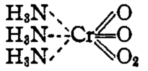
and bursts into flame. This decomposition takes place in two stages—swelling and ignition. The particles appear to swell considerably, and finally flash rapidly leaving a residue of finely divided chromic oxide. If struck a sudden blow the material decomposes with explosive violence. If allowed to remain for some time below, or at room temperature, the material becomes more stable and behaves in much the same manner as does ammonium dichromate. X-Ray diffraction patterns show the tan colored material to have a structure quite different from that of ammonium chromate or ammonium dichromate.

The physical and chemical properties of this material resemble those described by Riesenfeld[11] for the compound chromic tetroxide triammine. The formula given this compound is



Since the molecular weight of this material would be 167, and that of $H_2CrO_5{\cdot}2NH_3$ 168, it follows that the chromium content would not be a deciding factor in the determination of structure. Since but two ammonia groups could be accounted for by accurate ammonia analysis in the case of the material prepared in this study; it is assumed that these compounds are different in chemical constitution although very similar in chemical properties.

Summary

The reaction between hydrogen peroxide and chromic anhydride has been studied using dry ethyl acetate as the solvent. A tan ammonium salt of the blue colored peroxychromic acid has been prepared. Analyses of this salt are in accord with the formula $H_2CrO_5{\cdot}2NH_3$. From this information the formula of the blue peroxychromic acid probably is H_2CrO_5 or $CrO_3{\cdot}H_2O_2$. Some physical and chemical properties of the ammonium salt have been determined.

URBANA, ILLINOIS RECEIVED JULY 29, 1936

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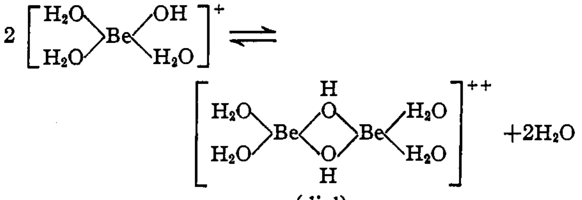
[11] Riesenfeld, *Ber.*, **41**, 3536–52 (1908).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Basic Beryllium and Complex Beryllate Hydrosols; an Additional Contribution to the Concept of Polyolated and Polyoxolated Structures

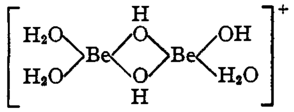
BY ARTHUR W. THOMAS AND HOKE S. MILLER

In previous publications from this Laboratory the properties of certain colloidally dispersed metallic "oxides" have been readily explained according to the concept that the micelles are polyolated and/or polyoxolated structures.[1] Application of this theory which involves the Werner–Pfeiffer ideas of hydrolysis and olation together with Stiasny's concept of the oxolation of ol groups, has produced a new and fundamental knowledge of beryllium "oxide" hydrosols.[2] Accepting the coördination number of 4 usually assigned to beryllium, the formation of a diol from triaquo monohydroxo beryllium ion would be



(diol)

The dissociation of an aquo group in this dinuclear diol ion, or the replacement of one of its aquo groups by OH would produce an ion such as



According to the theory, two of these in turn can olate, the result in this case being a tetranuclear olated ion. Since removal of H^+ ion favors olation, one would expect increase in size of the olated ions when a solution of a beryllium salt is made increasingly basic. Increases in basicity, however, and especially elevation of temperature

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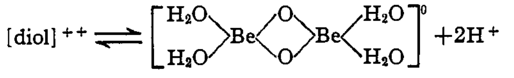
[1] (a) A. W. Thomas and T. H. Whitehead, *J. Phys. Chem.*, **35**, 27 (1931); (b) A. W. Thomas and A. P. Tai, THIS JOURNAL, **54**, 841 (1932); (c) A. W. Thomas and F. C. von Wicklen, *ibid.*, **56**, 794 (1934); (d) A. W. Thomas and R. D. Vartanian, *ibid.*, **57**, 4 (1935); (e) A. W. Thomas and C. B. Kremer, *ibid.*, **57**, 1821, 2538 (1935); (f) A. W. Thomas and H. S. Owens, *ibid.*, **57**, 1825, 2131 (1935).

