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EQUILIBRIUM IN THE SYSTEM BERYLLIUM OXIDE, OXALIC ANHYDRIDE AND WATER.

By Charles L. Parsons and Wm. O. Robinson.

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I. THE OXALATES OF BERYLLIUM.

The attempts of Vauquelin, 1798,[1] and of Debray, 1855,[2] to prepare the normal oxalate of beryllium resulted only in the formation of an indeterminate gummy mass. Their failure was due to the fact, only recently fully comprehended, that definite crystalline compounds of beryllium can be made only when exact equivalents of anion and cation are present or when there is an excess of the acid component. Atterberg, 1873,[3] had the same experience but gave the formula $BeC_2O_4.Be(OH)_2.H_2O$ to the gummy mass first obtained and $BeC_2O_4.6Be(OH)_2.6H_2O$ to the highly basic precipitate obtained by diluting the solution of the first with a large excess of water. Rosenheim and Woge, in 1897,[4] first prepared the normal oxalate $BeC_2O_4.3H_2O$ and described an acid salt, $2BeC_2O_4.H_2C_2O_4.5H_2O$, which, if it exists, is the only acid salt of beryllium known, with the possible exception of some very doubtful acid selenites described by Nilson,[5] the also doubtful acid arsenate and phosphate of Atterberg[6] and Scheffer's[7] acid

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[1] Allgem. J. Chem. 1, 590.

[2] Ann. chim. phys. [3] 44, 37.

[3] Kgl. Svenska Akad. Handl. 12, 51.

[4] Z. anorg. Chem. 15, 283.

[5] Bull. soc. chim. [2] 23, 355.

[6] Ofvegt. Akad. For. (Stockholm) 1875, No. 7, 33.

[7] Ann. 109, 144.

phosphates. Wyrouboff[1] confirms the results of Rosenheim and Woge as to the normal oxalate, although he claims for it the formula consistent with the completely discredited trivalency of beryllium. With the exception of Vauquelin all of the above-mentioned investigators, as well as Philipp,[2] made well-characterized double oxalates with the alkaline metals, but these double oxalates have no connection with the present paper.

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

$BeC_2O_4.H_2O$
$BeC_2O_4.3H_2O$
$2BeC_2O_4.H_2C_2O_4.5H_2O$
$BeC_2O_4.Be(OH)_2.H_2O$
$BeC_2O_4.6Be(OH)_2.6H_2O$

Attempts were made by us to prepare and study all of these substances and any other compound containing the three components, BeO, C_2O_3 and H_2O, that might be found under varying equilibrium conditions.

Purification of Material.—Previous work by one of us[3] had shown that the basic acetate of beryllium, discovered by Urbain and Lacombe,[4] possessed decidedly characteristic properties which might be applied to separating beryllium from aluminum and iron, the only two elements which present any real difficulty. It is easily sublimed and is soluble in glacial acetic acid, benzene, toluene, chloroform, all petroleum distillates, alcohols, ether, carbon disulphide, carbon tetrachloride, acetone, etc., to a greater or less extent. Iron and aluminum form no similar compound, and Haber and Van Oordt[5] have already proposed to separate their normal acetates from the basic acetate of beryllium by means of the solubility of the latter in chloroform. Parsons[6] has shown that glacial acetic acid is itself, when hot, a most excellent solvent for the basic acetate of beryllium, allowing the basic acetate to crystallize out on cooling in beautiful octahedra. We tried the effect of many solvents but found that none of them compared with glacial acetic acid for ease of manipulation and recrystalliza-

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[1] Bull. soc. franç. min. 25, 71.

[2] Ber. 16, 752.

[3] Parsons: This Journal, 26, 721.

[4] Compt. rend. 133, 874.

[5] Z. anorg. Chem. 40, 465.

[6] This Journal, 26, 738.

tion of the product, and since the small amounts of the acetates of iron and aluminum, which are soluble in this reagent when hot, are not precipitated on cooling it, offered a ready means of purification.

