

Contributions to the Chemistry of Beryllium

A THESIS

PRESENTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

By

PAUL HENRY MALLET-PREVOST BRINTON

SUBMITTED TO THE GRADUATE FACULTY OF THE UNIVERSITY OF
MINNESOTA

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Contributions to the Chemistry of Beryllium.

Introductory.

In 1798 Vauquelin¹ undertook the analysis of samples of emerald and beryl with a view to showing them to be merely varieties of the same mineral. De Haüy had already noticed the great similarity between the emerald and beryl, and had, in fact, made a statement as to the mineralogical identity of the two specimens. In the course of the analysis of the beryl Vauquelin obtained a precipitate with ammonium hydroxide which he supposed to be aluminum hydroxide. A peculiarity in this precipitate was noticed, however, in that while it dissolved completely in potassium hydroxide, yet upon boiling, a white flocculent precipitate was again thrown down. This behavior led Vauquelin to make a closer investigation of the precipitate, and he found among other things that the solution of the precipitate in sulphuric acid was incapable of forming an alum with potassium sulphate. The solubility of the new hydroxide in ammonium carbonate was another indication that it was not a compound of aluminum, and Vauquelin accordingly announced his discovery of the oxide of a new element, designating the oxide as the "earth of the beryl."

Although the name "Glucina" was soon applied to the oxide, owing to the sweetish taste of its salts, and later upon isolation of the metal it was called Glucinum, many favored the name "Beryllium" for the element, and that name is the one in most common use to-day, although "Glucinum" is still used by many chemists.

Vauquelin² in a series of papers, published during the year 1798, made known many of the principal properties of the compounds of the new element.

The first attempt to isolate the metal was made by Humphrey Davy,³ who tried electrolysis, as well as the action of potassium vapor on the oxide, but his results were unsatisfactory. In 1828 Wöhler,⁴ and Bussy,⁵ working independently, prepared the metal at about the same time, and, strangely enough, by the same method. This consisted in subjecting beryllium chloride to the action of potassium, and the product was a metallic powder of a low degree of purity, dark gray or brown in color, which assumed considerable luster on burnishing.

¹ *Ann. de Chim. et de Phys.*, [1] 26, 155.

² *Ibid.*, [1] 26, 155, 170, 259; *Allg. J. Chem.*, 1, 590.

³ *Phil. Trans.*, 100, 59.

⁴ *Pogg. Ann.*, 13, 577.

⁵ *J. de Chim. médicale*, 4, 453.

Nothing further was done in the attempt to prepare the element until 1855, when Debray¹ produced a metal of somewhat higher purity than that hitherto prepared, by passing vaporized chloride of beryllium over heated sodium metal. Debray's chief point of departure from the methods before used consisted in the separation of the alkali metal and the beryllium chloride during the heating, putting each material in a separate boat and allowing the beryllium chloride to come in contact with the sodium only after the former had been vaporized. A mixture of sodium chloride and metallic beryllium resulted, and this yielded upon extraction with water a purer metal than had before been prepared. The reaction used by Debray is found in practically all other published processes² for the production of beryllium metal up to the introduction of the electrolytic method. These other attempts differed only in details from that of Debray, although it should be mentioned that owing to the difficulty in preparing and handling beryllium chloride some of the subsequent investigators used the double fluorides of beryllium and the alkali metals. These salts are easily prepared in pure condition, and can be melted at a comparatively low temperature.

Winkler³ claims to have reduced the oxide of beryllium to the metal by the action of metallic magnesium, but it seems questionable as to whether or not he really obtained an appreciable reduction. Similarly Goldschmidt⁴ claimed to have attained at least a partial reduction of beryllium oxide by his aluminothermic method, but metal in sufficient quantity or of sufficient purity for investigational purposes does not appear to have been produced.

The first mention of an electrolytic method for the preparation of beryllium was a proposition by Grätzel,⁵ in which the oxide of beryllium was to be mixed with the chloride of a more electro-positive metal, and the mixture then electrolyzed. It is not stated that this patent has ever been put to the practical test. In 1895 Warren⁶ stated that he prepared the metal by electrolysis of the fused bromide, but inasmuch as the halides of beryllium do not conduct electricity it is difficult to understand how Warren got his metal by the process mentioned, unless, indeed, he happened to use a bromide sufficiently admixed with conducting impurities to allow passage of the current. A proposition by Borchers⁷ to electro-

¹ *Ann. de Chim. et de Phys.*, [3] 44, 1.

² See Reynolds, *Phil. Mag.* [5] 3, 38; Nilson and Pettersson, *Ber.*, 11, 381, and *Wied. Ann. der Physik.*, 4, 554; Humpidge, *Proc. Roy. Soc.*, 39, 1; Krüss and Moraht, *Ann. der Chem.*, 260, 161.

³ *Ber.*, 23, 120.

⁴ *Ztschr. f. angew. Chem.*, 11, 822 (1898)

⁵ German Patent 58,600 (1892).

⁶ *Chem. News*, 72, 310

⁷ *Z. f. Elektrochem.*, 2, 3, 9.

lyze the fused chloride, rendered conducting by the addition of a chloride of an alkali—or alkaline earth metal, seems to have resulted in the production of no metal.

Lebeau¹ was the first to produce enough metal by electrolysis to make a more or less complete study of the properties of the element. This investigator prepared double fluorides of sodium and beryllium, melted them in a nickel crucible which was attached to a negative pole, and a carbon rod having been inserted as anode, he passed through the melt the current from a dynamo which yielded normally 20 amperes at 80 volts. The beryllium was deposited on the sides and bottom of the crucible, and is said to have been easily obtained in practically pure condition by washing away the sodium fluoride with water. The metal obtained in this way consisted of hard, brittle, steel-grey hexagonal plates, which had a brilliant metallic luster. Fichter and Jablecznski,² in attempting to prepare the metal by the method of Lebeau, found no little difficulty in freeing the crystals from the difficultly soluble sodium fluoride, which was so interlaced with the metal that it could scarcely be removed. These authors recommend a melt for electrolysis which contains less sodium fluoride, for while Lebeau used the double salts, $\text{BeF}_2 \cdot 2\text{NaF}$, they took only one molecule of sodium fluoride to two molecules of beryllium fluoride. It is claimed that by this modification the separation of the metal by dissolving away the difficultly soluble sodium fluoride is made much more easy. The melt after electrolysis for two and one-half hours with 7–10 amperes at 15 volts (at the end of which time the "anode effect" occurred), was removed from the crucible while still hot. After cooling and finely pulverizing, the substance was thrown into a large volume of water (one to two liters), a little at a time with constant stirring. The salt is said to have dissolved almost immediately, while the metal fell to the bottom. The deleterious effect of the acid (HF due to hydrolysis) was counteracted by the addition, from time to time, of a little ammonium hydroxide, and by frequent renewal of the water. The metal, after washing with alcohol and drying over phosphorus pentoxide, was found by gasometric analysis to contain only about 92% of the pure metal. Microscopic examination revealed particles of white substance here and there through the mass of metallic crystals. The authors state that they consisted of beryllium oxide, resulting from the hydrolysis of the fluoride. Since beryllium metal has a specific gravity of only 1.842, according to Fichter and Jablecznski,³ while the oxide has a gravity of about 3.0, they state that no difficulty was experienced in obtaining a metal of almost perfect purity by centrifuging the crude metal in ethylene bromide, diluted with alcohol

¹ *Compt. rend.*, 126, 744.

² *Ber.*, 46, 1604.

³ *Loc. cit.*

to a specific gravity of 1.95. The oxide is said to have settled to the bottom, leaving the pure metal suspended in the liquid.

The work of Fichter and Jablcznski is the latest published account of the preparation of beryllium metal, and has been reviewed in considerable detail, as I shall have occasion to refer to it again in the "Experimental" part of the present paper.

The valence of beryllium and its position in the periodic table of the elements have been the subject of much discussion. The great similarity between many of the compounds of beryllium and aluminum led Berzelius¹ to assume the element as trivalent, assigning to the oxide the formula Be_2O_3 . This stand was opposed by many, and arguments for the bivalency of the element were numerous. Debray,² for example, showed that from a crystallographic standpoint the compounds of beryllium resembled those of zinc fully as much as they did those of aluminum, and that in the formation of double salts, and in certain other chemical relations the beryllium compounds were not unlike those of magnesium. Scheffer³ in studying the phosphates of beryllium made a triple salt to which the formula $\text{BeNa}_2(\text{NH}_4)_2(\text{PO}_4)_2 \cdot 7\text{H}_2\text{O}$ could be applied if beryllium were considered bivalent, and this was considered as further evidence that the element in reality was bivalent. An attempt by Nilson and Pettersson⁴ to settle the question of valency by a determination of the specific heat of the metal tended to indicate trivalency rather than bivalency, but later determination by Humpidge⁵ showed that beryllium had an abnormal specific heat at the lower temperatures, which had been used in the investigations of Nilson and Pettersson, while at higher temperatures, between 400 and 500 degrees, the specific heat became practically constant at about 0.62. If beryllium be assumed as bivalent this would give an atomic heat of about 5.64, which, while not very eloquent testimony, none the less indicates that the element is more probably a diad than a triad. The best evidence we have of the bivalency of beryllium,—which is now accepted by practically everyone,—lies in the determinations of the vapor density of the chloride,⁶ as well as that of the bromide.⁷ Further evidence by other investigators⁸ has not been lacking to show

¹ *Pogg. Ann.*, 8, 18.

² *Ann. de Chim. et de Phys.*, [3] 44, 5.

³ *Ann. der Chem.*, 109, 104.

⁴ *Ber.*, 11, 381.

⁵ *Proc. Roy. Soc.*, 39, 1.

⁶ *Ber.*, 17, 987; and *J. f. prakt. Chem.*, [2] 33, 1.

