(2) Both electromotive force measurements and chemical equilibrium determinations show that the effect of ferrocyanide in acidified solutions is proportional to the square of its concentration where theoretically it *should be proportional to the first power.*

Work on this problem will be continued.

In the experimental work of this paper I have been assisted by Mr. R. C. Pantermühl of this laboratory. I gladly take this occasion to express my appreciation of his assistance.

EQUILIBRIUM IN THE SYSTEM BeO : SO_3 : H_2O.

BY CHARLES LATHROP PARSONS.

Received August 9, 1904.

THE sulphates of beryllium were first studied by Berzelius in 1815,[1] although Vauquelin, in 1798,[2] had already produced a gummy basic sulphate. It was Berzelius who first found the necessary conditions to produce the neutral tetrahydrate, which he considered to be of an acid nature. He also produced basic substances to which he gave the formulas $3BeO.SO_3$, $2BeO.SO_3$ and $6BeO.SO_3 + 3H_2O$. Awdejew,[3] in 1842, first proved the neutral character of $BeSO_4.4H_2O$, carefully purified it and studied its properties in connection with his atomic weight determinations. Weeren,[4] in 1854, again used this salt for the same purpose and claimed that it loses one-third of its water of crystallization as low as 35°. Debray,[5] in the following year, used the properties of the basic sulphates as a means of separation from aluminum and states that the precipitated basic sulphate, on continued washing, left nothing but the hydroxide.

In 1869, Klatzo[6] took up the study of the sulphates and claimed to prepare the salt $BeSO_4.7H_2O$. Atterberg, 1873-74, in his extended study of the compounds of beryllium,[7] again prepared $BeSO_4.4H_2O$ and $BeSO_4.2H_2O$, and assigned the following formulas to the basic compounds prepared by him. $BeSO_4.Be(OH)_2$

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[1] Schweigger : *J. Chem. Phys.*, **15**, 296.

[2] *Allgem. Jour. der Chem. Scheerer*, **1**, 590.

[3] Pogg. *Ann.*, **56**, 101.

[4] *Ibid.*, **92**, 91.

[5] *Ann. chim. phys.* (3), **44**, 1.

[6] Inaugural dissertation, Dorpat, *Ztschr. Chem.*, **12**, 129.

[7] *Kongl. Svenska Vet. Akad. Hand.*, **12**, 1 ; also *Bull. Soc. Chim.* (2), **19**, 497, and (2), **21**, 157.

$+ 2H_2O$, $BeSO_4.2Be(OH)_2 + 2H_2O$, $BeSO_4.5Be(OH)_2 + 2H_2O$ and $BeSO_4.7Be(OH)_2 + H_2O$. Topsöe,[1] and Topsöe and Christiansen,[2] in 1873, studied the crystalline form, specific gravity, molecular volume and optical characters of $BeSO_4.4H_2O$. Thomson[3] determined its heat of solution. Nilson and Petterson[4] determined its molecular heat and specific gravity, and also that of the product obtained by drying at 250°, which they considered the anhydrous sulphate. Nilson and Petterson,[5] and Krüss and Moraht[6] again prepared and studied the hydrated sulphates and used the tetrahydrate in atomic weight determinations. The author[7] was unable to obtain satisfactory results from it for the atomic weight of beryllium, mainly owing to a slight but continuous loss of water over desiccating agents.

The following sulphates of beryllium have, therefore, more or less standing in chemical literature:

$BeSO_4$.
$BeSO_4.2H_2O$.
$BeSO_4.4H_2O$.
$BeSO_4.7H_2O$.

$BeSO_4.Be(OH)_2.H_2O$.
$BeSO_4.2Be(OH)_2.2H_2O$.
$BeSO_4.5Be(OH)_2.3H_2O$.
$BeSO_4.5Be(OH)_2.2H_2O$.
$BeSO_4.7Be(OH)_2.2H_2O$.

Attempts were made to prepare and study all of these substances and any other compounds containing the three components, BeO, SO_3 and H_2O, that might be formed under varying equilibrium conditions.

BERYLLIUM SULPHATE TETRAHYDRATE, $BeSO_4.4H_2O$.