Commercial beryllium hydroxide, containing notable quantities of iron and aluminum, was dissolved in acetic acid, evaporated and dried. The pulverized residue was boiled with glacial acetic acid and filtered through a funnel surrounded by a steam coil. On cooling, small octahedra of basic beryllium acetate separated in quantity. These were collected on a Buchner funnel and washed twice with cold glacial acetic acid. The residue was retreated with the same acetic acid. This can not be done continuously for the reason that the beryllium acetate first formed by solution of the hydroxide and evaporation always undergoes hydrolysis so that the residue, no matter how carefully dried, always contains beryllium hydroxide and yields more or less water to the glacial acetic acid. The presence of water, except in very small quantities, is fatal to the formation of the basic acetate, and even in small quantities causes a loss of beryllium in the mother-liquors. This can be recovered, however, by evaporation and retreatment. The crystals of beryllium basic acetate were recrystallized from glacial acetic acid and obtained pure. Some of this basic acetate was sublimed for further purification, but this was found to add but little to the quality of the product.

By far the most convenient compound of beryllium to use in the laboratory as a basis for the preparation of other compounds is the basic carbonate. Although of indefinite composition an analysis of any given preparation is easily made by simple ignition in platinum. To prepare this substance the basic acetate was hydrolyzed by hot water and dissolved by the addition of a slight excess of pure acetic acid. It was then precipitated by ammonia, filtered, dissolved in ammonium carbonate and precipitated by boiling with steam. The perfectly white and granular precipitate was washed and dried.

Analysis gave $BeO = 43.03$ per cent. and 43.08 per cent.

Beryllium Oxalate Trihydrate, $BeC_2O_4 + 3H_2O$.—Basic beryllium carbonate was treated with a slight excess above the equivalent amount of oxalic acid and dissolved readily with effervescence. On evaporation, needle-like crystals of oxalic acid separated out first and were removed. On further evaporation, orthorhombic crystals of a beryllium oxalate were deposited which contained notable quantities of oxalic acid. These crystals were dissolved and recrystallized, rejecting again the needle-like crystals of oxalic acid first deposited, and this operation was repeated nine times without securing crystals free from occluded oxalic acid. The separation is rendered very difficult, if not impossible, from the comparatively great solubility of both substances and from the fact that, at ordinary temperatures at least, they differ but little in solubility.

Analyses of the last five crops of crystals showed the following composition.

	BeO.	C_2O_3.	BeO/C_2O_3.
5	15.05	49.06	1.18
6	15.43	49.41	1.12
7	15.35	48.61	1.11
8[1]	16.90	51.87	1.07
9	15.85	48.68	1.06

Both Rosenheim and Woge[2] and Wyrouboff[3] claimed to obtain two forms of crystals of the normal oxalate of beryllium, the first needle-like and the second in plates. It is noteworthy that we were able to obtain only the latter form of crystals, and that invariably the first crops of these were mixed with needle-like crystals easily separated under the microscope and which proved to be oxalic acid in every instance. We were also unable to secure the pure oxalate by the method they used.

The pure normal oxalate was obtained in beautiful orthorhombic crystals by adding to the slightly acid oxalate of the ninth recrystallization the exact amount of basic beryllium carbonate necessary to neutralize the occluded oxalic acid. The crystals gave, on analysis, the theoretical composition of $BeC_2O_4.3H_2O$.

Great care was necessary that no excess of the carbonate be used or the oxalate would not crystallize but would simply evaporate to a thick, gummy glucose-like mass. So small an excess as 0.1 per cent. of the oxide completely prevented crystallization, and this apparently small amount added for experimental purposes must in reality have been larger than necessary for attempts to recrystallize the pure oxalate itself

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[1] 8 had lost some of its water of crystallization.

[2] Z. anorg. Chem. 15, 283.

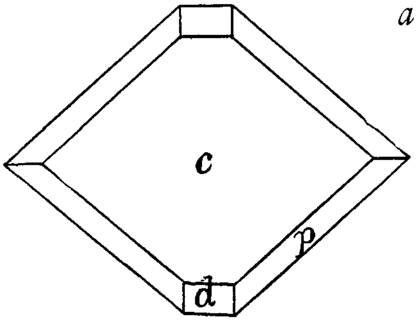
[3] Bull. soc. franç. min. 25, 71.

failed in several instances until a drop of oxalic acid solution was added, apparently from no other reason than a slight loss of oxalic acid when the crystals were dissolved in hot water and evaporated on the steam-bath. The addition of small crystals of the normal oxalate to the uncrystallizable mass in no wise affected the result.

