second crystallization from pure water the sulphate was again dissolved, precipitated by ammonia, filtered and washed, without any attempt, however, to free the gelatinous hydroxide entirely from sulphates. The removal of the main part of the ammonium sulphate is advisable, however, as the reverse reaction,

$$Be(Be(OH)_2)_3CO_3 + 4(NH_4)_2SO_4 = 4BeSO_4 + 8NH_3 + 7H_2O + CO_2,$$

takes place to a greater or less extent on continued boiling, after precipitating the basic carbonate from ammonium carbonate solution, and is, of course, proportional to the amount of sulphate present. The reaction may be easily complete if excess of sulphuric acid is present before neutralization. The beryllium hydroxide was transferred to a large bottle covered with an excess of dilute ammonia and carbon dioxide passed through the

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[1] This Journal, 17, 604.

liquid. When nearly saturated, more ammonia was added, the carbon dioxide shut off and the bottle allowed to stand in a warm place with occasional shaking. The liquid was filtered from some undissolved aluminum hydroxide and was treated with excess of ammonium sulphide as recommended by Scheerer[1] and Krüss and Moraht.[2] A small amount of a black precipitate was invariably thrown down at this stage. After standing for several days, the solution was filtered, with special care that the black precipitate was at all times in contact with liquid containing ammonium sulphide. It was then boiled with constant stirring until ammonia was evolved and precipitation was complete. Vigorous stirring of some form is absolutely necessary as the granular precipitate settles quickly and causes violent bumping which I have never been able to prevent by any other method. The basic carbonate thrown down varies continually in composition as precipitation progresses but the final product has the approximate formula $Be(Be(OH)_2)_3CO_3.2H_2O$ when dried over sulphuric acid. It is slightly soluble in water, so precipitation is never quite complete. At 100° it loses about 4.50 per cent. of water and contains about 44 per cent. of BeO. Like all the basic compounds of beryllium which have come under my observation except those of the acetate group to be described later, its composition is by no means definite. The carbonate was twice redissolved in pure sulphuric acid and reprecipitated from ammonium carbonate as described above except that the treatment with ammonium sulphide, although each time repeated, failed to separate any further black sulphide.

Kahlbaum's "Berylliumhydrat" contained quite notable amounts of aluminum and small quantities of iron. It was precipitated three times as basic carbonate, exactly as described above, and the small amount of dissolved iron thrown out by ammonium sulphide.

The basic carbonates so prepared were employed as a basis for the production of the purer salts used in the atomic weight determinations. They contained small amounts of aluminum, but were free from other admixture.

The Ammonium Sulphide Precipitate.—Krüss and Moraht lay special stress upon the removal of the black precipitate formed

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[1] *J. prakt. Chem.*, [1], **27**, 76.

[2] *Ann. Chem.* (Liebig), **262**, 47.

by adding ammonium sulphide to the ammonium carbonate solution and attribute the fact of their low results to its removal. In fact their investigation was undertaken with this idea in view. According to them[1] the precipitate was not due to iron but, while yielding a black sulphide, gave a white hydroxide. They promised further investigation. Apparently unknown to them, Scheerer had, on July 15, 1842,[2] read a paper at Stockholm in which he recommended the same procedure for the removal of the small amount of iron dissolved in the ammonium carbonate, and Vauquelin, in one of his early articles,[3] speaks of the difficulty of removing the last traces of iron, but says it can be done by means of potassium hydrosulphide. This must have been done in ammonium carbonate solution.