⁷ Humpidge, *Loc. cit.*

⁸ Brauner, *Ber.*, 11, 872; 14, 53; Rose, *Berlin Ber. Akad. der Wiss.*, 1855, 334; Nilson, *Ber.*, 8, 655; 9, 1056, 1145; Hartlet, *J. Chem. Soc.*, 43, 316; Coomes, *Compt. rend.*, 119, 1221; Prudhomme, *Bull. soc. chim.*, [3] 13, 509; Henry, *Compt. rend.*, 121, 600; Rosenheim and Woge, *Z. f. anorg. Chem.*, 15, 283; Urbain and Lacombe, *Compt. rend.*, 133, 874; Glassmann, *Chem. Ztg.*, 31, 8; also *Ber.*, 40, 3059; Galecki, *Z. f. Elektrochem.*, 14, 767.

that beryllium is bivalent, although a number¹ were firm in their contention for trivalency, while Tanatar² and Kurovski³ have advanced the theory that beryllium is quadrivalent. In the light of a survey of all the evidence offered, however, there seems but little room for doubting the bivalency of the element.

Beryllium has been placed at the head of the second group in the periodic table of the elements, and in spite of the strong resemblance to aluminum, particularly in the oxide, hydroxide, and metal, yet the relation of beryllium to magnesium is more clearly seen. For instance, it forms no alums and the general type of beryllium salts is quite similar to that of the magnesium salts, as well as that of the zinc salts. In its amphoteric character beryllium is more clearly allied to zinc than it is to aluminum. On the whole, there is clearly no place in the periodic table which beryllium could occupy other than that in which it is now placed.

The atomic weight of beryllium seems quite satisfactorily settled as 9.1, since the more recent determinations⁴ are nearly all in close agreement with this figure.

Beryllium salts are colorless when the acid is colorless, and a large majority dissolve in water. Such solutions have a sweet taste and give an acid reaction. A large number of the salts of beryllium have been prepared in a state of high purity, and have been well studied, but the binary compounds, with the exception of the halides and a few others, are comparatively unstudied.

As might be predicted from the weak basic nature of beryllium hydroxide, the carbonate and sulphide cannot be obtained by precipitation. The additions of ammonium sulphide to solutions of beryllium salts cause precipitation of the hydroxide, while the use of an alkali carbonate as reagent throws down a highly basic carbonate, which, when precipitated under some conditions, approaches very nearly the hydroxide in composition. The existence or non-existence of the normal carbonate of beryllium is a matter of some interest. Klatzo⁵ claimed to have prepared a crystalline film of the composition $\text{BeCO}_3 \cdot 4\text{H}_2\text{O}$ by long-continued passage of carbon dioxide into a suspension of beryllium hydroxide in water. This was filtered and evaporated in an atmosphere of carbon dioxide. Parsons⁶ denies the accuracy of Klatzo's report, and states that the normal car-

¹ Rose, *Berlin Ber. Akad. d. Wiss.*, 1855, 581; Meyer, *Ber.*, 11, 576; Blake, *Chem. News*, 45, 111; Traube, *Z. f. anorg. Chem.*, 8, 35; Wyruboff, *Bull. soc. franc. min.*, 19, 219; also *Ibid.*, 25, 71.

² *J. Russ. Phys.-Chem. Soc.*, 36, 82; 38, 850.

³ *Ibid.*, 39, 936, 1630.

⁴ For a list of these see Parsons, "Chemistry and Literature of Beryllium," page 14; and Brauner, in Abegg's *Handbuch der Anorganischen Chemie*, [2] II, 31.

⁵ *J. prakt. Chem.*, 106, 242.

⁶ *Op. cit.*, p. 38.

bonate has never been made, and can never be made unless from a non-aqueous solution. The compound nevertheless finds place in most of the handbooks, and the subject seems to merit further investigation.

The tendency of beryllium to form basic compounds, or basic mixtures, is very strong, and there can be no doubt that many of the compounds of high molecular weight which find place in the literature are nothing but indefinite basic mixtures, or solid solutions,¹ which should in reality find no place in a list of true chemical compounds. Beryllium does form a number of well-defined basic compounds, but these are formed only in the absence of notable quantities of water, *i. e.*, under conditions which render hydrolysis impossible. One of these compounds, the basic acetate, $\text{Be}_4\text{O}(\text{C}_2\text{H}_3\text{O}_2)_6$, prepared first by Urbain and Lacombe,² has been used by Parsons³ in the determination of the atomic weight of the element.

A few acid salts of beryllium are known, but the tendency in this direction is very limited.

Beryllium forms double salts readily, and these compounds are far more stable in solution than are the single salts. In addition to the considerable number of double salts of the inorganic acids which have been described, a good many double salts have been prepared in which the acids have been organic, and some very interesting problems have been opened up in this field.⁴

An interesting side light is thrown on the nature of the beryllium atom by its entrance into complex molecules. Of special importance are those of certain organic acids, in which beryllium appears capable of replacing not only the hydrogen of the carboxyl group, but also the hydroxyl hydrogen. These compounds with tartaric, malic, and racemic acids have been well studied,⁵ and it seems clear that the beryllium should be regarded in these compounds not as one of the metals of an ordinary double salt, but as a constituent of the negative radical. Thus the formula for sodium diberyllium tartrate may be written $\text{Na}_2\text{Be}_4\text{C}_8\text{H}_4\text{O}_{18} \cdot 10\text{H}_2\text{O}$, the beryllium occurring in the complex negative ion $\text{Be}_4\text{C}_8\text{H}_4\text{O}_{18}''$. It is interesting to note that the formation of this compound is further evidence of the bivalence of beryllium, for only bivalent metals are known to form complexes with tartaric acid.

On the ground of the solubility of beryllium hydroxide in solutions of the strong alkalies, we must assume that the hydroxide is amphoteric, and therefore we should expect to find beryllium in the negative radical as a beryllate. From the very weak acidic nature of beryllium hydroxide

¹ Parsons, *Loc. cit.*

² *Compt. rend.*, **133**, 874.

³ *J. Am. Chem. Soc.*, **26**, 721.

⁴ Rosenheim and Woge, *Z. anorg. Chem.*, **15**, 283; and Rosenheim and Itzig, *Ber.* **32**, 3424

⁵ Rosenheim and co-workers, *Loc. cit.*

the beryllate, if it exists at all, must be very strongly hydrolyzed, and this would render difficult the isolation and identification of the compound. Krüss and Moraht,¹ however, claim to have made and isolated a definite beryllate of potassium, with the formula K_2BeO_2 , by treating freshly precipitated beryllium hydroxide with pure, carbonate-free potassium hydroxide dissolved in absolute alcohol. In this way it is said the difficulties due to hydrolysis were surmounted, and by concentrating the clear solution in a vacuum, a snow-white mass, of silky luster, having the formula above given, was obtained. Sodium beryllate is said to have been prepared in the same way. These beryllates are very hygroscopic and are immediately decomposed by water. Rubenbauer,² from experiments on the solubility of beryllium hydroxide in solutions of sodium hydroxide of various strengths, found that the solubility increases with increasing concentrations of alkali, but no direct proportionality seems to exist. He contends that the alkali solutions do not contain beryllates of definitely fixed composition. Hantzsch³ approached the question by means of conductivity measurements of the solution of beryllium hydroxide in sodium hydroxide, comparing the conductivity, for example, of the system $Na_2SO_4 \cdot Be(OH)_2 : 8NaOH$, with that of $Na_2SO_4 : 8NaOH$. From such experiments he concludes that in the system $Be(OH)_2 : 8NaOH$ about one-half of the beryllium exists in the form of a true sodium beryllate, while the remainder probably exists as colloiddally dissolved hydroxide. Although unable to isolate the beryllate, he deduces the formula $(BeOH)(ONa)$.

Of far greater interest than the solubility of beryllium hydroxide in alkali hydroxides is the remarkable solubility of this hydroxide in aqueous solutions of normal beryllium salts. This property has long been known but the reasons for it are not altogether clear. This solvent action seems to vary with the different salts, although comprehensive quantitative data are not available. Some work by Parsons on this subject will receive attention later.

The normal compounds of beryllium when dissolved in water show in many ways actions which are characteristic of the acids from which the radicals are derived. Thus they dissolve beryllium hydroxide, liberate carbon dioxide from carbonates, and in some cases they dissolve metals. These actions suggest, of course, hydrolysis, and yet Leys⁴ and Brunner⁵ have shown that in some cases at least, the salts of beryllium are hydrolyzed to an extent less than that of either iron or aluminum salts. Par-

¹ *Ann. der Chem.*, 260, 161.

² *Z. anorg. Chem.*, 30, 331.

³ *Ibid.*, 30, 289.

⁴ *Z. phys. Chem.*, 30, 199.

⁵ *Ibid.*, 32, 132.

sons¹ suggests as an explanation of the phenomena the hypothesis that solid in solution may, and frequently does, act towards other solutes exactly as if it were a liquid miscible with the solvent in which the second solute was itself soluble; and he further argues that if this be the case, many of the so-called abnormal osmotic effects are readily explained qualitatively without any assumption other than that of simple solution.

In support of his general theory Parsons² studied the systems (1) camphor, acetic acid, and water; (2) lead oxide, lead acetate, and water; (3) iodine, acetic acid, and water; (4) iodine, potassium iodide, and water; (5) silver cyanide, potassium cyanide, and water; and (6) borax, boric acid, and water. Preliminary to the work just mentioned Parsons, Robinson and Fuller³ investigated the solution of beryllium hydroxide in beryllium sulphate to the extent of cryoscopic, dialysis, ion transference (qualitative), and conductivity measurements. It was shown that dissolving beryllium hydroxide in normal beryllium sulphate solution raises its freezing point, and diminishes its conductivity; that the solutions so obtained are not true colloids, and that they contain no beryllium in the anion.

From the work thus far cited, then, we seem justified in assuming that the act of a beryllium salt in dissolving beryllium hydroxide is one of simple solution, and therefore the solubility of the hydroxide may be expected to vary according to the salt employed as solvent.

Some work has been done recently⁴ with a view of establishing a connection between the extent of solubility and the nature of the solvent. Walden⁵ has shown that with a series of solvents the solubility of a salt was greater the more strongly associated the solvent. The same investigator⁶ also states that when salts are dissolved by various liquids the expression $\frac{\epsilon}{\sqrt[3]{\mu}}$ is approximately constant, where ϵ is the dielectric constant, and μ the percentage molecular solubility. Crompton, Turner, and others have also studied the relation of solubility to the nature of the solvent, but most of that work deals with liquid phases.

Some interesting statements in regard to the solubility of beryllium hydroxide in solutions of normal beryllium salts were made as early as 1858, by Ordway.⁷ His article is lacking in experimental details, and his statements as to the extent of these solubilities are made without referring to the experiments in which he obtained his results. He states that the

¹ *J. Phys. Chem.*, **11**, 659.