Beryllium oxalate is stable at room temperature. It is soluble in less than its own weight of water at 100° and is but little less soluble at ordinary temperatures. It is strongly acid in reaction, like all normal salts of beryllium, has a rather sharp, sweet taste and is easily decomposed by heat. It readily dissolves a large amount of its own carbonate, forming liquid and solid basic solutions as later described.

Through the courtesy of Prof. Samuel L. Penfield and Mr. F. H. Heath, who most kindly examined the crystals for us, we are able to add the following crystallographic characteristics.

Crystals of $BeC_2O_4.3H_2O$.—The crystals are orthorhombic, and the accompanying projections show the general development. The forms are as follows: *c* (001), *d* (101) and *p* (111).



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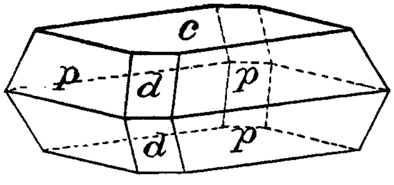

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The crystals were not very well suited for measurement with the goniometer, but the best ones were selected and the following observations made:

$p \wedge p'''$, $111 \wedge 1\bar{1}1 = 74° 16'*$
$p \wedge p'$, $111 \wedge \bar{1}11 = 90° 6'*$
$c \wedge p$, $001 \wedge 111 = 68° 30'$.
Calculated, 68° 20'.

The measurements marked by an asterisk yield the axial ratio $a:b:c=0.853:1.0:1.645$.

The *d* faces were so small and poorly developed that no satisfactory reflections could be obtained from them. On a second crop of crystals the *d* faces were absent and there was a greater development of the basal plane than shown in the accompanying figures, the crystals appearing as flat tables with beveled edges.

No distinct cleavage was observed. With a tabular crystal examined under the polariscope, it was seen that the *c* axis was a bisectrix, and that the plane of the optical axes was the brachypinacoid. The interference figure was, however, very indistinct and the axial angle was so large that the hyperbolas opened out beyond the field of view.

Beryllium Oxalate Monohydrate, $BeC_2O_4+H_2O$.—This oxalate is easily prepared by heating the trihydrate to 100–105°, at which temperature it is stable as well as at lower temperatures, if in dry air. Heated much above these temperatures it begins to lose water slowly but more rapidly as the temperature approaches 220°, about which temperature the oxalate begins to decompose, and at 350° is completely converted into the oxide. There is no apparent stage between the formation of the anhydrous oxalate and its decomposition, but decomposition sets in before all the water is driven off as in the case with the sulphate.

Acid Beryllium Oxalate.—The acid oxalate described by Rosenheim and Woge[1] could not be prepared although their directions were carefully followed and modifications tried. A single experiment is characteristic. Beryllium carbonate was dissolved in twice its equivalent of oxalic acid and subjected to fractional crystallization over sulphuric acid. The crystals of the first three crops were long and needle-like and gave no tests for beryllium. The fourth crop contained two forms, one long and needle-like, the other in orthorhombic plates. They were carefully separated under the microscope and the former proved to be only oxalic acid. In no case could a beryllium oxalate be obtained, after mechanically separating the admixed oxalic acid, that con-

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[1] Z. anorg. Chem. 15, 283.

tained a ratio of C_2O_3 to BeO greater than 1.18 to 1, due to occlusion of oxalic acid, while the crystals described by Rosenheim and Woge were assigned the formula $2BeC_2O_4.H_2C_2O_4.5H_2O$.

It had been our expectation to examine this oxalate in contact with its mother-liquors in a thermostat, as was done with the basic precipitates, to be described later, for the concentration of the mother-liquors would have shown at once whether it was a single phase or mixed crystals but the fact that the mixed crystals could be so easily separated mechanically under the microscope rendered this part of the work entirely unnecessary. We were unable to procure any single phase which even approached the acid oxalate of Rosenheim and Woge. The further consideration that no other well-authenticated acid salt of beryllium is known leads us to the conclusion that the existence of an acid oxalate of this metal is highly improbable.