The matter has been one of interest to chemists working on beryllium and its compounds since the article of Krüss and Moraht was written, for it appeared to follow that if their statement of a black sulphide and white hydroxide was true a new element was under consideration. As the amount of precipitate is small, I began, some three years ago, in the early part of my work on beryllium and while working on beryl, to save the small amounts of black precipitate obtained with each new lot of material. Fortunately I did not realize for some time the desirability of removing the ammonium sulphate previous to solution in ammonium carbonate, so that the filtering of the ammoniacal solution after precipitation of the hydroxide was omitted. In this way about a gram of the black precipitate was collected and on analysis it proved to be a mixture of the sulphides of iron and zinc, but mainly zinc. On adding ammonia, with care to avoid excess, it yielded a precipitate which, in small amounts, might easily have been called white, while on addition of ammonium sulphide the black iron sulphide immediately predominated. Over 0.5 gram of zinc oxide was separated in the pure state and was procured from several kilograms of beryl. I believe the presence of zinc in beryl has not before been noted.

The "Berylliumhydrat" was also carefully examined and the presence of zinc established, but in very small amounts. It is quite probable that this material had been washed from alkaline

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[1] *Ann. Chem.* (Liebig). **262**, 47.

[2] *J. prakt. Chem.* [1], **27**, 76; Pogg. *Ann.*, September, 1842.

[3] *Allg. Jour. du. Chem.*, **1**, 595.

solution which would, of course, have removed the greater part of the zinc.

Beryllium Chloride.—It is quite generally conceded that atomic weight determinations, based upon the analysis of the metallic halides, are among the most accurate made, and it is highly desirable that the beryllium equivalent be determined on the pure chloride. Unfortunately, however, it has properties which render the task extremely difficult, being immediately acted upon by the slightest trace of water, and according to Nilson and Pettersen,[1] and Humpedge[2] it attacks glass. In my earlier studies on the subject I had hoped to be able to purify the chloride by the same method that Richards[3] used for magnesium, by evaporating carefully a mixture of the chlorides of beryllium and ammonium in a perfectly dry current of hydrochloric acid gas and subliming off the ammonium chloride. Early experiments showed that the ammonium chloride did prevent the decomposition of the beryllium chloride and a dry mixture but little, if any, decomposed could be obtained. On heating, however, they both sublimed together and no separation could be made, in spite of the fact that Carnelley[4] places the melting-point of beryllium chloride as between 858° and 890°. If the mixture be dried and heated in air, the ammonium chloride alone sublimes, leaving the oxide of beryllium in so light and feathery a form that it is carried by air currents about the room.

The normal chloride, bromide and iodide were first made by Wöhler[5] by heating a mixture of the oxide and carbon in the appropriate gas and subliming the product. The chloride was also made from the metal itself by sublimation in dry hydrochloric acid gas by Nilson and Pettersen. Lebeau[6] has recently prepared the iodide from the carbide in a similar manner. The chloride and iodide have quite similar properties. The bromide has been little studied. All are attacked violently by water with evolution of the corresponding acid. The solution of the chloride is strongly acid in reaction, readily dissolves the car-

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[1] *Ann. chim. phys.* [5], **14**, 425.

[2] *Proc. Roy. Soc.*, **39**, 1.

[3] *Ztschr. anorg. Chem.*, **13**, 92.

[4] *Phil. Mag.* [5], **18**, 21.

[5] *Ann. der Phys.*, **13**, 577.

[6] *Compt. Rend.*, **126**, 1272.

bonate or loses hydrochloric acid on evaporation. Evaporation on the water-bath or *in vacuo* over sulphuric acid has, in my hands, invariably yielded basic compounds. I have made many analyses of these basic chlorides. but no two products have ever agreed in composition, nor has crystalline structure ever been observed. Heating to a high temperature yields the pure oxide, but a small amount of $BeCl_2$ seems to be always sublimed after the last traces of water have been driven off. Every attempt to make the compound $BeCl_2.4H_2O$, described by Awdejew, met with failure. No crystalline chloride of any degree of hydration could be prepared. I believe the existence of this compound to be highly improbable. Some recent experiments have led me to seriously doubt the conclusion of Nilson and Pettersen, and Humpedge as to the action of $BeCl_2$ on glass, at least upon Jena or hard potash glass, in both of which I have sublimed the chloride from place to place, and repeatedly from the same place without the slightest sign of action so long as all moisture was absent. The least moisture, however, caused a thin film of the oxide to form, which might easily be mistaken for corrosion and which adhered tenaciously to the glass.