Beryllium sulphate tetrahydrate is easily prepared when the components SO_3 and H_2O are in excess and should always be so made in practice. A very slight excess in solution of the BeO component will prevent the formation of the compound and only a non-crystallizable syrupy mass will result. In the presence of excess of sulphuric acid or the exact equivalent, it crystallizes readily. It is best prepared by dissolving beryllium carbonate or hydroxide in excess of moderately dilute sulphuric acid and evaporating to the crystallizing point. These crystals can then be

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[1] *Centrbl.*, 1873, p. 76.

[2] *Ann. chim. phys.* (5), 1, 5.

[3] *Ber. d. chem. Ges.*, **6**, 712.

[4] *Ibid.*, **13**, 1459.

[5] *Ibid.*, **13**, 1451.

[6] *Ann. chim. phys.*, **262**, 38.

[7] This Journal, **26**, 739.

purified by washing with strong alcohol, re-solution in water, evaporation to a syrup and turning, while hot, into excess of strong alcohol. The solution is at first colloidal, but after some hours the $BeSO_4.4H_2O$ crystallizes out almost completely. By repetition, the last traces of sulphuric acid may be removed; or, more quickly, beryllium oxide may be dissolved in concentrated sulphuric acid in a platinum dish and the excess of sulphuric acid be driven off by a Bunsen burner, held in the hand. Care must be used to heat but little higher than necessary to remove the excess of acid. The mixture of anhydrous sulphate with a little oxide, resulting from its own decomposition, is then treated with water and allowed to stand. While quite insoluble at first, the sulphate will have dissolved in the course of one or two days. Filtration from the undissolved oxide and crystallization yields a product of a fair degree of purity.

Beryllium sulphate tetrahydrate is stable in air having an aqueous vapor pressure equal to or greater than the pressure of its own water of crystallization. Tensimeter experiments show this pressure over phosphorus pentoxide at 20° to be equivalent to 20 mm. of olive oil and to increase rapidly with the temperature. At ordinary laboratory temperatures the pulverized salt slowly but surely lost water in a desiccator over phosphorus pentoxide. Many sets of weighings might be given, showing this slow but continuous loss, but as they bring forth no other fact they are scarcely worth entering in detail. The other properties of the tetrahydrated sulphate have been carefully determined by the authorities cited and need no repetition here.

BERYLLIUM SULPHATE DIHYDRATE, $BeSO_4.2H_2O$.

Beryllium sulphate dihydrate is easily prepared by heating the tetrahydrate to 100°. At this temperature it is fairly stable, but if kept in dry air from 100° to 110° it very slowly loses water. This loss is so slow that it would not be detected in ordinary work, but with sufficient time and careful weighing may be shown to be continuous. In dry air, at ordinary temperatures, it is quite stable. It has, in general, the same appearance and properties as the tetrahydrate.

ANHYDROUS BERYLLIUM SULPHATE, $BeSO_4$.

Two apparent methods present themselves for the preparation of this compound: First, by driving off the water of crystallization of the dihydrate, and second, by treating beryllium oxide with concentrated sulphuric acid. The first method was employed by Nilson and Petterson, who claimed it was rendered anhydrous at 250°. Such is, however, far from being the case, for water is given off at temperatures many degrees above this temperature. Repeated experiments, undertaken by me, have shown that there is no sharply defined line between the points where all water is driven off and where sulphuric anhydride begins to be evolved. In fact, they come off together through a considerable range of temperature. A product which is almost anhydrous and which has lost no sulphuric anhydride can be obtained near to the boiling-point of sulphuric acid. The second method, used by Lebeau,[1] is subject to the same objections, but to a less degree, if a very strong acid is used. It is next to impossible to evaporate the last traces of free acid and water resulting from its decomposition without decomposing a small amount of the sulphate, and I have never been able to make a sulphate in this manner which did not leave behind a small amount of insoluble residue after the main portion had been dissolved. The anhydrous sulphate is almost insoluble in water and is stable in dry air. It is gradually acted upon by cold water and more quickly by hot, and apparently has to be converted into the very soluble tetrahydrate before solution will take place. It certainly loses sulphuric anhydride as low as 400° and probably much below this temperature. The last traces are driven off only at a white heat.

BERYLLIUM SULPHATE HEPTAHYDRATE, $BeSO_4.7H_2O$.