Basic Beryllium Oxalates.—One of us[1] has already pointed out the property possessed by solutions of any of the salts of beryllium of dissolving large quantities of beryllium hydroxide giving rise to solutions decidedly basic in character, although acid in reaction, and which for the most part are precipitated by dilution with water after a certain concentration of the BeO component has been reached. The oxalate is perfectly analogous to the sulphate[2] in this respect, giving rise to both soluble and insoluble basic substances of indefinite composition.

Soluble Basic Oxalates.—If a hot saturated solution of oxalic acid is treated with an excess of basic beryllium carbonate or hydroxide, it dissolves the basic component until a concentration of 2.85 BeO to 1 C_2O_3 is reached, setting free carbon dioxide and giving rise to a thick syrupy solution. Any excess of carbonate, so long as the mass remains moist, also loses its carbon dioxide but remains insoluble in the form of the so-called solid basic oxalates to be described in the next section. The colorless solution still reacts acid to litmus. On drying, it becomes more and more viscous and finally glassy without the slightest evidence of crystalline structure. When diluted with water a white voluminous precipitate settles out. If solutions of oxalic acid growing less and less concentrated are used, the ratio of base soluble in the acid grows constantly smaller. No matter whether this con-

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[1] Parsons: This Journal, 26, 1437.

[2] Ibid. 26, 1438.

centration is 2.85 BeO: 1 C_2O_3 or only a very slight (less than 0.1 per cent.) excess over the ratio BeO: C_2O_3, the residues on evaporation are glutinous and glassy in character and are physically indistinguishable except that the compounds of higher ratio are soluble only in a minimum of water while, at least, those less than 1.5 BeO to 1 C_2O_3 will dissolve in any amount used.

A single experiment shows this relation clearly. Two cc. of the solution 2.85 BeO: 1 C_2O_3 were treated with successive quantities of water of 10 cc. each from concentration 1 to 0.01, then with 100 cc. portions. Each 10 cc. added caused a precipitate and each 100 cc. did the same until a concentration of 0.001 was reached, after which further dilution appeared to be without effect and the ratio of base to acid remained approximately 1.5: 1. On evaporating any one of these concentrations a glue-like film formed, hardened and became glassy. If a solution of concentration 0.001 was boiled down to small bulk, a small amount of a fine white precipitate settled out, resembling magnesium ammonium phosphate to the naked eye but showing no crystalline structure under the microscope.

The following table shows the composition of these soluble basic oxalates. The concentration is expressed in the first column in the ratio of cubic centimeters of saturated solution to cubic centimeters of water. A gram concentration would undoubtedly be preferable but in this case serves no useful purpose.

Concentration.	Ratio BeO/C_2O_3.
1 : 5	2.1 : 1
1 : 50	1.9 : 1
1 : 100	1.74 : 1
1 : 1000	1.5 . 1

These results were obtained at ordinary temperatures and as the reaction takes place more and more slowly with the dilution it is probable that complete equilibrium was reached in no instance.

The oxalate 2 : 1 is the one to which Atterberg[1] gives the formula $BeC_2O_4.Be(OH)_2.H_2O$ but it can have no claim to being a definite chemical compound. It is simply a degree of saturation and, except as shown by analysis, can not be distinguished from any other ratio near to its own. 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 make their complete drying

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[1] Kgl. Svenska Akad. Handl. 12, 51.

improbable. As it is impossible to obtain any degree of saturation that will yield a solid and liquid phase together for any concentration between 1.5 BeO: 1 C_2O_3 and 1 BeO: 1 C_2O_3 it is, of course, out of the question to apply the phase rule considerations used on the insoluble basic oxalates next to be considered.

Insoluble Basic Oxalates.—Rosenheim and Woge did not succeed in producing any oxalate of beryllium of greater basicity than 2.8 BeO to 1 C_2O_3, although they refer to Atterberg's work. This failure could have been due to no other cause than wrong conditions, for these highly basic precipitates are thrown out of any solution of the oxalate of a bascity greater than about 1.5 to 1 when sufficiently diluted with water, and the extent of the dilution necessary for precipitation to begin varies inversely as the basicity of the solution. The action is in all respects similar to that of the so-called basic sulphates except that the precipitation does not occur in even apparent stages, but takes place with every addition of water until complete.