² *Loc. cit.*

³ *Ibid.* **11**, 651.

⁴ Cf. "Modern Inorganic Chemistry," edited by J. N. Friend, **1**, 106.

⁵ *Z. phys. Chem.*, **55**, 703.

⁶ *Ibid.*, **61**, 633.

⁷ *Am. J. Sci.*, [2] **26**, 197.

"nitrate, formate, chloride, bromide, and iodide can be made nearly, but not quite, tribasic. By partial neutralization with ammonia the nitrate may become fully tribasic, and remain perfectly clear. * * * * The sulphate can be got almost tribasic, but will not bear large dilution." He states further that even the fluoride will take up some excess of base, while the acetate seems to have the highest solvent power, taking up the hydroxide until it is rendered almost sexibasic. Ordway calls attention to the fact that in studying salts rendered basic by the taking up of excess of hydroxide, due regard must be had to the fact that many hydroxides can exist in a more reactive form or in a less reactive form, according to the conditions of the precipitation. Thus he states that the reactive form of aluminum hydroxide is best obtained by precipitation with ammonium carbonate or an alkaline sulphate, rather than with ammonium hydroxide. In speaking of beryllium, Ordway says that the nitrate precipitated by excess of ammonia gives the hydroxide in the reactive form, and he continues: "Indeed it is not known that hydrate of glucina is ever passive with respect to acids, though that precipitated by boiling a diluted alkaline solution is said to be no longer soluble in alkalis."

The variation in the reactivity of beryllium hydroxide obtained under different conditions has been chronicled by several investigators. Van Bemmeln¹ designated two modifications of the hydroxide as alpha and beta. Of these the alpha, obtained by boiling diluted solutions of alkaline beryllates, was the less reactive, while the far more voluminous form of the hydroxide, the beta, obtained by precipitation of beryllium salts with ammonia, was more reactive in every way. The first form was held to be anhydrous $\text{Be}(\text{OH})_2$, while the beta was looked upon as highly hydrated. Haber and van Oordt² also called attention to the fact that the solubility, and other properties, of the hydroxide is in large measure dependent upon the method of preparation, and the treatment to which the hydroxide has been subjected. While beryllium hydroxide which has been freshly precipitated in the cold absorbs carbon dioxide greedily, and is very readily soluble in dilute alkalis, yet on heating or drying, this same hydroxide almost completely loses its power of absorbing carbon dioxide, and its solubility in dilute alkalis falls to about one-thirtieth of that which it possessed in the freshly precipitated condition. Hantzsch³ rather objects to the designation of these so-called varieties of a given hydroxide as allotropic modifications, and he finds ready explanation for the differing properties on grounds which are partly physical and partly chemical. In the behavior of metallic hydroxides toward alkalis, the decreased reactivity goes hand in hand with increasing density, or, what amounts

¹ *J. prakt. Chem.*, [2] 26, 227.

² *Z. anorg. Chem.*, 38, 377 and 40, 465.

³ *Ibid.*, 30, 338.

to the same thing, with decreasing surface. The directly precipitated, reactive hydroxides are very voluminous, but on drying they shrink, and their alkali solubility is decreased. On the other hand, the hydroxides which separate spontaneously from alkaline solutions are in the form of fine, heavy powders, as was mentioned by Van Bemmeln, and this condition reduces the combining capacity toward alkalies, as well as the acid solubility. Aside from the physical causes as just outlined, Hantzsch assumes as a chemical cause for the differing behavior of the hydroxides, a difference in the state of hydration. The views of Van Bemmeln and Hantzsch are really not at variance, and no essential incompatibility exists. But Hantzsch points out clearly the fact that it is not necessary to assume isomerism or polymerism (allotropism) in order to rationally explain the differing reactivity of most metallic hydroxides. More recently Bleyer¹ has investigated the hydroxide of beryllium, and he claims the existence of three chemical modifications, differing in stability, and hence in solubility and reactivity. On standing, it is asserted, the least stable and most reactive form passes into the more stable and less reactive modification, and this transition involves a change in the state of hydration.

The varying reactivity of beryllium hydroxide as brought out in the preceding paragraph, is of considerable interest, since it is hoped in the present investigation to throw some light on the relation existing between the solvent action on beryllium hydroxide of various normal salts of beryllium, and the chemical and physical characteristics of these salts.

Since it is purposed in this paper to deal with certain compounds of beryllium with some of the rarer elements a brief survey of the literature dealing with these compounds will here be given.

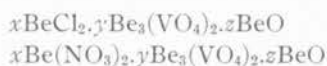
While making a general study of vanadates Berzelius² prepared what he describes as a yellow, neutral, difficultly soluble, and pulverulent salt, by the addition of ammonium vanadate to a solution of a beryllium salt. Berzelius made no analysis of the substance, and assigned no formula. The only other mention of a vanadate which I have been able to find in the literature of beryllium is in an article by Tanatar and Kurovski.³ These investigators obtained, by the action of sodium vanadate on beryllium chloride in water solution, a yellow amorphous precipitate which contained 47.28% of V_2O_5 . It was stated that this precipitate was soluble in dilute mineral acids, but insoluble in other solvents. Another precipitate, obtained from beryllium nitrate, contained 25.40% V_2O_5 , and 46.30% BeO ; and differed from the one before mentioned in being of somewhat lighter yellow color. These authors state

¹ *Apoth. Ztg.*, 28, 353.

² *Pogg. Ann.*, 22, 58.

³ *J. Russ. Phys.-Chem. Soc.*, 41, 813.

that the compositions of their salts correspond to formulas of the following types:



Practically no details are given beyond those mentioned in the preceding lines. The analytical method used in making the difficult separation of beryllium and vanadium is not stated, nor is any mention made of tests showing the presence of chloride or nitrate in the precipitates.

Normal, acid, and basic molybdates of beryllium have been reported in the literature. Atterberg¹ claims to have made the acid molybdate $\text{BeMoO}_4 \cdot \text{MoO}_3 \cdot x\text{H}_2\text{O}$, as well as the basic molybdate, $\text{NeMoO}_4 \cdot \text{Be}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$, but little detail is given in either case, and there is little to indicate that actual compounds of the above formulas really exist. Two notices are given of the preparation of a normal molybdate. Rosenheim and Woge² made the dihydrate, $\text{BeMoO}_4 \cdot 2\text{H}_2\text{O}$, by boiling equimolecular quantities of beryllium hydroxide and molybdic acid, suspended in water. The two solids dissolved in great measure, and upon evaporation of the clear filtrate a syrupy liquid separated from the concentrated solution. This was separated from the mother liquor by means of a separatory funnel, and allowed to stand in the air at a low temperature. After fourteen days the liquid set to a mass of crystals. Analysis showed considerably more BeO and less MoO_3 than corresponds with the formula given, but this was attributed by the authors to admixture of a little beryllium hydroxide which it was physically impossible to separate from the crystals. These investigators report unsuccessful attempts to prepare double salts with the molybdates of sodium, potassium, and ammonium.

Tanatar and Kurovski³ claim to have prepared the anhydrous molybdate, BeMoO_4 , as blue crystals by boiling together, suspended in water, equivalent quantities of basic beryllium carbonate and molybdenum trioxide. A very slight excess of beryllium carbonate was said to be necessary to insure the crystallization of the pure molybdate. It is interesting to note in this connection that the slightest excess of the hydroxide will make it impossible to obtain the sulphate of beryllium in well-crystallized form. Tanatar and Kurovski make no mention of the separation of the oily layer mentioned by Rosenheim and Woge, and they seem to have had no difficulty in preparing well-developed crystals in a state of perfect purity, since their test analyses checked almost perfectly with the calculated values. The difference in the state of hydration of the two molybdates obtained by the German and Russian investigators is not explained.

¹ *Kongl. Svenska Vet. Akad. Handlingar*, 12, 1; also *Ber.*, 7, 472.

² *Z. anorg. Chem.*, 15, 306.

³ *J. Russ. Phys.-Chem. Soc.*, 41, 813.

Experimental.

The Preparation of Beryllium Metal.—My experience in the preparation of metallic beryllium by the method of Fichter and Jablcznski shows that the process is not as ideally simple as one might infer from the literature, and while I obtained some apparently pure metal, the yield was so small and the method so time-consuming that from my own experiments I cannot now recommend this process as one for the production of beryllium in quantities sufficient for investigational purposes. As a basis for future work, I shall here record my experiences just as they came to me.

As starting material Merck's "Beryllium Oxide, hydrated," was used. Analysis by the conventional method of solution in water and nitric acid, precipitation by a slight excess of ammonium hydroxide, and ignition to oxide in platinum crucible over a large Bunsen burner, carried out in duplicate, gave the following results:

	No. 1.	No. 2.
BeO.....	31.41%	31.38%

Preparation of Melt for Electrolysis.—In all experiments the melt was prepared just as directed by the authors above mentioned, and the details may be here given once for all. Such quantities of the hydrated oxide of beryllium and pure anhydrous sodium carbonate were weighed out that the constituents were present in the molecular ratio of $4\text{BeO} : \text{Na}_2\text{CO}_3$. The beryllium oxide was first brought into a large platinum dish and dissolved by the gradual addition of concentrated hydrofluoric acid. It was found necessary to moisten the powder with water before adding the acid, to prevent mechanical loss from effervescence, as the action of the acid was very vigorous. With all precautions there was a very slight loss of material during the operation of solution. To the clear solution of the beryllium fluoride, in excess of HF, was added the weighed amount of sodium carbonate, in small portions at a time. In this operation there was also a very slight loss of the material added, and, roughly speaking, it was thought that the loss of sodium carbonate was probably approximately equal to that of the beryllium compound, so that the molecular ratios were not appreciably changed. Enough hydrofluoric acid was added to make certain that a generous excess was present, and then the dish was set on the hot plate to evaporate. After evaporation the dish was heated over a free flame, finishing the melting over a Meker burner, or a blast lamp, until a clear, quiet, homogeneous fusion was obtained. On cooling the mass set to a clear porcelain-like cake,—pure white, opaque, and of high luster. After standing a day in the air the surface lost a little of its luster, softened somewhat, and became a little sticky. Evidently the surface deliquesced to some extent, but below the surface the mass seemed unchanged. Kept in a desiccator, the original hardness, dryness, and luster were preserved.