Beryllium Sulphate.—Beryllium forms two normal sulphates, $BeSO_4.4H_2O$ and $BeSO_4.2H_2O$, which are definite in composition under proper equilibrium conditions. As will be shown in another paper soon to be published, the sulphate $BeSO_4.7H_2O$, described by Klatzo,[1] does not exist and it is doubtful if the anhydrous sulphate $BeSO_4$ has ever been prepared pure. It is upon the tetrahydrate that the accepted atomic weight of beryllium rests. The dehydrated salt is produced from the tetrahydrate by heating at 100° and is apparently stable in dry air below this temperature. It was an intermediate step in the work of both Nilson and Pettersen, and Krüss and Moraht and would have given a second ratio for the determination of the equivalent.

In the early stages of my work on the sulphate it became apparent that I could not dry the normal tetrahydrous salt over phosphorus pentoxide as Krüss and Moraht had done, for the material slowly but continuously lost in weight. No absolutely definite point could be taken as representing exactly the salt $BeSO_4.4H_2O$, although the powdered crystals are stable at ordinary temperatures and pressures when air-dried. Under these

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[1] *J. prakt. Chem.*, **106**, 233.

conditions they probably are as near to the accepted formula as is the case with most hydrous salts. Nilson and Pettersen seem to have recognized this fact, for they made no attempt to dry their air-dry material other than by pressing between filter-paper. To establish more definitely the instability of the water of crystallization I undertook a series of tensimeter experiments. With phosphorus pentoxide as the desiccating agent, the water of crystallization of the tetrahydrous salt shows a pressure of 20 mm. olive oil at 20° and this pressure increases rapidly as the temperature of the thermostat rises. The pressure in the tensimeter was many times equalized and the experiment repeated. Weeren[1] states that $BeSO_4.4H_2O$ loses one-third of its water at 35°. The dihydrous salt $BeSO_4.2H_2O$, while for all ordinary purposes stable at 100°, appears to very slowly lose its water of crystallization if continuously maintained at this temperature. I have never been able to obtain the same equivalent from the weight of $BeSO_4.4H_2O$ taken and the weight of $BeSO_4.2H_2O$ derived therefrom. One would naturally suppose, since Krüss and Moraht first dried their salt to slowly remove the first 2 molecules of water before ignition, that they arrived at a like conclusion. This fact in itself should, in the absence of other proof of definiteness of composition, render the use of either for atomic weight purposes, subject to question.

In order to repeat the work of previous investigators on the sulphate, I prepared a quantity of a very pure salt by first dissolving the carbonate, already mentioned, in hydrochloric acid and treating according to the method of Havens[2] to remove any aluminum remaining. During the course of this work it was discovered that if the filtered saturated solution of beryllium chloride in the ether hydrochloric acid mixture was cooled down or supersaturated, a mass of beautiful white needle-like crystals were formed, which could be separated from the mother-liquor by means of a Buchner funnel without the use of filter-paper. These crystals contain all the constituents of the solution, beryllium chloride, hydrochloric acid, ether and water. Their exact composition is yet to be determined, but as they seemed to offer a further means of purification all of the beryllium chloride used in the preparation of the sulphate was passed through this

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[1] *Ann. der Phys.*, **92**, 124.

[2] *Ztschr. anorg. Chem.*, **15**, 18.