Klatzo, in the course of his extended investigation on beryllium compounds, claimed to have produced the sulphate $BeSO_4.7H_2O$ and gives analyses of his product. From acid solution he first separated the normal sulphate $BeSO_4.4H_2O$ and then from a like mixture of substances by making more strongly acid and treating by long evaporation between 18° and 25° over sulphuric acid: first monoclinic crystals of a basic salt were thrown out and following them crystals of the normal $BeSO_4.7H_2O$, a truly astonishing sequence, especially when it is considered that by the evaporation the liquid phase was continually growing more concentrated in sulphuric acid and the higher hydrate was claimed to separate from this more strongly acid solution. Marignac[2] has already

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[1] *Compt. Rend.*, **123**, 818.

[2] *Ann. chim. phys.* (4), **30**, 45.

severely criticized certain parts of this investigation and certainly no other chemist has ever made the heptahydrate. A repetition of Klatzo's experiment, which was perhaps unnecessary, yielded nothing but the tetrahydrate. It can be safely stated that there is no evidence of the existence of $BeSO_4.7H_2O$.

Variously modified conditions have failed to yield any other definite sulphates of beryllium than those already mentioned.

BASIC COMPOUNDS.

The normal salts of beryllium are, in general, strongly acid to litmus when in solution and act like acids toward many substances, being acted upon by zinc and some other metals with evolution of hydrogen. They all dissolve large quantities of beryllium hydroxide and carbonate, evolving the carbon dioxide in the latter instance. The quantities of hydroxide or carbonate dissolved are proportional to the concentration in very strong solution, although this is not so apparent when the solutions are dilute. The extent of possible saturation varies with the acid used, but is usually as much as three equivalents of beryllium to one of the acid radical, and in the case of the acetate is nearly six. The addition of water to some of these basic solutions throws down immediately precipitates of a more highly basic character, non-crystallizable and of a gummy nature. On drying at 100° these precipitates are glassy and show no evidence of definite structure under the microscope. The remaining solution itself is also basic in character and its basicity depends on the dilution until a point is reached where the further addition of water throws out no further precipitate. On evaporation, the residues obtained are also gummy non-crystallizable masses and are physically undistinguishable from the basic precipitates except by the fact that they are soluble in water. The precipitates, on washing, continually grow more basic and rapidly approach the hydroxide in composition, although I have never been able to entirely eliminate the acid. To the precipitates themselves and to the residues left in solution, various formulas have been given. As they themselves are never definite in composition it is not strange that different chemists have seldom agreed as to the formulas assigned.

A lack of appreciation of the strong hydrolyzing action of water on beryllium compounds has caused many investigations to fail and has added many beryllium compounds to the literature which have no existence in fact. Still the normal salts themselves are but slightly dissociated, as Leys[1] and Bruner[2] have shown. In fact, they are not nearly so much dissociated as the corresponding salts of aluminum and iron, which possess the same power in a very much less degree of dissolving their hydroxides and precipitation by water.

This property of beryllium has led to much confusion in its literature, and in the opinion of the author, based upon an examination of many of these so-called basic compounds and upon the results which follow, it is very doubtful if any definite basic compounds of beryllium have been made in which beryllium is the only metal present, with the exception of the basic acetate of Urbain and Lacombe.[3] and others of the same group, as prepared by Lacombe.[4] These latter are a truly wonderful series of compounds, basic in nature, yet made in anhydrous acid. They, too, are hydrolyzed by water and then lose their crystalline character and definiteness of composition. Most of the so-called basic compounds are probably solid solutions of the hydroxide with the normal salt. Precipitated by water the hydroxide occludes large quantities of the normal salt, much of which can be removed by washing, but which, in turn, dissolves and carries some of the hydroxide with it as it is washed out. It is hoped to study more of the precipitates by phase-rule considerations and to arrive at some conclusion regarding the nature of the basic solutions through a study of the migration of the ions and the effect upon the freezing-point.

BASIC BERYLLIUM SULPHATES.

Of the basic sulphates already enumerated as claimed by Berzelius and Atterberg, those of a dibasic and tribasic nature are considered as soluble sulphates, it being possible to dissolve them while the hexabasic and octabasic sulphates are precipitated from the soluble basic sulphates by dilution with water.