Analyses of these basic precipitates were made showing variable composition. When freshly prepared they showed a ratio of about 10: 1 but this ratio was increased by washing with water, although the acid component washes out much less readily than was previously found to be the case with the corresponding sulphates.

As with the basic sulphates it was early apparent that the precipitates could not be completely separated from the mother-liquors for the 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 phase rule considerations, and the conditions of its applicability to such problems as the identification of individuals in a mixture of basic salts with mother-liquor have been most clearly pointed out by Miller and Kendrick.[1]

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

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

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 homogeneous solid phase of variable composition.

In order to study this question a series of experiments was carried out in the same large and especially constructed thermostat that had been used by one of us upon basic beryllium sulphate. The experiment began on April 13, 1905, and equilibrium was not reached until June 10th. The bottles were continuously agitated throughout this time at a temperature of 25°, being stopped only to remove samples of the mother-liquor for analysis.

The ratio of BeO to C_2O_3 taken is shown in the first column. The amounts taken and the composition of the mother-liquors are shown as indicated.

	Taken.				Found.		
No.	Ratio $BeO:C_2O_3$.	Grams BeO.	Grams C_2O_3.	Grams H_2O.	Gram BeO in 10 grams mother-liquors.	Gram C_2O_3 in 10 grams mother-liquors.	Gram BeO. / Gram C_2O_3 in mother-liquors.
1	2 : 1	0.6972	1	50	No solid phase at this dilution and temperature.		
2	2 : 1	1.0458	1.5	50			
3	2 : 1	0.6972	1	100			
4	2 : 1	1.0458	1.5	100	0.0958	0.1501	0.64+
5	$2\frac{1}{2}$: 1	0.8715	1	50	0.1108	0.1847	0.60
6	$2\frac{1}{2}$: 1	1.3073	1.5	50	0.1765	......	.....
7	$2\frac{1}{2}$: 1	1.7430	2	50	0.2254	0.3818	0.59
8	$2\frac{1}{2}$: 1	0.8715	1	100	0.0567	0.0969	0.58
9	$2\frac{1}{2}$: 1	1.3073	1.5	100	0.0867	0.1466	0.59
10	$2\frac{1}{2}$: 1	2.1788	2.5	100	0.1302	0.2361	0.55
11	3 : 1	1.0458	1	75	0.0750	0.1243	0.60
12	3 : 1	1.5687	1.5	75	0.1228	0.2000	0.61
13	3 : 1	2.0916	2	75	0.1598	......	......
14	3 : 1	1.0458	1	100	0.0562	0.0969	0.58
15	3 : 1	1.5687	1.5	100	0.0887	0.1460	0.61
16	3 : 1	1.8302	1.75	100	0.0901	0.1529	0.59
17	4 : 1	1.3944	1	75	0.0667	0.1257	0.53
18	4 : 1	2.0916	1.5	75	0.0953	0.1793	0.53
19	4 : 1	1.3944	1	100	0.0480	0.0935	0.51
20	4 : 1	2.0916	1.5	100	0.0787	0.1465	0.54
21	6 : 1	2.0916	1	75	0.0505	0.1180	0.43
23	6 : 1	2.0916	1	100	0.0390	0.0916	0.43

In examining these figures it should be remembered that ratios between 1.5 : 1 and 1 : 1 BeO could not be used, for they give no coexistent solid and liquid phase at any concentration.

A study of the above figures will show at once that the concentrations of the mother-liquors vary widely and therefore the precipitate can not consist of a mixture of two definite basic salts. It will also be evident that the concentration of the mother-liquors is almost exactly proportional to the initial concentration, which shows, as does also the ratio of base to acid, that at these dilutions and at 25° there was little additional precipitation by the dilution from 50 to 100 cc. By comparing Nos. 8, 14, 19 and 23; 11, 17 and 21; and 4, 9, 15, 20 it will also be evident that the composition of the mother-liquors depends almost solely upon the initial concentration of the acid component and is nearly independent of the basic, although a relatively large increase of the initial basic component does diminish the basic ratio in the mother-liquors. It will also be observed that almost all of the acid was left in solution while an increasingly large proportion of the base was thrown out into the precipitate, leaving in most of these experiments a solution of approximately 1.7 BeO : 1 C_2O_3. These facts are all in harmony with the conclusion that the solid phase was the hydroxide and that no basic salt exists.