medium. On exposure to air the crystals were decomposed, losing ether and hydrochloric acid. The purified material was dissolved in excess of ammonium carbonate, boiled, precipitated and washed free from chlorides and ammonia. The carbonate so produced was dissolved in slight excess of carefully purified sulphuric acid. On evaporation, crystals of $BeSO_4.4H_2O$ were obtained, which were four times crystallized from water, washing each time with absolute alcohol. The crystals so prepared were dissolved in pure water, evaporated to the crystallizing point and the viscous hot solution poured into a large excess of strong alcohol. No precipitation occurred at once although a milky, apparently colloidal, solution was produced which, on standing over night, crystallized out almost completely. This was repeated once and the crystals so obtained were dissolved in carefully purified water, evaporated and crystallized as small crystals by stirring. When air-dry, they were powdered and used for determination of the equivalent and for the experiments already briefly described. Determinations were made on both the air-dried sulphate and upon sulphate which had been, for a short time only, over phosphorus pentoxide. The sulphate was weighed into platinum crucibles, dried at 100°, reweighed, and dried at a gradually increasing temperature in a Jannash beaker until the remainder of the water and most of the sulphur trioxide was removed. It was then blasted to complete removal of the sulphur trioxide. This required a very high temperature and was not complete, with the blast at my command, if the platinum crucible was protected by enclosure in a second. Fortunately, however, the oxide produced from the sulphate did not in the least adhere to the platinum crucible. The final weight of the crucible was, therefore, taken in determining the weight of the oxide. Nilson and Pettersen, and Krüss and Moraht both blasted platinum direct and mention no correction therefor. It would seem likely, however, that Krüss and Moraht made such a correction, for they speak of having to diminish the weight of the platinum crucible used as a tare in order to balance the one used in analysis. They used such large amounts of material that this error would be comparatively small in their results.

It has not been deemed necessary to enter into details of manipulation, but full precautions were observed, as described in the analyses to follow. Results on the sulphate yielded atomic weights from 9.18 to 9.36. Sources of probable error were so apparent that I had no confidence in the results obtained, and they will not be included in the final summary. The work is described for its bearing on the investigations of others and to call attention again to the probable errors in using a hydrous salt as a basis for the determination of atomic weight. Unfortunately, until quite recently, no other salt seemed to be available in the case of beryllium.

II. DETERMINATIONS OF THE ATOMIC WEIGHT.

Since the last investigation of the atomic weight of beryllium was made by Krüss and Moraht, in 1890, two new anhydrous compounds of beryllium have been discovered which are especially fitted for a redetermination of this constant, *viz.*, the acetylacetonate and the basic acetate. The first has the disadvantage common to all compounds previously used in that it contains a small per cent. of beryllium, slightly less than the sulphate, in fact, and any variation in the per cent. of beryllium oxide is doubled in the atomic weight. The basic acetate fortunately contains a much larger proportion of beryllium and in this respect approaches to the composition of the chloride. Both are readily crystallized and sublimed, and lend themselves to a very complete separation of the element from others, which might interfere in the determination. The basic acetate, a compound with very unusual properties and peculiar to beryllium alone, would seem to be especially adapted for this purpose.

The Properties and Analysis of Beryllium Acetylacetonate.

Properties.—Beryllium acetylacetonate was first prepared by Combes,[1] the discoverer of acetylacetone itself,[2] and many of the interesting metallic derivatives of that compound. It is most readily prepared by the action of beryllium carbonate or hydroxide on acetylacetone. It is a perfectly white crystalline substance which is slightly soluble in cold water, more soluble in hot water and slowly decomposed by boiling water with loss of acetylacetone and precipitation of beryllium hydroxide. It is readily soluble in alcohol and is easily crystallized therefrom in rhombic plates, differing widely from the crystals of the corresponding aluminum

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[1] *Compt. Rend.*, **119**, 1221.

[2] *Ibid.*, **103**, 814.

salt. It is soluble in benzene, toluene, xylene, naphtha and all petroleum distillates, chloroform, turpentine, methyl alcohol, amyl alcohol, ether, ethyl acetate, acetone, carbon disulphide and all other solvents at my disposal. It melts at 108° and boils at 270° without decomposition.[1] It sublimes readily many degrees below its boiling-point and begins to sublime even below the boiling-point of water. The sublimed crystals are light and flocculent with a marked resemblance to flakes of snow. It is soluble in acids, setting free acetylacetone.

Preparation of Material.—Two separate lots of material were prepared for the atomic weight determinations.