[2] For convenience, those hydrosols in which the beryllium is in the cationic micelle will be called *basic beryllium* hydrosols and the name *complex beryllate* will signify hydrosols in which the beryllium exists in the form of an anionic micelle.

favor oxolation, which, taking the diol for simplicity, is represented by the reaction



the intermediate product, containing one ol and one oxo group being omitted to save space. Quite unlike metals having coördination numbers of 6 and 8, it is seen that the complete oxolation of a diol structure of beryllium with its coördination number of 4 produces a complex without a charge. This would suggest that oxolation of colloidal basic beryllium complexes would result in precipitation of the micelles. This prediction has been found to be correct because our basic beryllium hydrosols precipitate immediately when boiled, and in about two hours at 60°.[3]

According to the polynuclear theory proposed at this Laboratory, the formation of a hydrosol by peptization of the hydrous oxide with the acid, HA, consists in the interaction between the H^+ ion of the peptizing acid with OH groups of the hydrous oxide gel, thus converting the polynuclear olated hydrous oxide to a polynuclear cationic micelle. A cationic micelle arises, however, only when the anion, A^- of the acid is not a strong coördinative binder. If it, by displacing aquo groups, becomes coördinatively bound to the same extent that the H^+ ion reacts with the OH groups of the gel, then no colloidal dispersion occurs. However, if A^- has great tendency to displace aquo groups, it may actually produce anionic micelles, and in the case of even neutral salts of such anions, an anionic micelle arises by peptization of the oxide.[1e] Such phenomena previously reported for zirconium and thorium "oxide" hydrosols have also been found in the case of beryllium "oxide" hydrosols.

Preparation of Basic Beryllium Hydrosols.—Three methods were employed as follows:

(a) Sodium hydroxide was added dropwise to a mechanically stirred aqueous solution of beryllium nitrate until a decided turbidity was produced. The stirring was continued for about twenty hours, after which the hydrosol was dialyzed against running distilled water, using nitrocellulose membranes.

(b) Beryllium hydroxide was precipitated from aqueous beryllium nitrate solution, washed by centrifuging and peptized with tenth molar beryllium nitrate solution. During the peptization the system was stirred mechanically. The stirring was continued for twenty hours after the beryllium nitrate was added. The hydrosols thus formed were dialyzed as previously mentioned.

(c) Beryllium hydroxide precipitated by ammonium hydroxide from beryllium nitrate solution was washed by centrifuging until the supernatant liquid no longer gave the ferrous sulfate ring test for nitrate. A known amount of 0.05 *N* hydrochloric acid was added while the solution was stirred mechanically. It was observed that the ratio of equivalents of beryllium as the hydroxide, to the equivalents of chloride, as the acid, should be approximately 50:1. When too much acid was added, deolation seemed to occur. After peptization had continued for about twenty hours the hydrosols were dialyzed against distilled water.

In all cases, the dialysis was carried out by allowing distilled water to flow through nitrocellulose bags which were immersed in the colloidal solutions, the latter being stirred mechanically. All sols were centrifuged after dialysis to remove coarse suspended matter.

Table I summarizes briefly some of the properties of these hydrosols.

TABLE I

DATA CONCERNING HYDROSOLS[a] CONTAINING CATIONIC BERYLLIUM MICELLES

Designation[b]	Method preparation	Hours dialyzed	Be[c]	Cl[c]	NO_3[c]	Ratio equiv. Be/Cl or NO_3	*p*H[d]
cA	a	84	27.2	..	0.1	272	6.1
cB	a	70	41.7	..	5.6	7	5.9
cC	c	360	21.9	[e]	...	...	6.6
cD	b	40	22.3	..	6.0	4	5.6
cE	b	70	12.3	..	1.9	6	5.6
cM	c	72	84.7	0.40	...	212	6.0
cN	c	56	86.3	0.99	...	87	6.1
cO	c	50	60.4	7.88	...	8	5.8
cR	a	72	10.1	..	1.8	6	5.7

[a] All the hydrosols displayed particles in lively Brownian motion in a brilliant Tyndall cone. They were cloudy in appearance. [b] The initial letters (c) and (a) are used in Tables I and III to signify that the beryllium is in the cationic (c) or in the anionic (a) micelle. [c] In milliequivalents per liter. [d] *p*H values were measured immediately after centrifuging the dialyzed hydrosols. [e] 500 cc. of sol cC when decomposed with nitric acid gave no test for chloride with silver nitrate, nor did a portion of it give the ferrous sulfate ring test for the nitrate ion.

Effect of Neutral Salts upon Hydrosols.—In previous publications[1] it was shown that neutral salts raise the *p*H values of certain metallic

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(3) Some of our basic beryllium hydrosols precipitated after storage for two months at room temperature.