It was early apparent that, as with the basic sulphates, the errors of analysis of the liquid phase would be so multiplied in the calculation as to render any computation of the composition of the solid phase next to useless. It may be well to note, however, that such calculations give in every instance results showing a much higher basicity than those obtained by analysis, which is exactly as would be expected when it is considered that in no case was the precipitate completely separated from the mother-liquors. The precipitates were washed once with water, pressed between filter-paper, dried and analyzed. The results obtained on thirteen of these precipitates follow. The others were not obtained in sufficient quantity for accurate work except Nos. 9 and 10, which were lost through an error and not enough remained for a second determination.

SOLID PHASE.

No.	BeO. Per cent.	C_2O_3. Per cent.	Ratio BeO/C_2O_3.
8	53.2	6.2	23
11	49.7	5.5	26
12	47.8	6.5	21
13	46.3	5.1	26
14	50.6	4.4	34
15	50.1	5.3	27
16	53.2	7.0	22
17	50.5	6.0	26
18	48.3	6.3	22
19	49.6	6.4	22
20	51.2	5.6	26
21	51.0	5.2	28
23	52.8	4.2	35

It will be seen at once that all of these precipitates contain notable quantities of oxalic acid, but from the analysis of the solutions we must conclude that this is probably present in the form of occluded mother-liquors. This is further supported by the fact that the water present was more than sufficient in every instance for the formation of the hydroxide. The presence of this mother-liquor whether great or small in amount gives, of necessity, a resultant solid less basic than the original solid phase. The results themselves taken literally lead to formulas varying from $20Be(OH)_2.BeC_2O_4$ to $34Be(OH)_2.BeC_2O_4$ with a slight excess of water in each case. 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 the simple hydroxide, or a basic salt of a basicity of at least $25BeO$ to $1\ C_2O_3$, or that the precipitates vary in composition and, therefore, are solid solutions containing a small amount of the oxalate 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.

"SO-CALLED" BASIC BERYLLIUM COMPOUNDS.

We have tried in the preceding pages to point out clearly that no basic oxalate or basic sulphate of beryllium has ever been made, and that the indefinite mixtures which have been considered as such were in reality only solid solutions in the hydroxide, and that the two substances mix, as water and alcohol, in all proportions to form a homogeneous solid phase. From a study of the action of other acids on beryllium hydroxide; from the action of water on the truly basic acetate of Urbain and Lacombe and the formate, butyrate, valerate, etc., of Lacombe; and from a careful examination of the original articles cited below we feel confident in the claim that no basic compound of beryllium has been made or probably ever will be made where water is one of the constituents of the system or at least where water is present in sufficient amount to have its mass worthy of consideration in the mass of the system. It can be safely stated that no efforts to make definite salts of beryllium will be successful where attempts are made to saturate an acid with beryllium hydroxide and it is by that method that many of the formulas assigned to so-called compounds of beryllium have been attained.

Among the compounds generally assigned to beryllium the following, in our opinion, have no place and are probably simply solid solutions of the normal salt in the hydroxide.

Basic sulphates and oxalates as cited above.

Basic sulphites:

$2BeSO_3.9Be(OH)_2.6H_2O$;[1]
$BeSO_3.Be(OH)_2+5H_2O$;[2]
$BeSO_3.Be(OH)_2+Aq$;[3]
$3BeSO_3.Be(OH)_2+Aq$.[3]

Basic dithionate:

$2BeS_2O_6.3Be(OH)_2+14H_2O$.[4]

Basic carbonates:

$BeCO_3.5Be(OH)_2+3H_2O$;[5]
$BeCO_3.2Be(OH)_2+Aq$;[6]
$BeCO_3.2Be(OH)_2+3H_2O$;[7]

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[1] Seubert and Elten: Z. anorg. Chem. 4, 52.

[2] Atterberg: K. Svenska Vet. Akad. Handl. 12, 51 (1873).

[3] Krüss and Moraht: Annalen, 260, 161.

[4] Krüss: Ann. 246, 195.