Electrolysis.—It will be remembered that Fichter and Jablcznski electrolyzed with 7-10 amperes at 15 volts. My first attempt was with a bank of nine storage batteries, but it was hard to get more than about an ampere through, and in trying to reduce the resistance of the bath by thorough melting, I raised the temperature too high, with the result that a hole was put in the bottom of the crucible. This, according to Fichter and Jablcznski, would be due to the formation of an alloy of beryllium and nickel of low melting point.

One more attempt with the nine storage batteries, having first melted the mixed fluorides in a platinum dish, and then pouring them into a heated nickel crucible, and immediately introducing a preheated anode, consisting of three carbons wired together, resulted in practical failure to get the current through, and it then became evident that a more powerful source of current must be employed.

In the next attempt the melt was prepared as before, and poured in molten condition into the heated nickel crucible which served as the cathode. The anode, as described above, was introduced, and a current of about 20 amperes, at 60 volts, was sent through from a large motor generator. A small gas flame was kept under the crucible to assist in keeping the contents fluid. It should be mentioned that at the very first there was practically no action, and the ammeter registered zero, but after a very few minutes the melt heated up, 20 amperes passed through, and a brisk evolution of gas—odor of fluorine—started. Jets of flame were visible all over the surface of the melt. These I take to be carbon monoxide from the anode, possibly in presence of a slight amount of retained water in the melt. The current was far from steady, the voltage varying from 35 to 75, and the amperage from zero to 22 or more (limit of ammeter); but the average was 15-20 amperes at 40-60 volts. After about an hour the current became very irregular, and the amperage went to the limit of the number (22 amperes), even when the volts were cut down to 35. At this point the carbons glowed at the contact with the melt, but the latter seemed cool—just liquid—at the edges of the crucible. The current was interrupted, the melt scraped out with a nickel spatula, and allowed to cool. It was dark gray in color and was glistening with bright specks of crystallized metal. The cooled melt was finely ground and brought in small portions into a large beaker (1400 cc.) of water. Most of the substance dissolved, but an insoluble residue which looked like a gray powder settled to the bottom. The water was frequently renewed, and a little ammonia was added now and then, as Fichter and Jablcznski recommend, for the partial neutralization of the hydrofluoric acid resulting from the hydrolysis. The ammonia was never added to full alkalinity. It should have been mentioned that when the melt was brought into water there was a slight evolution of gas. It could not be

collected in appreciable quantities, but it was taken to be methane, resulting from the action of water on a little beryllium carbide, which might have been formed during the electrolysis. The odor resembled that furnished by the unsaturated hydrocarbons accompanying the hydrogen evolved from common iron treated with an acid; and this same odor could be easily detected in the cold melt before it was brought into water. The gray powder which had settled to the bottom was well washed, first repeatedly with water, then with alcohol, and finally dried in a desiccator over sulphuric acid.

Microscopic examination of the gray powder above mentioned revealed an intimate mixture of glistening steel-gray crystalline plates of the metal, and white sharp particles which might be sodium fluoride, or beryllium oxide. Doubtless there was some of both substances present, but it is worthy of note that these particles resembled the original melt after it had been pulverized, thus revealing sharp, broken angles, far more than they did the kind of substance one should expect from the hydrolysis of a beryllium salt. From the description of the process by Fichter and Jablecznski, they obtained at this stage a metal of about 92.0% purity, whereas my gray powder could not have contained over 30-50% at the very highest. By the method of suspension, or rather centrifuging, in ethylene bromide these authors obtained practically pure metal, so this method was next tried on my gray powder. Ethylene bromide was diluted with alcohol until a specific gravity of 1.95 was obtained. The gray powder was then brought into a separatory funnel together with the heavy liquid, but upon shaking and allowing to stand for a moment the whole of the solid settled rapidly to the bottom. Since beryllium has a specific gravity of only 1.842 it is evident that the metal was so entangled with the heavy beryllium oxide (specific gravity about 3.0) or sodium fluoride (sp. gr. 2.55) that the metal was carried down by its heavier associates. By triturating the mixture with undiluted ethylene bromide of sp. gr. 2.05, in an agate mortar, and again shaking in the separatory funnel, a film of metal crystals formed on top of the liquid, while all the white substance, and most of the metal, again fell to the bottom, and these were drained off. The crystals of metal were caught by passing the upper layer through a filter paper. After washing with alcohol, the filter and its contents were allowed to dry in the air. The heavy portion which had been drained off was again triturated with a view to destroying the intimacy of the mixture of the metal with its contaminating substances, and the separatory operation was repeated. Again a light film of metal floated on the surface of the liquid, and this was separated, dried, and collected as before. By repeated treatment as just outlined more and more of the metal could be obtained but only a comparatively small proportion of the metal which was readily present could be separated from the

white substance. Here again, then, my experience differs from that of Fichter and Jablcznski. It will be seen, however, that our differences are rather quantitative than qualitative, for I found it quite possible to prepare the metal by the process outlined, but the yield was far too small in comparison with the expenditure of time and material to allow the method to be used for preparing beryllium as a basis for the study of the binary compounds,—and it was for this purpose that I undertook the preparation of the metal.

The experiments just described were all made in the laboratory of the University of Arizona, and to be sure that the method was being given a fair trial, the whole operation was tried again in the laboratory of the University of Minnesota. In this last test everything connected with the experiment was new, and different from that used in Arizona, with the single exception of the "Beryllium Oxide, hydrated" from Merck. The details of the work were identical with those laid down by Fichter and Jablcznski, with the exception that a nickel crucible of 100 cc. capacity was used instead of one with a capacity of 150 cc., which is the size they mention. The graphite anode agreed with theirs in size, *viz.*, 30 mm. in diameter. A current of 7 to 8 amperes, at 53 volts, was maintained, while they mention 7–10 amperes, at 15 volts. The current was allowed to pass for two and one-half hours, as was the case with their experiment; but I saw no evidence of any "anode effect" at the end of this time, as they observed. It may also be added that in spite of the small gas flame kept under the crucible through the whole of the electrolysis, the surface of the melt had solidified toward the end of the time, but since the current remained constant it seems fair to assume that the mass was in a state of fusion below the surface.

The results of this new experiment agree in every particular with those of the experiments made previously at the University of Arizona, and I feel forced, therefore, to record the fact that my experience with the method of Fichter and Jablcznski is at variance with their published statements as to the facility with which metallic beryllium can be obtained by their procedure.

Pressure of work along other lines of investigation, and shortage of material, due to the European war, necessitates a temporary cessation of the study of the metal and its preparation by the electrolytic method. By way of suggestion for future work, it may be said that enough of the gray mixture of metal and white substance should be prepared to allow the separation of a sufficient quantity of the white substance for identification. The knowledge so gained might lead to a better method of separation. Also it seems worth while to try the electrolysis of some aqueous solutions of beryllium salts with a mercury cathode, and distillation in atmosphere of hydrogen of the resulting amalgam,—if indeed an

amalgam be formed. Attempts to form an amalgam by grinding some beryllium metal with mercury in an agate mortar, and also by heating at about the boiling point of mercury, gave apparently negative results; but the metal at my disposal was so small in amount that these experiments should not be regarded as conclusive. The difficulty offered by a thin coating of oxide over the metal might be eliminated by the presence of a trace of acid. Since beryllium does not react with hydrogen there should be no difficulty in distilling off the mercury from an amalgam, without danger of oxidizing the metallic beryllium.

The Vanadates of Beryllium.—The indefinite and meagre nature of the information offered up to the present time on the vanadates of beryllium seemed to justify an attempt to repeat the precipitation as made by Berzelius,¹ and Tanatar and Kurovski,² and to analyze the product.

A solution of ammonium vanadate was made by dissolving vanadium pentoxide in concentrated ammonium hydroxide, and evaporating to small volume. This reagent was then added to a rather dilute solution of beryllium nitrate. The latter gave a strongly acid reaction, doubtless due to hydrolysis, and there was no precipitation on mixing the two solutions. Very dilute ammonium hydroxide was then added drop by drop, with constant stirring. A yellow precipitate formed, which increased with each addition of ammonia. This was continued until a very heavy, slightly flocculent precipitate had been obtained. This precipitate was filtered off, and the filtrate, yellow in color, was found to be distinctly acid. Upon the addition of more ammonia to the filtrate a further precipitation occurred, and this precipitate was decidedly lighter in color than the one first filtered. No sudden change in the appearance of the precipitate was observed as the mixture passed through the neutral stage,—the precipitate simply became lighter and lighter in color. Analysis, the methods for which will be discussed later, showed that this substance contained about $60\text{BeO} : 1\text{V}_2\text{O}_5$.

Analysis of the yellow substance first filtered off was made after drying for a week over sulphuric acid under reduced pressure, and led to a formula approximately expressed as $4\text{BeO} \cdot \text{V}_2\text{O}_5 \cdot 6\text{H}_2\text{O}$. One molecule of water differed from the others in that it was given off at 105° . For the purpose of showing that in all probability this substance is not a compound, but simply an indefinite basic mixture, the following is tabulated:

	Calculated.	Found.
H_2O , at 105°	4.61	4.28
BeO	25.69	26.45
V_2O_5	46.67	48.30
H_2O , by difference.....	23.03	20.97

¹ *Pogg. Ann.*, 22, 58.

² *J. Russ. Phys.-Chem. Soc.*, 41, 813.

From the fact that the last filtrate of the very basic whitish mixture above mentioned was colorless, it seems that I must have been working with an insufficient amount of ammonium vanadate to insure excess of this reagent, and it was therefore deemed advisable to make another attempt to obtain a precipitate in the presence of excess of the vanadate.

Ammonium vanadate solution was added to a solution of beryllium nitrate until when a few drops of the mixture were made alkaline with ammonium hydroxide, and the resulting precipitate filtered, a yellow filtrate was obtained, thus showing an excess of the ammonium vanadate. To the main solution was then added dilute ammonia in small portions, with constant stirring, until present in slight excess. The very voluminous lemon-orange-yellow precipitate was filtered and washed very thoroughly with cold water, using suction to render the process more complete. A portion of the precipitate when heated with sodium hydroxide solution showed no trace of ammonia, thus proving the absence of ammonium compounds in the substance.