SOLUBLE BASIC SULPHATES.

When neutral beryllium sulphate is treated with the basic carbonate, carbon dioxide is evolved and an amount of the base is dissolved, depending on the concentration of the solution. If the

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[1] *Ztschr. phys. Chem.*, **30**, 218.

[2] *Ibid.*, **32**, 133.

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

[4] *Ibid.*, **134**, 772.

solution of the basic sulphate is fairly concentrated (about 1 : 3), the final saturation ratio of base to acid is as 3 : 1. If the solution is quite dilute (1 : 1000) this saturation ratio does not usually exceed 1.5 : 1. Solutions have, however, been obtained by washing the insoluble basic sulphates having as high a ratio as 2.1 : 1, which were apparently not altered by dilution, while others of a less basicity have thrown out small amounts of the insoluble compounds. The conditions causing this variation have not been determined. A very small amount of carbonate dissolved in the normal sulphate takes from it its power of crystallization on evaporation. Accordingly, a substance of any degree of basicity up to tribasic can be produced by evaporation of the corresponding solution and drying the residue. Several of these substances have been produced and analyzed. They separate as gummy glucose-like masses, which, on drying at 100°, are still soft, but on cooling become glassy, hard and brittle, and can be easily pulverized. On heating over a Bunsen burner they swell up to an immense volume, losing water and yielding a glistening foamy mass, which, if ignited over the blast-lamp, is reduced to oxide. The powder itself can be dissolved in a minimum of water depending on its basicity and the solution, if precipitable by water, may be diluted to an amount inversely proportional to its basicity before the more highly basic sulphates, soon to be considered, are thrown out. The less basic are similar in composition, physical and chemical properties with the sulphates left in solution when the more basic of these substances are, by the hydrolytic action of water on dilution, separated into a soluble and an insoluble constituent. The tribasic sulphate is simply the limit of saturation, the dibasic the half-saturated solution at full concentration. There is no other reason at present to consider them as definite compounds, for the ratio base to acid in fully precipitated solutions is seldom, if ever, exactly 2 : 1, as supposed by Berzelius and Atterberg. On drying at 100° the amount of water left is generally in excess of the theoretical amount necessary to produce the hydroxide, but this has little significance, as the gummy character of the substances makes their complete drying improbable.

The following analyses of these soluble basic powders will serve as examples. Many others were made. Nos. 1 and 2 are of the saturated concentrated solution; Nos. 3 and 4 of the soluble residues after apparently complete precipitation. Their difference is quite probably due to variation of temperature, as no thermostat was used in this preliminary work.

No.	BeO. Per cent.	SO_3. Per cent.	H_2O. Per cent.	Approximate ratio.
1	30.09	32.94	36.97	$3BeO : SO_3 : 5H_2O$.
2	29.98	33.26	36.76	$3BeO : SO_3 : 5H_2O$.
3	21.00	44.50	34.50	$1.5\ BeO : SO_3 : 3.5\ H_2O$.
4	24.56	43.26	32.18	$1.8\ BeO : SO_3 : 3H_2O$.

The saturated sulphate is still slightly acid to litmus and has a slightly sweetish acid taste. It does not show any hydrolyzing action on sugar solution. In fact the H ions which are present to a slight extent in a solution of the normal sulphate (0.02 mol per mol of $BeSO_4$ in 0.2 molar solution) are thrown back long before the dibasic condition is reached. The soluble basic solutions are unaffected by dialysis.

INSOLUBLE BASIC SULPHATES.

If a sufficiently basic solution of beryllium sulphate is diluted with water, precipitates of much greater basicity than the dissolved sulphates are thrown out. The necessary amount of dilution depends upon the basicity. If the tribasic solution is used, there are three distinct precipitations, the different stages of which are probably more apparent than real, since the precipitates themselves vary little in composition. The point of the beginning of each precipitation and its end are not sharp, so that only very rough approximations of the necessary dilutions can be given, but the periods between the different precipitates where the further addition of water caused no apparent effect are prolonged and not to be mistaken. The extent to which this hydrolytic action proceeds is truly remarkable.