"oxide" hydrosols, the action being ascribed to the displacement of OH groups in the micelle by the added neutral salt anions. The relative potencies of neutral salt anions to raise the *p*H value have been ascribed to their relative coördinative binding tendencies.

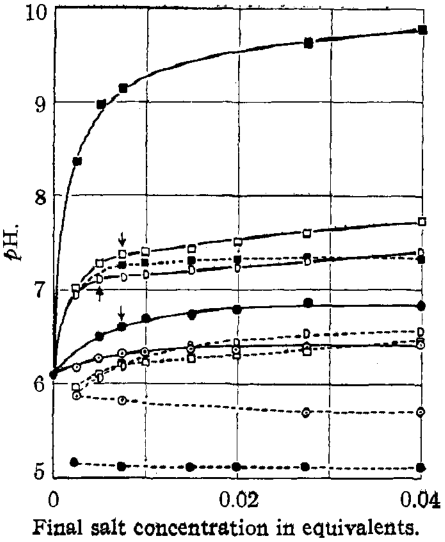

Fig. 1.—Effect of potassium salts on the *p*H of sol cA. Sol six days old. Broken lines represent *p*H values of pure aqueous salt solutions. Continuous lines record *p*H values of sol-salt mixtures. ■, Citrate; ⊙, chloride; □, oxalate; ●, sulfate; D, tartrate.

In the experimental work, with the exception of all the data given in Fig. 1 and that for the potassium citrate solution in Fig. 3, 0.08 *N* stock solutions of the salts were adjusted to *p*H values below 7 and above 6 by the addition of potassium hydroxide or of the appropriate acid. The *p*H values of these stock solutions are recorded in Table II. These solutions with added water, when necessary, were added to equal volumes of the hydrosol in small bottles and rotated at 7 r. p. m. for twelve to twenty hours at 25°.[4] The hydrogen ion activity was then measured by the quinhydrone electrode if the *p*H value was less than 7.5 and by the hydrogen-platinized-platinum electrode when it was above 7.5.

TABLE II

*p*H VALUES OF 0.08 *N* POTASSIUM SALT SOLUTIONS

Acetate	6.3	Maleinate	6.5
Citrate	6.3	Malonate	6.7
Chloride	6.3	Nitrate	6.6
Formate	6.1	Oxalate	6.3
Fumarate	6.2	Sulfate	6.2
Lactate	6.7	Tartrate	6.4
Malate	6.4		

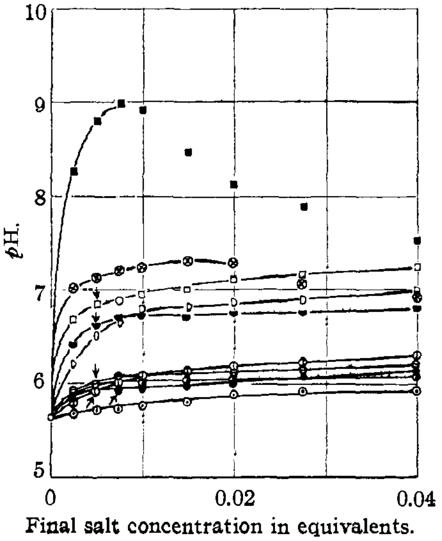

Fig. 2.—Effect of potassium salts on *p*H of sol cE. Sol one day old. Salt solutions were those described in Table II. ⦶, Acetate; ■, citrate; ⊙, chloride; ⊖, formate; ◑, fumarate; ⊗, malate; ▾, maleinate; □, oxalate; ●, sulfate; D, tartrate.

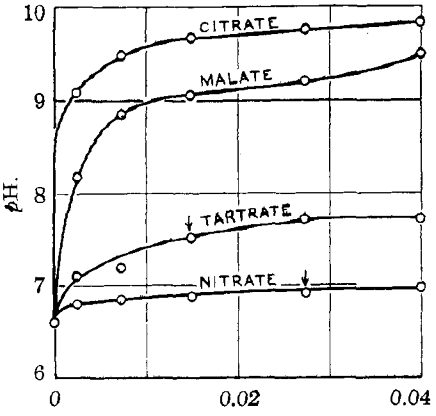

Fig. 3.—Effect of potassium salts on *p*H of sol cC. Sol one day old and apparently devoid of chloride or nitrate ion. Salt solutions used were those described in Table II with exception of the citrate solution which in this instance was at *p*H = 6.9.