Having in mind the statement of Tanatar and Kurowski¹ as to their compounds such as $x\text{BeCl}_2 \cdot y\text{Be}_3(\text{VO}_4)_2 \cdot z\text{BeO}$, I tested this yellow precipitate for nitrates but obtained an entirely negative result. The method of the zone reaction with sulphuric acid and ferrous sulphate was employed for this test, and to be certain that the vanadate would not mask the coloration a trial was made with a part of the precipitate to which a very small amount of nitric acid had been added. With this substance the test showed clearly, and I feel justified, therefore, in reporting this basic vanadate of beryllium, or rather this basic mixture, as free from nitrate. Analysis of the yellow precipitate showed a molecular ratio for $\text{BeO} : \text{V}_2\text{O}_5$ of 4.3 : 1. The ratio of $\text{H}_2\text{O} : \text{V}_2\text{O}_5$ was 9.7 : 1 in the substance dried at 105° , while it was 3.1 : 1 in the substance which had been ignited at red heat.

From these results, then, it seems fair to assume that the yellow precipitate obtained by Berzelius was simply a more or less hydrated mixture containing about four equivalents of BeO to one of V_2O_5 . The assumption of a definite basic vanadate of beryllium is not justified. In comparing my results with those of Tanatar and Kurowski the fact that in my precipitates the ratio of $\text{BeO} : \text{V}_2\text{O}_5$ is about 4 : 1, while in theirs it is about 13 : 1 seems to require explanation. The fact that I used ammonium vanadate while they used sodium vanadate as precipitant can hardly be looked to as explanation. If they precipitated in presence of excess of beryllium salt the matter is readily explained, for according to my investigation the ratio of base to acid in such cases can easily go as high as 60 : 1, or even higher. If the precipitate was obtained in the presence of excess of vanadate the matter is not so easily explained. I am inclined,

¹ *Loc. cit.*

however, to attribute the difference in composition to varying degrees of washing. I found that the washings from the yellow precipitate, although apparently colorless, none the less contained notable quantities of the vanadate which gave a very distinct yellow color upon concentration by evaporation. From this it appears that the vanadate of beryllium is considerably soluble in water, and it is therefore easy to see how these precipitates could become more basic by long-continued washing.

It being evident that a normal beryllium vanadate was not to be obtained by precipitation with a soluble vanadate, other means were tried for the preparation of such a compound.

The most important thing to guard against in the preparation of normal beryllium compounds is the introduction of an excess of beryllium hydroxide, and it was thought that by working with two oxides, or hydroxides, each being individually almost insoluble, a compound of beryllium and vanadium might be prepared in which there was no excess of beryllium oxide. My first attempt was to prepare a normal orthovanadate, $\text{Be}_3(\text{VO}_4)_2$, and with this end in view such weights of beryllium hydroxide and vanadium pentoxide were taken that the ratio was $\text{Be}(\text{OH})_2 : \text{V}_2\text{O}_5 : - 3 : 1$. About half a gram of this mixture was boiled with 150 cc. of water for an hour. The solution gradually took on a yellow color which became deeper as the boiling continued. It looked as if about half of the solid mixture had gone in solution. The mixture was filtered hot, and upon cooling the clear yellow filtrate became turbid. Set to evaporate on the water bath the solution again became clear, and when considerably concentrated the solution remained clear when allowed to stand in the cold overnight. The next morning the evaporation was continued until a deep orange-red syrupy liquid was obtained. This was allowed to cool and stand. After two days the whole had set to a solid mass of fascicular crystals. Upon repeating the above experiment with larger quantities of material,—6 grams of the mixed oxides, boiled with three successive liters of water,—and evaporating to about 40 cc., it took nine days' standing before any separation of crystals took place. At the end of that period the whole had set to a mass of dark yellow crystals, which seemed to get a little darker on standing. The mass was so hard that it was difficult to scratch out a sample with a knife. The mass seemed to consist of crystals of two colors, some yellow and some brown. The yellow ones were more distinctly crystalline than the brown. The effect of adding alcohol to some of the crystal mixture was to convert the whole of the surface to a uniform yellow crystal mass. When the alcohol was poured off the surface became brown again, and the individual crystals seemed to lose to some extent the sharpness of their outline.

A rough preliminary analysis of a small portion of this heterogeneous mass seemed to indicate that there was probably present a normal meta-

vanadate instead of an orthovanadate, and this metavanadate had either three or four waters of crystallization, and a slight excess of BeO mixed with it. This analysis was not regarded as very reliable, and it is not worthy of record. It suggested two points, however, and they were that I should take equimolecular weights of the two oxides to boil together, and that since alcohol seemed to have the effect of transforming the surface of the heterogeneous mass into fine yellow crystals it might be able to precipitate out these yellow crystals from the concentrated syrupy liquid obtained by evaporating the water extract of the oxide mixture, and these crystals might then be free from basicity.

Equimolecular proportions of beryllium hydroxide and vanadium pentoxide were boiled up with water as before, the yellow liquid freed from the insoluble residue by filtration, and evaporated to an orange-red syrup. This was poured while still hot into a large crystallizing dish full of 95% alcohol. A copious separation of lemon-yellow particles immediately took place, and after standing twelve hours a thick layer of yellow crystals had settled to the bottom of the dish. These were well washed with alcohol, and allowed to dry in the air. Under the microscope the crystals seemed perfectly homogeneous, consisting of lemon-orange-yellow, waxy plates. Later attempts at the preparation of these crystals, in which conditions were so regulated that the precipitation by alcohol took place more slowly, *i. e.*, by adding the alcohol to a less concentrated solution so that the separation was more in the nature of a crystallization than a precipitation, the crystals were obtained in far more definite form. Under the microscope it could be seen that there were really two sets of crystals, the main mass consisting of particles of about 0.25 mm. average diameter, but scattered among these was a very small percentage of little, flat, tabular crystals, the largest of which did not exceed 0.05 mm. across, and far less than this in thickness. These last-mentioned crystals surely did not make up as much as one per cent. of the total mass.

The main crystals are evidently isometric, being cubes modified by an octahedron. The polar angle (Rho, according to Goldschmidt's method) gives a value of $54^{\circ} 46'$. The theoretical value is $54^{\circ} 44'$. The cubic face in contact with the glass does not show the octahedral modifications. One face of the cube, that lying horizontally in the crystallizing dish, is in nearly all cases characterized by a quadrangular embayment, or negative development. This feature being developed on only one face of the cube suggests a tetragonal habit, but the values given above for the polar angle seem to prove conclusively that the crystals are isometric. The embayments, then, seem to result from physical position only, and not from any crystallographic consideration. Thin fragments of these crystals, mounted on a slide under a petrographical microscope, do not polarize light.

The little tabular crystals, which were found in very small quantity between the larger ones just described, do polarize light, and seem to show an orthorhombic habit. One of these crystals was mounted on a goniometer, and, although six faces in the prismatic zone gave signals, they were too irregular to yield satisfactory measurements. The base also was plainly visible in the goniometer.

For the crystallographic determinations, which were made on a two-circle Goldschmidt goniometer, I am indebted to Prof. F. N. Guild, of the University of Arizona.

Whether or not these very small crystals were the same in substance as the larger ones I cannot say. Making up as small a percentage of the whole as they did, it is certain that they could not have had very much effect on the analytical results, and it was physically impossible to isolate enough of the little particles to obtain an independent analysis of them.

Several batches of the yellow crystals were made at different times, and the following analyses were made on three different lots. The results show clearly that the salt is a normal Beryllium Metavanadate Tetrahydrate, a compound which has not heretofore been prepared.

$\text{Be}(\text{VO}_3)_2 \cdot 4\text{H}_2\text{O}$.				
	Calculated.	Found.		
BeO.....	9.00	8.44	9.74	9.18
V_2O_5	65.22	66.60	65.38	66.86
$4\text{H}_2\text{O}$	25.78	24.96	24.88	23.96

The material represented by the first analysis was crystallized from water, the other two by precipitation with alcohol. The amounts used for analysis in the first two samples were small, and in view of the somewhat unsatisfactory method of separation used, the results are perhaps as concordant as might be expected. The third analysis was made on a good sized sample, and is in all respects the most reliable. The ratio of $\text{BeO} : \text{V}_2\text{O}_5$ in this analysis is found to be 1 : 1.002, and this may be taken as conclusive proof that we are dealing with a normal metavanadate of beryllium, with four waters of crystallization, though a little of the latter is evidently easily lost.

Some difficulty was experienced in finding a method suitable for the exact, quantitative separation of beryllium and vanadium in the scheme for analysis. Precipitation of the beryllium by ammonia was, of course, out of the question, since under such conditions the vanadium is precipitated as basic vanadate of beryllium. Attempts to separate the vanadium first as lead vanadate were unsuccessful, for it seemed that a concentration of acetic acid sufficient to prevent the co-precipitation of beryllium caused incompleteness in the precipitation of the lead vanadate, and in all cases the beryllium subsequently precipitated was strongly contami-

nated by vanadium. The method finally adopted was essentially that laid down by Noyes, Bray and Spear¹ for the qualitative separation, but it was found necessary to make additional operations to insure quantitative separation. The method as used is as follows:

The crystals of beryllium metavanadate were dissolved in very dilute nitric acid in a small pressure flask, and the solution was nearly neutralized with sodium bicarbonate, added in solid form in such quantity that the precipitate at first formed by the last addition of the reagent dissolved very slowly on shaking. One gram more of the solid bicarbonate was then added, the flask immediately closed, the cork screwed down in a pressure frame, and the whole brought into a bath of warm water which was then heated to gentle boiling, and thus kept for twenty minutes. The flask was then rapidly cooled, opened, and the contents promptly filtered, using warm water for washing. The precipitate had, as a rule, a slight yellowish tinge, so it was dissolved in nitric acid, and the precipitation was repeated under pressure as before. The second precipitate seemed perfectly white, so it was dissolved in nitric acid and precipitated by ammonia to free it from occluded sodium salts. The final precipitates after igniting and weighing usually had a slight yellowish tinge, and this was corrected for by dissolving the weighed precipitate in sulfuric acid, reducing with sulphur dioxide, and titrating with potassium permanganate, as in the case of the main portion for vanadium. The amount of vanadium oxide thus found, amounting as a rule to a few milligrams, was deducted from the weight of the beryllium oxide and added to the vanadium oxide found in the main portion. The combined filtrates from the precipitation of the beryllium were warmed on the water bath to see if any more beryllium precipitate would separate. After an hour or so a slight, but easily ponderable, white precipitate had separated. Further digestion seemed to cause no increase of this precipitate, so it was filtered off and ignited with the main portion of the beryllium. This little precipitate seemed pure white, but if it did contain any vanadium compound, this would be corrected for by the determination of the vanadium pentoxide in the ignited precipitate, as just described.