The two following experiments will lead to a better understanding of exactly what takes place. The tribasic solution used was prepared by adding an excess of basic beryllium carbonate to a 10 per cent. solution of the neutral sulphate or to a corresponding amount of sulphuric acid and evaporating on the water-bath. Under these conditions the carbonate is dissolved until the tribasic conditions are reached. At this point a reaction sets in between a part of the soluble tribasic sulphate and the remaining carbonate by means of which the latter loses all of its carbon dioxide and forms a gum-like insoluble basic substance, of similar composition to those precipitated by water. The evaporation should not be carried too far, for if the solution becomes thick and syrupy it will be difficult to separate from the gummy residue and it can not be diluted. If this precaution is observed, the solution of the tribasic sulphate can be easily decanted from the residue.

(1) Three cc. of a syrupy solution, showing, on analysis, a ratio of $3BeO : SO_3$ was diluted with water at laboratory temperature. Precipitation was not permanent until about its own volume of water was added. Further addition of water threw down a voluminous white precipitate which momentarily appears gelatinous, but soon becomes snow-white and flocculent. Precipitation was complete before 50 cc. of water had been added. The precipitate was filtered, washed once and the solution further diluted without apparent effect to 400 cc., when it became milky, and on the further addition of water a second flocculent precipitate, resembling the first, but much less in amount, was thrown out. This second precipitate was washed once with a few cubic centimeters of water, the washings, as in the first instance, being added to the filtrate. Again on addition of pure water there was no apparent action until 1200 cc. in volume was attained when the solution again became slightly milky. This third precipitate does not easily gather together and, in fact, in repetition of this experiment it has not made itself manifest until the solution has stood some hours. On boiling down the solution the milkiness disappeared and was gradually replaced by a fine granular precipitate adhering firmly to the beaker, especially where it had been rubbed with a glass rod. To the unaided eye it exactly resembled ammonium magnesium phosphate, but under the microscrope showed an entire lack of crystalline structure, as did also the first two precipitates. The relative quantities of beryllium oxide in each precipitate and of that left in solution were as follows:

	Per cent.
First precipitate	29.37
Second precipitate	7.63
Third precipitate	10.78
Left in solution	52.22

(2) Approximately 2 grams of a basic sulphate showing, by analysis, a ratio of $2.3BeO : SO_3$ was dissolved in water and di-

luted. No precipitation whatever occurred until 50 cc. of water had been added, after which the precipitates came down in order as in the experiment already cited and, after the first, at about the same degree of dilution. The relative amounts of the beryllium oxide in each fraction were as follows:

	Per cent.
First precipitate	10.45
Second precipitate	5.37
Third precipitate	10.71
In solution	73.47

It will be seen at once that none of the residues left in solution after any precipitation could have been in the exact ratio of $2BeO : SO_3$.

The last precipitate being gathered together in large excess of water at the boiling temperature was more basic in character, even as high as 23 : 1, but was variable and differed little from the first two when they were subjected to the same treatment. Many analyses were made and the first two precipitates, when dried by pressure between filter-papers, also showed, on analysis, a variable composition. In no case was a basic ratio obtained as low as that given by Atterberg of 8 : 1. When freshly prepared they showed a ratio varying between 9 : 1 and 12 : 1, and the ratio was seldom one of whole numbers. On washing, they grew rapidly more basic in character and in one instance, a precipitate washed continuously for several weeks, reached a ratio as high as $35BeO : 1SO_3$. It appeared almost impossible, however, to remove the last traces of sulphuric anhydride by washing.

It was early apparent that the precipitates could not be separated from the mother-liquor for purposes of analysis and that it was by no means certain that a single basic salt or two different salts might not be present which were themselves decomposable by water. Fortunately the question can be settled by means of the phase-rule of Gibbs, and the conditions of its applicability to such problems as the identification of individuals in a mixture of basic salts with the mother-liquor have been most clearly pointed out by Miller and Kenrick,[1] and applied by Allen[2] and others.

In this case we have a system consisting of three components and if these have arrived at equilibrium at a fixed temperature and

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[1] *Trans. Roy. Soc. of Canada*, **7**, III, 35.