(1) Basic beryllium carbonate, prepared as before described from beryl, was carefully washed with ammonia-free water until absolutely free from sulphates and while still moist was treated with Kahlbaum's acetylacetone, which was first redistilled. Carbon dioxide was slowly evolved and the insoluble beryllium acetylacetonate left behind. This was pulverized and washed with pure water to remove excess of acetylacetone and was then dissolved in redistilled absolute alcohol and filtered to remove any unchanged carbonate. On partial evaporation, beryllium acetylacetonate was deposited. The clear plate-like crystals showed no color, but were again pulverized, washed with water, dissolved in absolute alcohol and recrystallized. This operation was repeated for the third time and the mother-liquors each time rejected. The crystals so produced were absolutely free from iron and not the slightest residue of aluminum chloride could be obtained by Havens' method of separation.[2] They were pulverized and dried for several hours in an air-bath. After drying they were introduced into a Jena glass retort, connected with a receiver of the same material and were sublimed in a current of dry carbon dioxide many degrees below their boiling-point. The retort was heated evenly on a bath of rosin kept at 230° and the neck of the receiver was covered with a piece of silk bolting-cloth, which allowed only the carbon dioxide to pass. The perfectly white, light and feathery acetylacetonate was again introduced into the freshly prepared apparatus, melted and resublimed. The sublimed crystals were kept over phosphorus pentoxide until ready for use.

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[1] Combes: *Compt. Rend.*, **119**, 1222.

[2] *Ztschr. anorg. Chem.*, **16**, 15-18.

(2) Kahlbaum's "Berylliumhydrat," containing a small amount of iron and some aluminum hydroxide, was treated direct with acetylacetone. The reddish color of the iron salt became immediately apparent and the main part of the beryllium hydroxide was converted into the acetylacetonate. Some aluminum hydroxide was also converted into aluminum acetylacetonate, although Urbain and Debierne[1] state that the aluminum derivative is not easily prepared from the hydroxide. The acetylacetonate was dissolved in alcohol, filtered and crystallized, rejecting the mother-liquor which contained almost all of the small amount of iron and aluminum acetylacetonates. The deep red color of the iron salt is a very delicate test for the presence of iron, even the slightest traces in an otherwise apparently pure beryllium carbonate being made evident at once by the yellowish tinge of the acetylacetonate. The crystals, still slightly colored, were pulverized and washed in water in which the iron salt is much more soluble and again crystallized from alcohol. This was repeated until crystals were obtained which yielded a clear colorless solution in absolute alcohol. These crystals were recrystallized three times, as in preparation (1), were dried, sublimed and resublimed, as already described. No evidence of any impurity could be found.

The Analysis.—The analyses were carried out in platinum crucibles without any transfer of material. The crucibles had been ignited for several hours in an atmosphere of hydrochloric acid gas containing a small amount of chlorine, to remove iron, after which they were submerged in fused acid potassium sulphate, cleaned and finally boiled in concentrated hydrochloric acid. Light, glass weighing-bottles were procured of a convenient size to contain these crucibles and in each was placed a thin porcelain dish so that the crucibles could be enclosed in the weighing-bottles while still warm without danger of fracturing the glass. A platinum cone was weighed with each crucible. Before each weighing, the weighing-bottles and contents were placed in a desiccator over phosphorus pentoxide, the desiccator being so constructed that the bottles could be closed before removal and the air of the desiccator, which always contains some moisture after being opened, replaced by perfectly dry air before

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[1] *Compt. Rend.*, **129**, 302-305.

the crucibles had cooled. The crucibles were placed in the desiccator warm before each weighing, except the initial weighing of the acetylacetonate.

Beryllium acetylacetonate is not hygroscopic, nor is the oxide, although Nilson and Pettersen[1] seem to have had a contrary experience. Still every precaution was taken to have the conditions of weighing as nearly identical as possible. As before stated, all weighings were made by the method of substitution and against a tare treated in like manner and of the same material and shape and of but slightly greater mass than the weighing-bottles and contents against which it was balanced. The crucible forming a part of the tare was not blasted.