Figures 1 to 3 provide some typical results. In Fig. 1, the broken curves show the *p*H values of pure aqueous solutions of the salts while the continuous curves represent the *p*H values of the salt-hydrosol mixtures. There can be no doubt concerning the *p*H increasing effect of the added anions. The marked buffer effect of the *p*H =

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(4) The reaction is practically complete in one to three hours.

6.3 citrate solution used in the experiments plotted in Fig. 2 led us to use a stock citrate solution of *p*H = 6.9 in the work recorded in Fig. 3. The arrows on Figs. 1, 2, 3 and 7 indicate where precipitation was observed. In the cases of added citrate and malate, precipitation occurred at extremely low concentrations of the added salt, higher concentrations of these salts producing no precipitate but having converted the cationic beryllium micelles to anionic citrato (or malato) beryllate micelles. A summary of all of our measurements showed that the *p*H raising order for the anions upon cationic beryllium hydrosols is citrate > malonate > oxalate > malate > tartrate > maleinate > acetate > formate ≧ fumarate ≧ sulfate > chloride ≧ nitrate. This series resembles that found in this Laboratory for thorium oxychloride sols[1e] and for zirconium oxychloride sols.[1f]

With the *cis-trans* isomers, potassium maleinate proved to be more effective than potassium fumarate. This is in agreement with the action of these salts on thorium oxychloride sols as reported by Thomas and Kremer.[1e]

One might ask whether there is any relationship between the *p*H raising effect of the added salts and their precipitating potencies upon basic beryllium hydrosols. A few experiments were performed to throw light upon this question.

Liminal Values[5] of Salts.—The procedure adopted for the measurement of liminal values was as follows. Into each of four 30-cc. volume test-tubes was placed 5 cc. of the hydrosol. Five cubic centimeter portions of varying concentrations of the salt were placed in four other tubes. The salt solution was poured into the hydrosol; the contents were poured back into the salt solution tube; then back to the hydrosol tube, after which they were centrifuged for two minutes at 1000 r. p. m. (radius, 21 cm.). This procedure was repeated until the liminal value was finally obtained.

From the results given in Table III it can be seen that the effectiveness of certain potassium salts as precipitants of cationic basic beryllium hydrosols is in general: citrate > malate = tartrate > oxalate > sulfate > fumarate > maleinate > chloride. It is interesting to note that tartrate is a more powerful precipitant than oxalate although the reverse is true for their *p*H raising potencies. Inasmuch as inorganic micelles are, in general, precipitated when the charge is reduced to a certain extent, and since in this instance the positive charge must be reduced by displacement of aquo groups of negatively charged ions, it would seem that tartrate is a more potent displacer of aquo groups than is oxalate. The same may be said for sulfate as compared with maleinate where the precipitating potency is sulfate > maleinate, the reverse of the *p*H raising tendency.

TABLE III

LIMINAL VALUES

Sol	Citrate	Tartrate	Malate	Oxalate	Sulfate	Fumarate	Maleinate	Chloride
cA	0.08	0.19	..	0.33	0.53	..	..	600
cB	.41	.62	..	1.08	.78	..	..	>1500
cR	.36	.58	..	0.76	1.64	..	..	>1000
cD	.27	.76	..	1.62	1.64	..	..	>1000
cE	.25	.44	0.44	0.76	0.88	1.24	1.96	>1000

Conductance Titrations.—Another means of comparing the tendencies of anions to displace aquo groups from the central metallic ions of the micelle is offered by measurement of changes in conductivity resulting upon addition of very small amounts of salts to the hydrosol and to water. Such measurements are shown in Fig. 4 where the conductivities of mixtures of hydrosol "cN" and potassium salts (solid lines) are compared with the conductivities of the pure salt solutions (broken lines). If the anion of an added salt enters the micelle, displacing an aquo group therefrom, the conductivity of the salt–hydrosol mixture will obviously be less than if there were no reaction between the added anion and the colloidal micelle. Convergence of the solid line and broken line curves in Fig. 4 is evidence for such displacement, while parallelism of the solid and broken lines for a given salt means no such reaction. Inspection of the figure reveals that the nitrate curves have practically identical slopes and hence at the low concentrations used, nitrate has only a negligible (if any) effect in replacing aquo groups from the central beryllium ions of the micelle. The tartrate curves are not of the same slope, showing that tartrate has an aquo group replacing tendency which is, however, less than that of citrate where the curves converge at the concentration of 15 milliequivalents of potassium citrate per 50 cc. of solution. It must be remembered that some replacement of OH groups also is effected by an ion such as citrate (and to a less extent by tartrate). This