[2] *Am. Chem. J.*, **25**, 308; **27**, 284.

pressure, the chances of having more than three phases (not considering the gaseous phase) are negligible. Thus in a series of experiments, if the mother-liquors have a constant concentration while the precipitates vary in composition when equilibrium is reached, then the precipitate is a mixture of two solid phases. If the mother-liquors vary in concentration while the precipitates have the same composition then the precipitate is a single chemical compound. If the precipitates and mother-liquors both vary in composition then the precipitate is a "solid solution," *i. e.,* a single solid phase of variable composition.

In order to study this question a series of experiments was carried out in a large, specially constructed thermostat, in which the solutions were agitated continuously in contact with the precipitates for several weeks at 25°. The experiment began on November 19, 1903, and the first samples of the mother-liquor were drawn for analysis on November 29th. Like samples were taken on December 7th and it being evident that equilibrium had been reached, all were sampled for analysis on December 10th. The thermostat was, however, kept running and on December 23rd further determinations were made which confirmed the previous condition of equilibrium. During the analyses it was noted that further precipitation took place on diluting the members of Groups III and IV, and in one or two instances in the other groups. It did not take place in Group V. The BeO and SO_3 are present in Groups I and II in the proportion of $3BeO : SO_3$; in Groups III and IV in the proportion of $2BeO : SO_3$; in Group V in the proportion of $6BeO : SO_3$; in Group VI in the proportion of $4BeO : SO_3$. The results follow:

		Taken.			Found.		
Group.	No.	Grams BeO.	Grams SO_3.	Grams H_2O.	Grams BeO in 10 cc. solution.	Grams SO_3 in 10 cc. solution.	Grams BeO / Grams SO_3 in solution.
	1	0.7560	0.3000	50	0.0802	0.1473	0.54
	2	1.1340	1.2000	50	0.1216	0.2147	0.57
I	3	1.5120	1.6000	50	0.1627	0.2844	0.57
	4	1.8900	2.0000	50	0.1995	0.3500	0.57
	5	2.2680	2.4000	50	0.2437	0.4193	0.58
	6	0.7560	0.8000	100	0.0382	0.0738	0.52
	7	1.1340	1.2000	100	0.0613	0.1142	0.53
II	8	1.5120	1.6000	100	0.0813	0.1457	0.56
	9	1.8900	2.0000	100	0.1014	0.1811	0.56
	10	2.2680	2.4000	100	0.1231	0.2132	0.58

		Taken.			Found.		
Group.	No.	Grams BeO.	Grams SO_3.	Grams H_2O.	Grams BeO in 10 cc. solution.	Grams SO_3 in 10 cc. solution.	$\frac{\text{Grams BeO}}{\text{Grams } SO_3}$ in solution.
III	11	0.5040	0.8000	50	0.0943	0.1536	0.61
	12	0.7560	1.2000	50	0.1400	0.2269	0.61
	13	1.0080	1.6000	50	0.1867	0.3002	0.60
	14	1.2600	2.0000	50	0.2293	0.3731	0.62
	15	1.5120	2.4000	50	0.2785	0.4622	0.60
IV	16	0.5040	0.8000	100	0.0462	0.0776	0.60
	17	0.7560	1.2000	100	0.0703	0.1159	0.61
	18	1.0080	1.6000	100	0.0942	0.1517	0.62
	19	1.2600	2.0000	100	0.1177	0.1925	0.61
	20	1.5120	2.4000	100	0.1394	0.2268	0.61
V	21	5.2920	2.8000	50	0.1710	0.4316	0.40
	22	5.2920	2.8000	100	0.0876	0.2241	0.39
VI	23	3.5280	2.8000	50	0.2360	0.4648	0.51
	24	3.5280	2.8000	100	0.1239	0.2432	0.51

A glance over the preceding figures will show at once that the concentrations of the mother-liquors vary widely and, therefore, the precipitates can not consist of a mixture of two definite basic salts. Other conclusions to be drawn are that an increase in the relative amount of BeO present diminishes the necessary amount of water to cause precipitation and also the basicity of the mother-liquors; that the concentration of the mother-liquors on equal dilution is directly proportional to the initial amount of the basic substance present and that a dilution from 50 to 100 cc., with the quantities present, does not appear to have caused further precipitation, since the ratio of base to acid is little, if any, changed. This last is in accord with the preliminary experiments and would seem to confirm the fact of the precipitation at different stages, which is difficult to understand. Further, a comparison of 1 and 11, 6 and 16, 21 and 23, and other corresponding numbers throughout shows that while an increase in the BeO present diminishes the ratio of BeO : SO_3 in solution it diminishes the total amount of SO_3, and in a greater relative proportion. This would tend toward similar composition for the precipitates, which is borne out by the results to follow.