For the determination of the main portion of the vanadium the filtrate from the last separation of the beryllium was strongly acidified with sulphuric acid, evaporated to heavy fumes, diluted, reduced at boiling temperature by sulphur dioxide, the excess of the latter being then displaced by passing a current of carbon dioxide through the boiling solution for about an hour, or until the issuing gas no longer decolorized a very dilute solution of potassium permanganate, and the hot solution containing the vanadium in the quadrivalent form was then titrated with permanganate.

¹ *J. Am. Chem. Soc.*, 30, 481.

The percentage of water of crystallization was taken by difference, having first made sure that there was no alcohol of crystallization present.

In studying the properties of beryllium metavanadate a determination of the solubility in water at 25° was made by agitating some fine crystals in a sealed test-tube with water for five days in a thermostat kept at 25°. In the filtrate the vanadium was determined by titration, and the solubility thus calculated. One part by weight of beryllium metavanadate was found to dissolve in a thousand parts of water at 25°. In hot water the crystals are readily soluble, and on cooling there seems to be a strong tendency toward supersaturation.

In pyridine the solubility seems to be of the same order as that in water. Chloroform and ether do not dissolve the salt, nor does absolute alcohol. In 95% alcohol the crystals are very slightly soluble,—just enough to give the faintest yellow color, but this solubility becomes more perceptible as the alcohol is diluted.

The specific gravity of the metavanadate was determined by the suspension method, using methylene iodide diluted with benzol. The specific gravity was found to be 2.273.

Since this metavanadate of beryllium is made by boiling together two oxides, both of which are far less soluble than the resulting salt it seemed a point of interest to determine the conductivity of the saturated solution of the salt. The saturated solution, according to the solubility determination, is 0.007 normal, and the molecular conductivity of this solution was found to be only 5.56. The slight degree of ionization thus indicated is probably in some measure responsible for the formation of this salt by boiling two relatively "insoluble" oxides, BeO and V₂O₅, and the displacement of equilibrium by the withdrawal of beryllium ions and metavanadate ions according to the equation



is probably the determining factor in causing the solution of the constituent oxides.

The tetrahydrate crystals lose water slowly, but continuously over sulphuric acid. No definite endpoint of dehydration could be obtained. On heating over a flame the color of the crystals passes through gray-green, blue-gray, orange, russet, to black, cooling again to a russet-brown.

The Molybdates of Beryllium.—Since the results of the attempts of Rosenheim and Woge to prepare the normal molybdate did not agree in all points with those of Tanatar and Kurovski, it was thought advisable to try to reproduce one or both of the compounds recorded. I took approximately equivalent weights of beryllium hydroxide and molybdenum trioxide. These were ground together to secure intimate mixture, and this mixture was brought in small quantities at a time into a large beaker

of boiling water. Almost complete solution resulted. The small insoluble residue was filtered off and proved to be beryllium hydroxide. Not having at that time noticed the precaution of Tanatar and Kurovski as to the necessity for an excess of beryllium hydroxide, and fearing basicity in the solution I added more molybdenum trioxide to the filtrate in the same way that the mixture had been added. A considerable amount of the trioxide dissolved. The greenish yellow solution was evaporated to small bulk—the color becoming yellowish green—and allowed to cool. The next morning it had set to a white amorphous mass which looked like molybdenum trioxide. I then read again the article of Tanatar and Kurovski, and noting what they say in regard to an excess of beryllium hydroxide, I redissolved the white mass in boiling water and added $\text{Be}(\text{OH})_2$ in small quantities as long as it would dissolve, finally filtering off the excess. Upon evaporation to small bulk the color became deep green, and evaporation was continued to incipient crystallization. There was no evidence of the two layers mentioned by Rosenheim and Woge, but just a regular separation of what seemed to be small, clear crystals, with a slight greenish blue cast. Allowed to stand overnight the liquid became thick and syrupy with crystals, but there seemed to be no gummy material. A little of the mixture was treated with alcohol, but it immediately became gummy, showing that this liquid could not be used in washing. The rest of the mixture was brought onto a filter paper, and washed with small portions of cold water. The air-dry crystals were analyzed by dissolving in dilute nitric acid, and precipitating the beryllium by ammonium hydroxide in the regular way. According to Rosenheim and Woge¹ this gives a beryllium hydroxide free from molybdenum. After removal of nitric acid from the filtrate by evaporation with sulphuric acid, the molybdenum was precipitated as sulphide in a pressure flask, and the sulphide converted to oxide by gentle ignition, a small amount of mercuric oxide, suspended in water, having been added to complete the oxidation of the filter paper at a low temperature.

The results of the analysis lead to no definite simple formula, but it is not impossible that a definite basic beryllium decamolybdate may have been prepared. It is to be noted that a sodium decamolybdate of formula $\text{Na}_2\text{Mo}_{10}\text{O}_{31}\cdot 2\text{H}_2\text{O}$ is known.² Analogous to this, though basic, the greenish crystals obtained may be looked upon as having the following formula:



The agreement between the theoretical figures for this compound and the figures actually found is seen to be satisfactorily close from the following comparison:

¹ *Loc. cit.*

² Roscoe-Schorlemmer, II, 1067.

	Calculated.	Found.	
BeO.....	8.36	8.44	8.39
MoO ₃	68.52	68.83	68.98
H ₂ O.....	23.12	22.73	22.63

Another attempt was made, using this time larger quantities, and substituting pure basic carbonate of beryllium for the hydroxide used in the previous trial. About 35 grams of a mixture of the carbonate and molybdenum trioxide of the highest purity, with BeO and MoO₃ in equimolecular proportions, were introduced in small portions into about two liters of boiling water. Nearly all dissolved, with greenish color. The slight residue was filtered off, and the filtrate was evaporated to small volume. Flakes began separating, and considerable material had thus separated by the time the volume had been reduced to 200 cc. After filtering, the liquid was further evaporated, and flakes continued to separate. Qualitative tests showed that these flakes consisted of MoO₃, or some molybdenum compound, but no beryllium could be detected in them. The liquid was strongly acid to litmus paper. More beryllium carbonate was added, and a good deal dissolved, with vigorous evolution of carbon dioxide. The volume had come down to about 100 cc. and the mixture was again filtered. When about half had gone through the paper a whitish substance began to run through which at first looked like a precipitate, but examination under the lens showed it to consist of drops of oily liquid in emulsion in the other liquid; and when the filtration was completed there were two distinct layers in the filtrate, the heavier layer being somewhat larger in volume than the lighter layer. This observation seems to be in strict agreement with the statement of Rosenheim and Woge, who also obtained these layers.

The material was transferred to a separatory funnel, and after eighteen hours the separation into two layers was complete. The two liquids were perfectly clear and of almost the same light green color. The lower, oily layer was just a shade the darker, and was very viscous. The oily layer was run into a crystallizing dish, and allowed to stand in the air. In a week spots of incipient solidification could be seen, and while under the microscope the spots showed something of a stringy, or thread-like, structure, yet, on the whole, the separation seemed to be more in the nature of a "skin" than of a group of definite crystals. After another week the whole mass had solidified to a hard, white, porcelain-like substance of very high lustre. The mass was perfectly homogeneous in appearance, except that the surface was light green. This was attributed to partial reduction, and the surface layer was rejected in selecting the samples for analysis.

The substance was analyzed by precipitation of the beryllium hydroxide with ammonia in the regular way. For the sake of greater convenience,

however, the molybdenum was determined volumetrically, by dissolving the material in water with a few drops of sulphuric acid, adding powdered zinc and sulphuric acid, and titrating the reduction product with potassium permanganate. A blank was run on the zinc, and applied in correction. The factor for molybdenum trioxide when the reduction is carried out in this way¹ was obtained by multiplying the iron value of the permanganate by 0.85714.

The following figures show the comparison between the results obtained and the theoretical percentage for the dihydrate of the normal salt:

BeMoO ₄ ·2H ₂ O.			
	Calculated.	Found.	
BeO.....	12.24	11.99	11.81
MoO ₃	70.21	68.68	68.64
2H ₂ O.....	17.55	19.33	19.55
	100.00	100.00	100.00

As a result of the method by which the substance was obtained it seems natural to suppose that some excess of water would be mechanically held by the material, and the high values for water, with corresponding depression in the values for the other constituents, is not surprising. A calculation of the molecular ratio of BeO/MoO₃ gives the figure 0.995. The analysis, together with this ratio, shows clearly that the material prepared is a normal beryllium molybdate dihydrate. This corroborates the statement of Rosenheim and Woge, and the ratio of BeO/MoO₃ shows no basicity, thus establishing their claim that in spite of the poor agreement in their analyses, they had really prepared the normal dihydrate.

Attempts to prepare the anhydrous molybdate recorded by Tanatar and Kurovski met with no success.

From the results of the experiments of Rosenheim and Woge, Tanatar and Kurovski, and the author, it seems that the exact product of the reaction between beryllium oxide (hydroxide or basic carbonate) and molybdenum trioxide depends largely on the particular conditions obtaining in the experiment.

The Solubility of Basic Beryllium Carbonate in Solutions of Normal Beryllium Salts.—The solvent action of solutions of normal beryllium salts on the hydroxide and basic carbonate of beryllium has been mentioned earlier in this paper. Parsons² made a study of the equilibria in the system BeO, SO₃, and H₂O, and concluded that no definite compound resulted from the solution, as the ratios of BeO to acid radical were in no case exactly integral. He states in a general way that 3BeO : SO₃ seems to be the limit of saturation in the most concentrated solutions.

¹ White, "Methods in Metallurgical Analysis," page 83.

² *J. Am. Chem. Soc.*, **26**, 1433.

Ordway¹ made some general statements as to the extent of solubility of the hydroxide in various salt solutions, but no definite figures were given.

It seemed worth while to get comparative figures for the solubility of beryllium base in solutions of several beryllium salts of equivalent concentration, to see whether any relationship existed between the solvent action and the nature of the salts, as figures of this kind are not to be found in the literature of this element.