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(5) "Liminal value" as used in this paper is defined as the lowest concentration of salt, expressed in millimoles per liter of final mixture, that just completely precipitates the micelles under the described procedure.

would cause the curves to diverge with increasing concentration, however. In view of the fact that both OH replacement and aquo group replacement may occur, one is obliged to be content with the solely qualitative nature of the evidence given in Fig. 4, namely, aquo group replacement potency is citrate > tartrate > nitrate.[6]

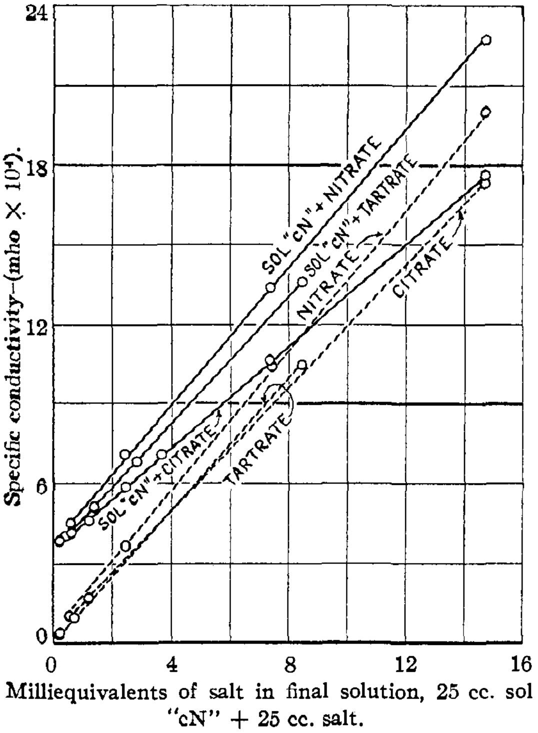

Fig. 4.—Potassium salt conductivity titrations of sol cN. Sol three days old. Continuous lines represent mixtures of sol and salt solutions. Broken lines represent salt solutions diluted with water.

Another method of measuring the tendency of anions to replace aquo groups is by means of the observation of the effect of added silver salts upon the conductivity of the hydrosol. By means of a technique previously described[1b] the results shown in Fig. 5 were given by sol "cM."

All the chloride in the hydrosols was precipitated by each of the silver salts added since the value of the chloride content determined by the conductivity method agreed with the gravimetric results. When an amount of silver salt just in excess of equivalence to the chloride content of the hydrosol was added, a sharp change in direction of the curve occurred.

It is seen that added amounts of silver nitrate caused an increase in conductivity in the first segment of the curve, while the reverse was found true for lactate and citrate. These experimental data may be explained as follows. When silver ion is added to the hydrosol it combines with the unbound chloride ion to form silver chloride. As the chloride ion is removed from solution, any coördinatively bound chloride moves out of the micelle. This reaction continues until all the chloride has been converted to silver chloride, when the inflection point occurs; further additions of silver salt obviously increase the conductivity of the system. Since the nitrate ion has only a very feeble tendency to become coördinatively bound, we may assume that as the chloride groups move out of the micelle, aquo groups enter to satisfy the coördination number of the beryllium atom, thus the positive charge of the micelle increases, and consequently the conductivity increases also. This is, of course, superimposed upon the increase in conductivity resulting from the addition of silver and nitrate ions.

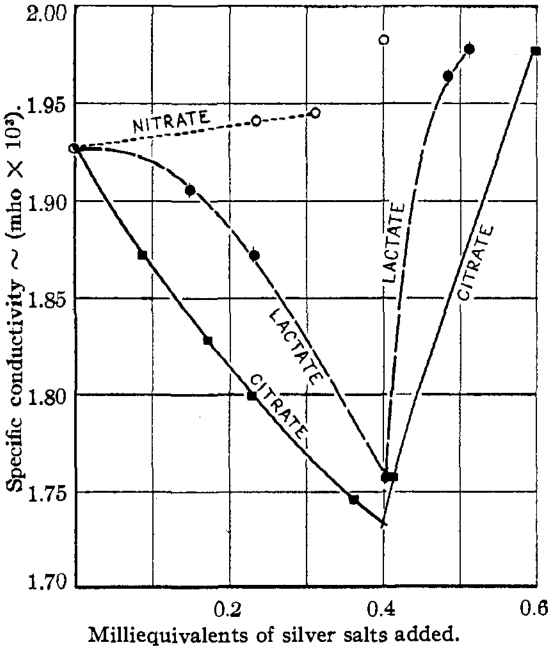

Fig. 5.—Conductivity titrations of sol cM with silver salts. Sol three days old.