After standing for some hours in the desiccator, the weighing-bottles, containing the empty crucibles and cones, were closed, removed, placed in the balance case and after standing for one-half hour were weighed. The acetylacetonate was now placed in the crucibles and the whole returned to the desiccator and allowed to stand for at least twelve hours, when they were again closed, removed and weighed. Although subsequent weighings were always made, there was no further loss in weight.

The crucibles were then taken from the weighing-bottles and redistilled pure nitric acid, leaving no residue on evaporation, was added. The acetylacetonate dissolved to a perfectly colorless solution, which was diluted with twice its own volume of water, that had been redistilled through block-tin and caught in platinum. The crucibles and contents were then placed upon a small platinum dish in an air-bath at 50°. It was kept at this temperature for from twenty-four to forty-eight hours, a further addition of water being once made. During this heating the acetylacetone was almost completely evaporated. Any considerable rise in temperature caused the nitric acid to attack the liberated acetylacetone, decomposing it with foaming, which invariably ruined the determination. If the temperature was carefully regulated, however, no trouble whatever was experienced. After the removal of the acetylacetone, the temperature was slowly raised during another forty-eight hours to 100°, which served to remove most of the remaining liquid, leaving a clear glucose-like nitrate already basic in character from loss of nitric anhydride.

[1] *Ber. d. chem. Ges.*, **13**, 1451.

Perforated platinum cones, previously weighed with the crucibles and of such size and shape that when inserted they fitted tightly in the crucibles above the nitrate, were now placed in an inverted position in the crucibles and the temperature again gradually raised during several hours to 175°. The use of the cones was thought advisable from noticing in a preliminary experiment that the last traces of water escaped through the viscous material in small bubbles and it was thought that possibly in breaking, a loss might occur through spurting. The inner surface of the cones showed no trace of this, however, when later removed. The heating to 175° left the nitrate as a slightly porous white solid which had already lost more than 75 per cent. of the nitric anhydride, equivalent to the beryllium present. The crucible was next supported in a Jannash beaker upon a platinum triangle and slowly heated over a Bunsen burner to decompose the last traces of nitrate, which was accomplished at a low heat and without any danger of loss of material. The crucible and contents were finally placed inside of a second platinum crucible, as recommended by Brauner,[1] to prevent loss of weight of the crucible itself, as Beilstein[2] and Hall[3] have shown can so easily occur and the whole blasted at a bright red heat until the crucible and contents showed no further loss of weight.

Corrections.—All weights are corrected to a vacuum standard and the weights of beryllium oxide are also corrected for occluded gases.

Specific Gravity.—Unexpected difficulty was encountered in determining the specific gravity of the beryllium acetylacetonate as no liquid could be found in which it was insoluble. It was but very slightly soluble in water at 20° and it was found necessary to determine its specific gravity in an aqueous solution of itself at this temperature. This was not all that could be desired, but gave results which vary but little from the truth and introduce an error into the subsequent corrections of weight so small that it can be entirely disregarded. In determining the specific gravity of the water, saturated with beryllium acetylacetonate, the pycnometer was filled to a mark on its outer surface and evacuated for the same length of time as employed in the

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[1] *J. Chem. Soc.*, **81**, 1249.

[2] *Chem. Centrbl.*, 1880, p. 614.

[3] This Journal, **22**, 496.

actual determinations of the specific gravity of the solid. No acetylacetonate separated. The pycnometer was then filled as usual and its weight determined. The average of closely agreeing determinations gave sp. gr. $Be(C_5H_7O_2)_2 = 1.168$, compared to water at 4°. The determination of the specific gravity of beryllium oxide needs no special comment. Krüss and Moraht obtained the value 2.9644.[1] My results gave sp. gr. $BeO = 2.9640$, compared to water at 4°.