[5] Seubert and Elten: Loc. cit.

[6] Parkman: Am. J. Sci. [2], 34, 326.

[7] Debray: Ann. chim. phys. [3], 44, 1.

$4BeCO_3.8Be(OH)_2+5H_2O$;[1]
$2BeCO_3.7Be(OH)_2+3H_2O$;[1]
$2BeCO_3.7Be(OH)_2+2H_2O$.[2]

Basic chlorides:

$3BeCl_2.2Be(OH)_2$;[3]
$BeCl_2.3Be(OH)_2$;[3]
$BeCl_2.12Be(OH)_2+10H_2O$;[3]
$BeCl_2.12Be(OH)_2+4H_2O$;[3]
$Be(OH)Cl$.[3]

Basic selenites:

$2BeSeO_3.Be(OH)_2+2H_2O$;[3]
$BeSeO_3.Be(OH)_2.H_2O$;[3]
$2BeSeO_3.3Be(OH)_2.7H_2O$.[4]

Basic borates:

$Be(BO_3)_2.2Be(OH)_2+Aq$.[5]

Basic nitrate:

$Be(NO_3)_2.Be(OH)_2.2H_2O$.[6]

Basic chromate:

$BeCrO_4.13Be(OH)_2+10H_2O$.[7]

Basic molybdate:

$BeMoO_4.Be(OH)_2.2H_2O$.[7]

Basic succinate:

$BeC_4H_4O_4.Be(OH)_2+2H_2O$.[7]

Basic ferrocyanide:

$Be_2FeCy_6.4Be(OH)_2+7H_2O$.[7]

Basic beryllium hypophosphites,[8] valerates,[9] oxalates, citrates, tartrates, acetates,[10] to which no formulas were assigned nor analyses made.

On the other hand, it must not be forgotten that the truly basic and beautifully crystalline series of salts of the general formula $Be_4O(Ac)_6$, in which the acid constitutent is the radical of formic

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[1] Weeren: Ann. Physik. 92, 91. Weeren seems to have clearly understood that these were no true compounds.

[2] Schaffgotsch: Ann. Physik. 50, 183.

[3] Atterberg: Loc. cit.

[4] Nilson : Bull. soc. chim. [2], 23, 355.

[5] Krüss and Moraht : Ann. 260, 161.

[6] Ordway : Amer. J. Sci. [2], 26, 197.

[7] Atterberg : Loc. cit.

[8] Rose: Ann. Physik. 12, 86.

[9] Trommsdorff: Ann. Pharm. 6, 194.

[10] Vauquelin: Allgem. J. Chem. 1, 590.

acid or one of its homologues are among some of the most interesting compounds of inorganic chemistry for, although basic in composition, they are all crystallized from anhydrous acid.[1]

CONCLUSIONS.

The following conclusions seem warranted for the ranges of temperature covered by our experiments:

That the only definite hydrated oxalates are $BeC_2O_4.3H_2O$ and $BeC_2O_4.H_2O$.

That no acid oxalate of beryllium exists.

That the anhydrous oxalate BeC_2O_4 is difficult, if not impossible to produce, owing to the difficulty of removing the last trace of water without at the same time decomposing the oxalate.

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

NEW HAMPSHIRE COLLEGE,
DURHAM, N. H.

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AN ELEMENTARY PROOF OF THE RELATION BETWEEN THE VAPOR PRESSURES AND THE COMPOSITION OF A BINARY MIXTURE.

BY GILBERT NEWTON LEWIS.

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BOTH partial vapor pressures from a mixture of two liquids are changed by a change in the composition of the mixture, but not independently. As one decreases, the other invariably increases according to the simple law discovered by Duhem,[2] namely,

$$N\frac{dp}{p}+N'\frac{dp'}{p'}=0,$$

where p and p' are the respective partial vapor pressures from a mixture containing N gram-molecules of the first substance and N' gram-molecules of the second, and dp and dp' are the changes in p and p' accompanying a slight change in composition.

No satisfactory elementary proof of this very important equa-

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[1] Urbain and Lacombe: Compt. rend. 133, 874; Lacombe: Ibid. 134, 772.

[2] Compt. rend. 102, 1449 (1887).