The decrease in conductivity when either silver lactate or silver citrate is added may be explained in the following manner. As the coördinatively bound chlorido groups move out of the complex they are replaced by negatively charged lactate or citrate ions as the case may be. The combination between chloride and silver ions reduces the

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[6] The reaction between citrate ion and the micelle was rather slow, four hours being required for attainment of equilibrium at the highest concentration of added citrate.

conductivity of the system as in the first instance. At the same time, since lactate or citrate ions displace aquo groups, the charge of the micelle is reduced. These ions no longer contribute to the conductivity of the system and hence there are introduced two additional conductivity-lowering factors.

The steeper slope for citrate is ascribed to its greater tendency than lactate to become coördinatively bound to the central beryllium ions and to replace aquo groups therefrom.

A similar series of titrations of sol "cO" is given in Fig. 6. This sol differed from "cM" in its lower basicity or higher ratio of chloride to beryllium. It is noted that nitrate ion showed a slight tendency to combine with the micelles.

Complex Beryllate Hydrosols

Thomas and Owens[1f] and Thomas and Kremer[1e] found that a reversal of the sign of charge of cationic zirconium "oxide" and thorium "oxide" micelles occurred upon the addition to the hydrosols of specified concentrations of salts and acids of strong coördinative binding anions. These authors also demonstrated that upon direct peptization of zirconium or thorium hydrous oxides with certain salts or acids, anionic basic "oxide" sols were produced. Thomas and Owens reported also that anionic zirconium micelles could be produced by boiling a crystalloidal solution of a complex zirconeate.

Search of the literature failed to locate any statement concerning the reversal of the sign of the charge of cationic beryllium "oxide" micelles other than the report that attempts to accomplish such a result by use of potassium ferrocyanide[7] did not meet with success. Following the theoretical prediction that anions which are powerful coördinative binders should produce anionic micelles provided that they replace a sufficient number of aquo groups from the cationic micelle or from the hydrous oxide, it was found that stable hydrosols of anionato complex beryllate micelles could be produced. Some remarks concerning these systems follow.

Preparation of Complex Beryllate Hydrosols.—These hydrosols can be prepared by either of the following methods: (1) by the addition of either potassium citrate, malate or tartrate to a cationic beryllium hydrosol, producing a precipitate which redisperses;[8] (2) by the peptization of freshly precipitated hydrous beryllium oxide with an aqueous solution of either potassium citrate or malate, or tartrate; (3) by dropwise addition of ammonium hydroxide solution to a complex crystalloidal beryllate, prepared by adding potassium tartrate to beryllium nitrate solution, with immediate and subsequent dialysis. Care must be exercised not to add too much ammonium hydroxide. An excess of this reagent precipitates the beryllium as hydroxide.[9]

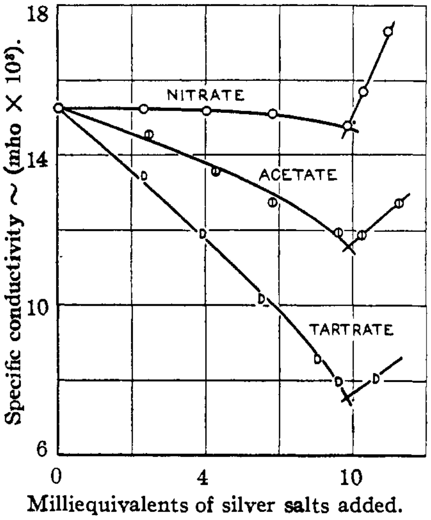

Fig. 6.—Conductivity titration sof sol cO with silver salts. Sol three days old.

A description of a few of these sols is given in Table IV.

TABLE IV

DATA CONCERNING COMPLEX BERYLLATE HYDROSOLS[a]

Designation	Method of preparation	Hours dialyzed	Be[b]	pH[c]
aJ	3	186	40.1	7.8
aK	2 (citrate)	237	19.5	6.3
aH	2 (tartrate)	113	41.6	6.4
aL	2 (malate)	223	29.1	6.9
aQ	2 (tartrate)	77	74.5	6.9

[a] These hydrosols were cloudy in appearance, displaying particles in lively Brownian motion in a brilliant Tyndall cone. [b] In milliequivalents per liter. [c] The *p*H values were measured immediately after centrifuging the dialyzed hydrosols.