Occluded Gases.—Richards[2] has shown that oxides, derived from the ignition of nitrates, contain occluded nitrogen and generally oxygen. Beryllium oxide is no exception to this rule, but the conditions of its formation by the very slow and gradual decomposition of the nitrate were peculiarly favorable to the removal of these gases. Gas was evolved on solution in strong sulphuric acid to the extent of 0.35 cc. for each gram of beryllium oxide, of which almost exactly one-third was soluble in alkaline pyrogallate. A correction was, therefore, made on the weights obtained of 0.00047 gram per gram of BeO.

No.	$Be(C_5H_7O_2)_2$. Grams.	BeO. Gram.	BeO. Per cent.	Equivalent BeO.
1	2.62245	0.31798	12.125	25.142
2	3.28037	0.39757	12.119	25.129
3	2.08993	0.25286	12.099	25.081
4	2.41401	0.29233	12.109	25.105
5	1.61353	0.19554	12.118	25.127
6	1.39714	0.16905	12.100	25.083
7	1.85023	0.22419	12.117	25.122
			Mean,	25.113

Analyses 1, 2, 3, 4, and 5 were made on preparation 1.
Analyses 6 and 7 were made on preparation 2.

The Properties and Analysis of Beryllium Basic Acetate.

Properties.—This unique and interesting chemical compound appears to be peculiar to beryllium alone. It was discovered by Urbain and Lacombe in 1901,[3] and Lacombe, a year later,[4] produced the basic formate, propionate, butyrate, isobutyrate and isovalerianate of the same type. The formate having the highest percentage of beryllium would be excellent for determining the

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[1] *Ann. Chem.* (Liebig), **262**, 57.
[2] *Am. Chem. J.*, **20**, 702.
[3] *Compt. Rend.*, **133**, 874.
[4] *Ibid.*, **134**, 772.

relative proportion of that element, but unfortunately it sublimes at so high a temperature and consequently condenses so quickly that it is extremely difficult to purify, especially as it is quite easily decomposed, even under much reduced pressure, at the temperature required for its sublimation. The basic acetate, however, has properties peculiarly fitting it for very complete purification and also contains nearly twice as great a percentage of beryllium as any substance heretofore used for the determination of the atomic weight.

Basic beryllium acetate, $Be_4O(C_2H_3O_2)_6$, melts at 283°-284° and boils at 330°-331°,[1] and is readily sublimed without decomposition. It is itself almost insoluble in water, but is slowly hydrolyzed by cold water and quickly by hot, after which it dissolves. It is easily soluble, unchanged in absolute alcohol and in chloroform, and is soluble in all the solvents already mentioned for the acetylacetonate (p. 733). It is also soluble in acetic anhydride and glacial acetic acid. Although a basic compound, its solution in glacial acetic acid can be saturated with hydrochloric acid gas and remain unchanged. It has not been found possible to produce the normal salt. It is unaffected in dry air. Ordinary acids attack it setting free acetic acid, probably through the agency of water they contain. It is much more soluble in boiling glacial acetic acid than in cold and is most readily crystallized in this manner. On cooling, it separates from boiling glacial acetic acid as small shining grains which, under a magnifying glass, are seen to be almost perfect octahedrons.

Preparation of Material.—(1) Basic beryllium carbonate prepared, as already described, from "Kahlbaum's hydrate" was dissolved in pure concentrated hydrochloric acid, ether added and the small amount of aluminum, which it still contained, was separated by Havens'[2] method. The pure chloride was precipitated by ammonia, dissolved in ammonium carbonate, ammonium sulphide added, allowed to stand, filtered and boiled to precipitate the carbonate. The carbonate so produced was thoroughly washed with carefully purified water and dissolved in excess of Kahlbaum's "Eisessig," which had been redistilled and which left no residue on evaporation. The excess of glacial acetic

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[1] *Compt. Rend.*, **133**, 874.