For the purpose of comparison four salts were selected: the sulphate, the selenate, the chloride, and the bromide. Since the solvent action of the salts varies—though not in exact proportion—with the concentration, it was necessary to select one concentration for all the salts, in order that a basis for comparison might be had; and it was decided to set the normality of all the solutions equal to one.

Owing to the varying degrees of reactivity of beryllium hydroxide, depending upon degree of hydration, conditions of precipitation, temperature of drying, and other factors, some of which are not fully understood, it is essential for an investigation of this kind that one uniform source of beryllium base be selected and used in all the tests. After some trials with the hydroxide prepared in different ways it seemed evident that it was harder to prepare a stable, air-dry sample of this material, without too much heating, than it was to secure a uniform sample of the basic carbonate. Moreover the latter can be much more thoroughly washed, as well as more easily dried, than the hydroxide, and it was decided to employ an air-dry sample of the pure basic carbonate, which contained 42.13 % BeO.

As the accuracy of the analyses in this investigation was of utmost importance, it was essential that weighings should be accurate. A Troemner No. 10 analytical balance was used, and it was so adjusted that the readings were easily accurate to $\frac{1}{20}$ of a milligram. The weights were carefully calibrated. The weighing room was free from direct sunlight, free from jars, and almost constant in temperature.

Glassware used for volume measurements, and for making up solutions of definite strengths, was calibrated with all precautions, against weights checked with standards from the German Reichsanstalt.

Preparation of Materials.

Distilled Water.—All water used in final operations was made by redistilling the distilled water from the laboratory tanks. Barium hydroxide was added before the last distillation, and the operation was carried out under a vacuum of about 15 centimeters of mercury. A condenser of thoroughly seasoned block tin was used. For use in con-

¹ *Loc. cit.*

nection with the conductivity measurements the water was received and stored in one liter flasks of fully seasoned Jena glass. The laboratory air was replaced in these by air purified from carbon dioxide and other foreign gases, before the receivers were connected to the condenser, and soda-lime guard tubes prevented the access of laboratory air during the distillation. These flasks were closed with thoroughly cleansed paraffined corks, which carried a siphon tube having a glass stopcock, and a short glass tube ordinarily closed by a cap, but through which compressed air, purified by passing through three soda-lime tubes, was forced when it was desired to start the water in the siphon tube. The conductivity of each batch was tested before use, and was found as a rule to be between 1.0 and 1.3×10^{-6} .

Basic Beryllium Carbonate.—Merck's beryllium oxide was used as raw material, and it was found to contain alumina in considerable quantities, as well as iron and other impurities in smaller amounts. The impure oxide was dissolved in dilute sulphuric acid, the small insoluble residue filtered off, the clear filtrate, which had a slight yellow tinge, was boiled with nitric to insure complete oxidation of the iron, ammonia was added to alkaline reaction, and an excess of sodium bicarbonate crystals added, as suggested by Parsons.¹ The mixture was allowed to stand for two days and then filtered. In order to remove any iron which might have been dissolved with the beryllium a little ammonium sulphide was added. There was quite a precipitate of ferrous sulphide, showing that under the conditions here obtaining the iron is dissolved to a very appreciable extent by the sodium bicarbonate. The ferrous sulphide was filtered off, and the clear filtrate which contained the beryllium was largely diluted, after which the beryllium was precipitated as basic carbonate by passing steam through the solution. The precipitate was filtered and washed by decantation and suction, then rinsed back into the beaker, a large volume of cold water was added, and this was brought to the boiling point by passing steam through it. This method of washing was repeated three times and the basic carbonate was then well washed with hot water on the filter. After drying for ten hours at 90 degrees, the fine white powder was bottled for use as starting point in the preparation of the different pure beryllium salts. Parsons states that the basic carbonate prepared in this manner is pure with the exception of about 2% of occluded sodium salt. Since each salt must be analyzed after it has been prepared, and any impurity would be there detected, it was not thought necessary to test the purity of the basic carbonate.

Beryllium Sulphate Tetrahydrate.—The pure basic beryllium carbonate just described was dissolved in an excess of dilute sulphuric acid, filtered from shreds of filter paper, evaporated to dryness in a large platinum

¹ "Chemistry and Literature of Beryllium," page 4.

dish, and then heated over a free flame, at a temperature just sufficient to maintain fuming, until fumes of sulphur trioxide were copiously evolved. After cooling the residue, it was dissolved in water, filtered, evaporated in platinum until thick and just ready to crystallize, and then poured into 95% alcohol. After standing several hours the mother liquor was decanted, the fine crystal meal was washed with alcohol, redissolved in water, concentrated by evaporation, and again poured into alcohol. A third recrystallization by alcohol was made in the same way, and the crystals were then dissolved in highly purified water, evaporated in platinum to incipient crystallization, and the mass well stirred during the cooling so that the salt was obtained in the form of a very fine crystal meal. This was washed several times with alcohol, well drained by suction, and spread out on a watch glass to air-dry in a room where no other work was being carried on.

The salt was analyzed by making a double precipitation of the beryllium with ammonium hydroxide, using the filtrate for the determination of the sulphate in the regular way. The analysis next tabulated shows a satisfactory degree of purity for the salt.

$\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$.			
	Calculated.	Found.	
Be.....	14.17	14.12	14.26
So ₃	45.19	45.10	45.11
4 H ₂ O.....	40.64	40.78	40.63
	100.00	100.00	100.00

Beryllium Selenate Tetrahydrate.—Having on hand a good supply of selenious acid crystals the method selected for the preparation of beryllium selenate was to prepare silver selenite, from that, selenic acid by oxidation, and then to dissolve basic beryllium carbonate in the selenic acid, and crystallize out the salt.

The selenious acid was dissolved in water, silver nitrate solution added in slight excess, the precipitate of silver selenite well washed, suspended in water, bromine water added carefully until the supernatant liquid showed a slight color due to excess bromine, and the silver bromide then filtered off from the solution of selenic acid. The clear solution of the latter tinged yellow from bromine, was evaporated to small volume on the water bath, during which operation the color due to bromine was completely removed. Some pure basic carbonate of beryllium was dissolved in this selenic acid, and the solution concentrated by evaporation. The substance failed to crystallize, giving instead a reddish yellow, gummy mass. It being evident that an insufficient amount of selenic acid was present, this gummy mass was dissolved in more of the acid, evaporated to syrupy consistency, and poured into 95% alcohol. The action here was similar

to that in the case of the sulphate, a milkiness being first formed, and a well-crystallized precipitate being deposited on standing for several hours. The precipitate was indistinguishable from the sulphate under the microscope. The crystals were dissolved in water, in which they are extremely soluble, the solution concentrated by evaporation and poured into absolute alcohol. The crystals were well washed with absolute alcohol with the aid of suction and then air-dried. Absolute alcohol was used for the second precipitation and for the washing because it was found that the selenate was much more soluble in 95% alcohol than was the sulphate.

The air-dried sample of the selenate crystals was analyzed as follows: After solution in 50 cc. of water, 25 cc. of concentrated hydrochloric acid were added, and the solution gently boiled for one hour in a flask which was connected with a reflux condenser to prevent loss of selenium through volatilization of the acid. The solution, containing all the selenium now in the form of selenious acid, was saturated with sulphur dioxide in the cold, and then heated to boiling. The precipitated selenium was filtered on a Gooch crucible, washed with water, and then with absolute alcohol, dried at 105°, and weighed. The filtrate was again tested by passing sulphur dioxide, and boiling; and after being proved free from selenium, it was treated with ammonium hydroxide for the precipitation of beryllium hydroxide. The beryllium was weighed as oxide in the usual way. The following figures attest the purity of the beryllium selenate:

BeSeO ₄ ·4H ₂ O.		Found.	
	Calculated.		
BeO.....	11.19	11.24	11.25
SeO ₃	56.71	56.82	56.73
4 H ₂ O.....	32.10	31.94	32.02
	100.00	100.00	100.00

Beryllium Chloride.—Owing to the great difficulties and uncertainty connected with the preparation of pure beryllium chloride in the dry state it seemed best to prepare directly the solution of the salt by precipitation of barium sulphate from a solution of purest beryllium sulphate by the addition of the calculated amount of specially purified barium chloride.

The purest barium chloride dihydrate of commerce was dissolved in pure water, and acidified with a few drops of hydrochloric acid. The nearly saturated hot solution was filtered, and allowed to stand until precipitation had begun. Pure concentrated hydrochloric acid was then added to complete the precipitation, and the crystals were washed first with cold water, then with alcohol, and dried by suction. The crystals were again dissolved in purest water, and further purified by repeated recrystallizations with alcohol. The final product was dried in pure air at room tem-

perature, and then bottled. A sample of this material was placed upon a watch glass, weighed, and then exposed to the atmosphere for five hours. A second weighing showed exact concordance with the first, and the crystals were therefore in equilibrium with the atmosphere. Two samples of the material were analyzed by the approved methods, the details of which need not be given. The results follow:

BaCl ₂ ·2H ₂ O.			
	Calculated.	Found.	
Ba.....	56.23	56.22	56.19
2 Cl.....	29.03	29.01	29.04
2 H ₂ O.....	14.74	14.77	14.77
	100.00	100.00	100.00

This analysis showed the salt to be practically pure, and of the proper degree of hydration. 22.1450 grams of the beryllium sulphate tetrahydrate before described were weighed out and dissolved in conductivity water in a 250 cc. graduated flask. 30.5363 grams of the barium chloride crystals were then dissolved in water and poured into the flask, rinsing out the beaker quantitatively. According to de Schulten¹ the density of precipitated barium sulphate is 4.499, and this means that the amount produced in this operation would occupy 6.49 cc. This volume of water, therefore, was added to the flask after the contents had been diluted exactly to the mark. When the precipitate had fully settled the solution was filtered into a dry flask, through dry paper, discarding the first runnings to avoid any change of concentration due to adsorption by the filter. The solution so prepared was regarded as a normal solution of pure beryllium chloride.

Beryllium Bromide.—The statements as to the difficulty of preparing pure dry beryllium chloride apply with even greater force to the preparation of the bromide, and for this reason a solution of beryllium bromide was prepared in essentially the same manner as the chloride.