Some Properties of Complex Beryllate Hydrosols.—It was found that addition of potassium salts to these hydrosols results in an increase in *p*H value. A typical result is shown in Fig. 7

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(7) W. H. Madson and F. C. Krauskopf, *J. Phys. Chem.*, **35**, 3237 (1931).

(8) The redispersion of the precipitate with potassium tartrate is slow, several days being necessary for the formation of a hydrosol.

(9) This affords a means for the separation of beryllium from certain other metals which is to be described by one of us (H. S. M.) in a subsequent paper.

where the effectiveness of the anions is seen to be citrate > malate > malonate > tartrate > oxalate > lactate > formate > maleinate. In the concentration range shown in Fig. 7, precipitation of the micelles occurred only with the last four salts mentioned and then only slightly at a concentration of 0.028 milliequivalent.

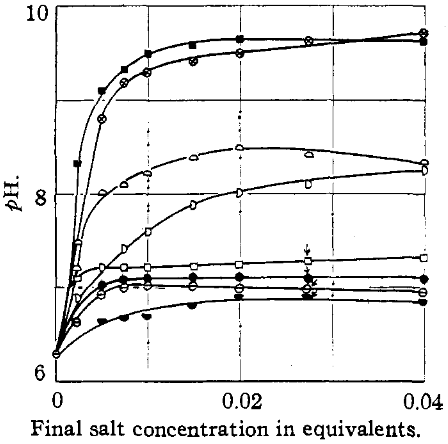
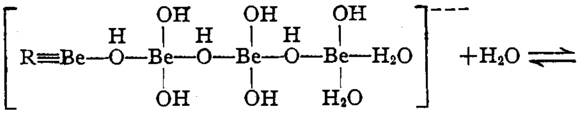


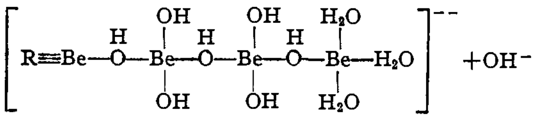
Fig. 7.—Effect of potassium salts on the *p*H of sol aK. Sol five days old. Salt solutions used were those described in Table II. ■, Citrate; ⊖, formate; ●, lactate; ⊗, malate; ▾, maleinate; ⌓, malonate; □, oxalate; D, tartrate.

It will be recalled that hydrosols of the cationic metallic micelles become more acid on storage at room temperature owing to oxolation and possibly to dissociation of aquo groups. The complex beryllate hydrosols, on the contrary, become less acid on aging at 25°. The *p*H value of sol "aK" which was 6.3 at the conclusion of dialysis rose to 7.2 in one month. Six weeks later it was 7.4. Sols "aL" and "aQ" also increased in *p*H value but to a less extent.

This increase in *p*H might be ascribed to the action of free citrate, malate or tartrate ions (possibly present) in replacing coördinatively bound OH groups. But the phenomenon of aquotization would seem to offer a more plausible explanation. An aquotization reaction of a hypothetical basic citrato beryllate[10] may be illustrated as follows, where R = $C_6H_5O_7^{---}$



$$\left[\mathrm{R{\equiv}Be{-}\overset{H}{O}{-}\underset{OH}{\overset{OH}{Be}}{-}\overset{H}{O}{-}\underset{OH}{\overset{OH}{Be}}{-}\overset{H}{O}{-}\underset{H_2O}{\overset{OH}{Be}}{-}H_2O}\right]^{---} + H_2O \rightleftharpoons$$



$$\left[\mathrm{R{\equiv}Be{-}\overset{H}{O}{-}\underset{OH}{\overset{OH}{Be}}{-}\overset{H}{O}{-}\underset{OH}{\overset{OH}{Be}}{-}\overset{H}{O}{-}\underset{H_2O}{\overset{H_2O}{Be}}{-}H_2O}\right]^{--} + OH^-$$

As a precedent for this type of reaction we would cite Sandved's[11] measurements of the equilibrium constants of the reversible aquotization reactions

$$\left[\mathrm{Co}^{X}_{(NH_3)_5}\right]^{++} + H_2O \rightleftharpoons \left[\mathrm{Co}^{H_2O}_{(NH_3)_5}\right]^{+++} + X^-$$

where X = Cl or NO_3

Heating of beryllate sols produced an unexpected change in that cationic beryllium micelles arose. Sols "aK" and "aL" were heated at 95° in sealed containers for ninety-six and fifteen hours, respectively. As a result of the heating, the conductivities rose in the case of "aK" from 4.24×10^{-5} to 5.84×10^{-5} mho and in the case of "aL" from 13.76×10^{-5} to 13.98×10^{-5} mho.