It was hoped in the earlier stages of the work that the composition of the precipitates could be determined by calculations based on the amounts of material originally present and the amounts left in solution. This was found not possible from the facts that the precipitates carried so little sulphuric anhydride, and in the case of Groups III and IV, while always present, were very small in amount. Consequently any error in the analyses of the portion of the solution taken, or in the determination of its fractional quantity, was many times multiplied in the calculation and made any conclusion as to the composition of the precipitates out of the question. The precipitates were, therefore, freed from the mother-liquors as completely as possible, were pressed between filter-paper so long as liquid was absorbed and were dried for several days to constant weight at 100° in air, free from carbon dioxide. The analyses of ten of these precipitates follow. The others were not analyzed, some being obtained in too small quantity for accurate work.

No.	BeO. Per cent.	SO_3. Per cent.	H_2O by difference. Per cent.
1	53.9	6.9	39.2
2	53.8	6.8	39.4
3	52.3	7.2	40.5
6	53.1	7.3	39.6
7	53.2	..	...
9	...	6.1	...
21	53.6	6.5	39.1
22	53.4	5.8	40.8
23	53.5	7.2	39.3
24	53.2	7.5	39.3

It will be seen at once that all of these precipitates contained notable quantities of sulphuric anhydride and much more than could be accounted for from any possible adhering mother-liquor. The presence of the small amount of mother-liquor introduces a slight unavoidable error, the effect of which is, however, to give a resultant solid less basic than the actual. The results themselves, taken literally, lead to formulas varying from $22Be(OH)_2.BeSO_4$ to $28Be(OH)_2.BeSO_4$, with a slight excess of water in every instance. The analyses are, however, subject to error and a slight error evidently has large effect in the calculation of such highly basic formulas. The possibility of the presence of two definite basic salts having been eliminated by the variation in concentration of the solutions, two propositions alone remain to us. First, that the precipitates are a single solid phase of definite composition which would prove the presence of a basic salt of a basicity of at least $25BeO$ to $1SO_3$, or that the precipitates vary in composition and, therefore, are solid solutions containing a small amount of the sulphate in the hydroxide. In view of the well-known property of hydroxides to carry down other substances with them when precipitated and the utter improbability of any molecule of so large a ratio of base to acid, the latter conclusion seems justifiable.

I am pleased to acknowledge the efficient help of my assistant, Mr. H. B. Pulsifer, who did much of the analytical work and of Mr. M. A. Stewart, who determined the extent of hydrolysis of the normal sulphate in solution and the effect upon the amount of $\overset{+}{H}$ ions present obtained by saturating the same solution with its own carbonate.

The following conclusions seem warranted:

That the only known definite hydrated sulphates of beryllium are $BeSO_4 + 4H_2O$ and $BeSO_4 + 2H_2O$.

That the anhydrous sulphate $BeSO_4$ is difficult to produce entirely free from water or excess of oxide, owing to the difficulty of removing the last traces of water without at the same time driving off sulphuric anhydride.

That the so-called basic sulphates of beryllium do not exist as separate and definite chemical compounds, but are in reality solid solutions of the sulphate in the hydroxide. These are much more basic in composition when equilibrium with the mother-liquors is reached than when first precipitated.

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ON THE MOLECULAR DEPRESSION CONSTANT OF *p*-AZOXYANISOL.

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Received August 1, 1904.

GATTERMANN and Ritschke[1] first prepared *p*-azoxyanisol and found that at 116° it passed into a turbid liquid of fluid crystals, which at 134° became a clear, transparent yellow liquid. Schenck,[2] in studying the compound, showed that both these transition points undergo abnormally large depressions, and from the depression of the "clear-turbid" transition point by seven

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[1] *Ber. d. chem. Ges.*, **23**, 1738.

[2] *Ztschr. phys. Chem.*, **25**, 349.