[2] *Ztschr. anorg. Chem.*, **16**, 15-18; *Am. J. Sci.*, [4] **4**, 111-114.

acid was boiled off, with constant stirring, by means of a Bunsen burner held in the hand under the porcelain evaporator, and the residue dried. A large excess of glacial acetic acid was now added and boiled. Solution immediately took place and, on cooling, the basic salt crystallized out in small shining octahedrons, which in the mass much resembled granulated sugar. The mother-liquor was rejected and the crystals washed with cold glacial acetic acid. They were again twice dissolved in hot, and recrystallized in cold glacial acetic acid, rejecting the mother-liquors and washing as before. The basic acetate so produced was dried at 150° to remove all excess of acid. It was then twice sublimed in Jena glass under a pressure of 250 mm. and in a current of dry air free from water and carbon dioxide. The sublimation was brought about by means of a bath of cylinder oil maintained at a temperature varying little from 290°. The perfectly white crystalline product so obtained was kept over phosphorus pentoxide until wanted.

(2) Another lot of the acetate was prepared in a manner differing little from that already described, except that it was sublimed at normal pressure and the bath kept at 305°-310°.

Analysis of the Basic Acetate.—The method used for the analysis of the basic acetate was almost identical with that employed for the acetylacetonate. The initial temperature was 70°, however, as the decomposing action of the nitric acid was no longer to be feared. At this temperature most of the acetic acid was removed, but to be sure that no acetate remained undecomposed, concentrated nitric acid was added twice more and the evaporation repeated. The basic acetate dissolved readily in nitric acid to a colorless nitrate.

Corrections.—The specific gravity of the basic beryllium acetate was determined in gasoline in which liquid it is less soluble than in any other investigated. Unfortunately, it is slightly soluble in this liquid, 50 cc. dissolving 0.054 gram, and the gasoline was first saturated with the basic acetate before its own gravity was determined. Closely agreeing results yielded specific gravity $Be_4O(C_2H_3O_2)_6 = 1.362$. Determinations of the gases, occluded by the oxide produced from the basic acetate, agreed with those from the acetylacetonate. In fact, the figure given is the average of several results on both. The variation of all results was from

0.32 to 0.39 cc. per gram of oxide. Occluded gases = 0.0047 gram per gram BeO.

ANALYSES OF BASIC BERYLLIUM ACETATE.

No.	$Be_4O(C_2H_3O_2)_6$. Grams.	BeO. Gram.	BeO. Per cent.	Equivalent. BeO.
1	1.89291	0.46788	24.717	25.139
2	1.47931	0.36534	24.703	25.111
3	1.09012	0.26911	24.686	25.097
4	1.35642	0.33493	24.692	25.105
5	1.56787	0.38715	24.693	25.106
6	1.34465	0.33204	24.693	35.106
7	2.61484	0.64630	24.716	25.137
8	2.67721	0.66109	24.693	25.107
9	3.11534	0.76930	24.693	25.107
			Mean,	25.113

Results 1 to 6 were obtained on preparation 1.
Results 7 to 9 were obtained on preparation 2.

ATOMIC WEIGHT OF BERYLLIUM.

O = 16, H = 1.008, C = 12.01

	from acetylacetonate.		from basic acetate.
	9.142		9.139
	9.129		9.111
	9.081		9.097
	9.105		9.105
	9.127		9.106
	9.083		9.106
	9.122		9.137
			9.107
Mean,	9.113 ±0.0059		9.107
		Mean,	9.113 ±0.0033
		General mean, Be =	9.113 ±0.0043

Samples of the oxide produced from both the beryllium acetylacetonate and the basic acetate were dissolved in pure hydrochloric acid and sent to Professor Charles C. Hutchins, of Bowdoin College, who kindly consented to examine them with the special spectroscopic facilities at his command. He reported that they were absolutely free from iron and aluminum, and that he was unable to find any other impurity. My acknowledgment and sincere thanks are due him for this part of the work.

In connection with this investigation I have prepared a bibliography of beryllium, with abstracts, which I believe to be complete and which will shortly be published separately.

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