Upon electrophoresis of the sols which had been heated, it was observed that about half the beryllium in the case of sol "aK" and about four-fifths in the case of "aL" migrated to the anode, the remainder being cationic.[12] These results may be explained on the assumption that heating causes some of the citrato or malato groups to move out of the micelles, thus reducing the negative charge and even reversing it on some of the particles. The citrato or malato groups which move out of the micelles cause an increase in conductivity, the increase depending upon the length of time of heating the hydrosols. Thus, oppositely charged micelles may exist in basic beryllium hydrosols as previously mentioned for basic zirconium complexes.[1f]

Action of Acids upon Hydrous Beryllium Oxide.—It was shown previously that acids containing weakly coördinative binding anions peptize hydrous alumina at room temperature to the colloidal state while those whose anions have powerful coördinative binding tendency do not.[1d] The following experiment was performed in order to see whether hydrous beryllium oxide acted similarly. A suspension of freshly precipitated and washed hydrous beryllium oxide (precipitated from the nitrate with ammonium hydroxide) equal to 0.1 g. equivalent of beryllium oxide was agitated for forty-eight hours at 25° with 195 cc. of water containing 0.005 g. equivalent of acid. The reaction mixtures were filtered and examined.

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(10) It is to be understood that the hypothetical compound formulated is not intended to describe the structure of a complex beryllate micelle.

(11) K. Sandved, *Tids. Kjemi Bergvesen*, **15**, 21 (1935).

(12) The colloidal nature of the migrating particles was evidenced by the turbid appearance of the contents of both arms of the electrophoresis U-tube.

In the cases of citric and malic acids (citrate and malate ions have powerful coördinative binding affinity for beryllium) the filtrates contained some beryllium ion but no colloid. In the case of tartaric acid (tartrate ion is not so powerful a coordinative binder as citrate or malate), the slightly turbid filtrate was found to consist of a dispersion of colloidal complex beryllate micelles ("negatively charged beryllium oxide"). In the case of lactic acid (lactate ion is not a strong coordinative binder to beryllium), the very turbid filtrate was a dispersion of cationic basic beryllium micelles ("positively charged beryllium oxide").

Thus, it is indicated that the reaction of hydrous beryllium oxide to acids can be included under the same theoretical treatment as aluminum oxide. More will be reported on this topic in a subsequent publication.

Summary

For convenience of expression the term "beryllium hydrosol" will be used to designate hydrosols wherein the beryllium is in the complex cationic micelles; and the term "beryllate hydrosol" will refer to those hydrosols wherein the beryllium is in the anionic micelles.

1. Some methods for the preparation of beryllium and beryllate hydrosols have been described.
2. Addition of neutral salts to beryllium and to beryllate hydrosols produces marked decreases in hydrogen ion activity, the decrease being dependent upon the nature and concentration of the anion of the salt added.
3. The effectiveness of potassium salts in decreasing the hydrogen ion activity of beryllium hydrosol–salt systems was in general: citrate > malonate > oxalate > malate > tartrate > maleinate > acetate > formate ≧ fumarate ≧ sulfate > chloride ≧ nitrate; while that for a beryllate hydrosol–salt system was: citrate > malate > malonate > tartrate > oxalate > lactate > formate > maleinate.
4. Heating to 60° precipitated the beryllium hydrosols, whereas the beryllate hydrosols did not precipitate[13] when raised to 100°.
5. Aging at 25° caused an increase in hydrogen ion activity of the beryllium hydrosols, while in case of the beryllate hydrosols a decrease in hydrogen ion activity was noted on aging.
6. The order of silver salts in decreasing conductivity is: nitrate < lactate < citrate; and nitrate < acetate < tartrate.
7. Conductance titrations of beryllium hydrosols with potassium salts indicate the following order with respect to the tendency of the anions of the salts to become coördinatively bound to the beryllium atom: citrate > tartrate > nitrate.
8. It has been shown that heat increases the conductivity of beryllate hydrosols, converting some of the anionic beryllium to the cationic state.
9. It is evident that the order of peptization of hydrous beryllia with acids is the reverse of the *p*H raising potencies of the corresponding neutral salts of the acids.

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[13] After standing for two months at room temperature tartrato beryllate began to precipitate, while the citrato and malato beryllates were still stable.