The barium bromide of commerce was repeatedly recrystallized from pure water to which a few drops of hydrobromic acid had been added, and the final crop of crystals was well washed with absolute alcohol, dried by suction and then air-dried to approximately constant weight. As a test of the equilibrium of the salt with the atmosphere, a sample of about 38 grams was left on a watch glass on the balance pan for an hour. At the end of this time a gain of 0.2 mg. in weight was observed, and the sample was then bottled and tightly corked. Two analyses showed the following results:

¹ *Compt. rend.*, 136, 1444.

BaBr ₂ ·2H ₂ O.		Found.	
	Calculated.		
Ba.....	41.22	41.15	41.10
2 Br.....	47.97	47.81	47.85
2 H ₂ O.....	10.81	11.04	11.05
	100.00	100.00	100.00

In view of the well-known fact that barium bromide is somewhat hygroscopic it is not surprising that the figures for water should be a little high, while those for the other constituents are correspondingly low. The fact that the sample gained a little in weight on exposure to the atmosphere leads to the anticipation of this discrepancy.

Since the analysis showed that these crystals contained only 88.96% BaBr₂, instead of the theoretical 89.19%, the amount of barium bromide found necessary by calculation for the precipitation of the beryllium sulphate was multiplied by the factor 89.19/88.96. The precipitation and dilution were carried out in exactly the same way as was described for the chloride, thus furnishing a normal solution of pure beryllium bromide.

The Solubility Tests.—The method of carrying out these tests was the same in all cases, and the details can be given once for all. A large water thermostat was maintained at 25°±0.2° day and night, by a gas regulator of the conventional toluene-mercury type. In the thermostat was set a shaft to which were attached six aluminum tubes fastened at their centers to the shaft, and perpendicular to it. One end of these tubes was left open for the introduction of the test-tubes, the end being closed by a cloth cap held in place by a rubber band after the test-tube had been introduced. The rotation of the shaft was operated by a motor, whose speed was stepped down so that the tubes made twenty-five revolutions per minute.

In making a test an excess of the dry basic beryllium carbonate was placed in the bottom of a dry test-tube, and the neck of the latter was then narrowed near the top by a small sharp blast flame. This could be done without appreciable heating of the carbonate in the bottom of the tube. When the neck had cooled, the normal solution of the salt under investigation was introduced by a pipette, and the neck of the tube was then sealed off. By this method there was no danger of leakage or of contamination from stoppers. After the tube had been agitated for a sufficient time it was removed from the case, wrapped in a thick cloth to prevent change of temperature while the neck of the tube was rapidly filed and broken off. The contents of the tube were then poured upon a dry filter, rejecting the first runnings, and the clear filtrate analyzed by suitable means. It is evident that the absolute volume of the solution taken

for analysis is of no importance, since the relation of base to acid is the thing to be determined.

A series of experiments made with the various salts as to the time necessary for the attainment of the full solvent action showed that in all cases the maximum solubility was reached within twenty-four hours, and this time was adopted as a standard for the tests. There was a little indication in the case of the sulphate that the solubility decreased just a little during very prolonged agitation (five days), but whether this observed difference was real or accidental must be the subject of later investigation.

The methods of analysis used in these determinations were the standard ones used in the analysis of the pure salts, so further description is unnecessary. The final weighing forms are indicated in the following table, in which are given the weights of the precipitates, and the ratios of beryllium to the respective acid radicals:

BeO. Gm.	BaSO ₄ . Gm.	Ratio $\frac{\text{Be}}{\text{SO}_4}$
0.0824	0.2840	2.70
0.1168	0.3998	2.72
BeO. Gm.	Se. Gm.	Ratio $\frac{\text{Be}}{\text{SeO}_4}$
0.0405	0.0404	3.16
0.0558	0.0552	3.19
BeO. Gm.	AgCl. Gm.	Ratio $\frac{\text{Be}}{2 \text{ Cl}}$
0.0928	0.4254	2.49
0.0991	0.4553	2.49
BeO. Gm.	AgBr. Gm.	Ratio $\frac{\text{Be}}{2 \text{ Br}}$
0.0995	0.6162	2.42
0.0979	0.6086	2.41

From these figures it will be seen that the solubility of the beryllium base is very different in equivalent solutions of the various salts, the selenate having the greatest solvent action, and the bromide having the least. The difference between the solvent action of the sulphate and selenate is far greater than that between the bromide and chloride. In the case of the bromide and chloride the observed difference is quite small, but it is believed to be far greater than the experimental error. Evidently no relation exists between the positions of the various acid-forming elements in their respective groups, and the solvent action of their salts.

As already pointed out, the action of the beryllium salts in dissolving beryllium hydroxide, liberating carbon dioxide from carbonates, and in some cases even attacking metals, suggests hydrolysis. Ley¹ and Brunner²

¹ *Z. phys. Chem.*, 30, 218.

² *Ibid.*, 32, 133.

has determined the percentage hydrolysis in solutions of the chloride and sulphate of beryllium, and from the results of Brunner in particular, we seem justified in assuming that the extent of hydrolysis of the chloride is about four times that of the sulphate, as the following table shows.

The figures are those determined by Brunner at 40° by the sugar inversion method, at various dilutions indicated by "v".

BeCl ₂ .		BeSO ₄ .	
v.	% hydrolyzed.	v.	% hydrolyzed.
12	2.1	4	0.52
20	2.2	12	0.58
40	2.2	20	0.68

It seems evident that hydrolysis plays no part in the solvent action of the beryllium salts, for the less hydrolyzed sulphate is a better solvent than the chloride, which undergoes hydrolysis to about four times the extent of that of the sulphate. In this connection it is worthy of note that the salts of iron and aluminum are hydrolyzed to a much greater extent than those of beryllium, yet the solvent action of the salts of these two elements on their hydroxides is far less than in the case of beryllium.

The Electrical Conductivities of the Salt Solutions.—In the hope that a determination of the relative degrees of ionization of the four salts might throw some light on this solvent action, the electrical conductivities of the salt solutions were determined.

No special description of the method and apparatus is needed. The well-known method of Kohlrausch, using the Wheatstone bridge, induction coil, and telephone receiver, was employed. The bridge wire was accurately calibrated, as had been also the Koehler resistance boxes. The conductivity water was prepared as described earlier in this paper, and its conductivity was deducted from that of the dilute solutions. The conductivity of this water was 1×10^{-6} . The solutions were kept in the thermostat at $25^\circ \pm 0.02^\circ$ during the measurements.

In the following table the Equivalent Conductivities of the four salt solutions are given. The dilutions are expressed in liters. Temperature 25°:

v.	BeSO ₄ .	BeSeO ₄ .	BeCl ₂ .	BeBr ₂ .
1	28.04	31.02	69.23	74.45
50	74.18	76.88	110.65	113.28
100	85.65	87.03	115.00	118.76
200	97.69	97.48	121.2	123.40
400	109.44	107.48	125.8	127.9
800	120.0	116.7	130.9	132.3
1600	128.0	124.0	135.0	136.0
$\frac{\lambda_1}{\lambda_{1600}}$	0.22	0.25	0.51	0.54

We are not entitled to look upon $\frac{\lambda_1}{\lambda_{1600}}$ as a true measure of the degree of ionization, since λ_∞ was not reached, and it is certain that the hydrolysis of the salts exerted a very great influence on the conductivity measurements; yet this ratio may perhaps be taken as at least an indication of the order of the ionization. From whatever angle viewed, however, it would seem that the order of ionization violates, and in an irregular manner, the order of the solvent power of the salts.

From this investigation, then, it is seen that no regularity has yet been observed between the solvent action of the normal salts of beryllium upon beryllium hydroxide or basic carbonate, and any of the properties of the salts, and my conclusions confirm those of Parsons, that there is in all probability no definite compound formed in these basic solutions, but that we are dealing with a case of simple solution. If these salt solutions act merely as physical solvents, it is not to be wondered at that the different solvents dissolve differing amounts of the beryllium base.

Summary.

In this paper an investigation has been made of the method for the preparation of metallic beryllium.

The vanadates of beryllium have been studied, and the hitherto unknown normal beryllium metavanadate tetrahydrate has been prepared. The basic nature of the mixture termed the vanadate by Berzelius has been shown.

Some study of the molybdates of beryllium was also made, and a substance which may be regarded as a definite basic beryllium decamolybdate, of formula $\text{BeMo}_{10}\text{O}_{31} \cdot 6\text{Be}(\text{OH})_2 \cdot 21\text{H}_2\text{O}$, was prepared. The existence of the normal beryllium molybdate dihydrate was confirmed. The anhydrous salt could not be prepared.

The solubility of basic beryllium carbonate in solutions of four typical beryllium normal salt solutions was studied, and exact figures for the relative solvent powers of normal solutions of the sulphate, selenate, chloride and bromide were established. Electrical conductivity measurements of the four salt solutions were made, and it was shown that in all probability there is no relation between the solvent power of the beryllium salts for the beryllium base, and the other properties of the salts, such as the degree of hydrolysis, the degree of ionization, position in the periodic groups, etc. Further evidence has been presented in support of the theory of Parsons that no definite compound results from the solution of beryllium hydroxide in solutions of normal beryllium salts, but that the phenomenon is one of simple solution, varying in degree with the particular salt used as solvent.

APPENDIX.

Since writing the record of my experience with the method of Fichter and Jablcznski¹ for the preparation of metallic beryllium, and criticising the recorded simplicity and ease of manipulation of the method outlined, there has come to my notice a second communication,—this one by Fichter and Brunner,² and received by the library on January 11, 1916, six months after that part of my paper had been completed. In this article the defects of the first method are acknowledged by giving directions which are said to overcome the very difficulties which I have pointed out in the early part of this paper. In the new method special emphasis is laid on the necessity for dehydrating the beryllium fluoride, and then adding the sodium fluoride in solid form, instead of dissolving the mixture of the carbonates of beryllium and sodium in hydrofluoric acid. By the process last outlined it is said that a melt which is perfectly soluble in water is obtained. Revised directions for heating the melt, and for current strength are also given. Finally, directions for the thorough trituration of the electrolyzed melt are given. This operation I have stated was absolutely essential to the even moderate success of the method. Lack of time and material renders it impossible for me at present to make experimental investigation of the newly proposed method.

¹ *Ber.*, 46, 1604.

² *Zeit. anorg. Chem.*, 93, 84.