[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Basic Zirconium Chloride Hydrosols

BY ARTHUR W. THOMAS AND HARRY S. OWENS

Studies upon metallic "oxide" hydrosols previously reported from this Laboratory[1,2,3] have been extended to include basic zirconium chloride hydrosols (generally known as "zirconium oxide" hydrosols).

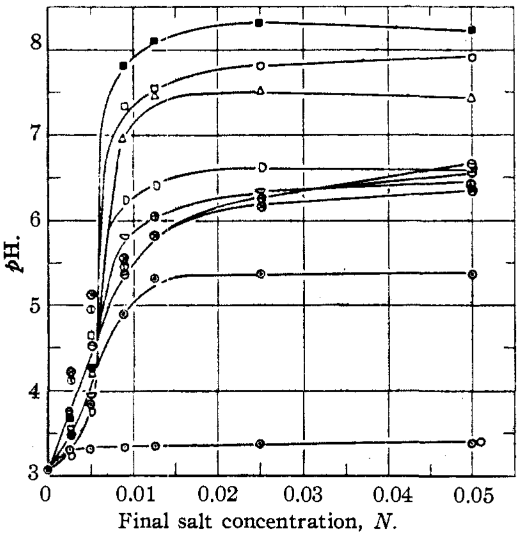

Fig. 1.—Effect of potassium salts on the pH value of Sol B; sol one day old: ⦶, acetate; ⊙, chloride; ■, citrate; ⊖, formate; ◡, glycolate; △, malate; ○, nitrate; □, oxalate; ⊗, propionate; ●, sulfate; D, tartrate.

The behavior of fifteen different basic zirconium chloride hydrosols was investigated, the results obtained with three which were typical of all being submitted here.

Preparation and Description of Hydrosols.—Hydrosols "B" and "F" were prepared in the following manner. Hydrous zirconium oxide precipitated from an aqueous solution of pure zirconyl chloride by redistilled ammonium hydroxide was washed by centrifugal decantations to the absence of a test for chloride ion. Portions of this oxide were rotated in contact with a 0,4 M zirconyl chloride solution at 25° for twenty-four hours in water-resistant glass-stoppered bottles. They were then dialyzed as previously described,[3] "B" for twenty hours and "F" for one hundred hours. Hydrosol "D" was prepared by boiling a 0.6 M aqueous zirconyl chloride solution in a glass-joined Pyrex reflux apparatus for twenty-four hours when it was dialyzed for one hundred and four hours. All sols were then centrifuged for one hour at 120 r. p. m. and a 42-cm. rotating diameter.

These hydrosols were turbid in reflected light, "D" exhibiting a bluish cast. To transmitted light "B" and "F" were colorless and clear while "D" was clear but orange-red in color. The micelles were positively charged in each case. Quantitative data are given in Table I.

TABLE I

COMPOSITION OF HYDROSOLS

The pH values are those obtained immediately at the completion of dialysis.

Sol	Zirconium milliequiv. per liter	Chloride milliequiv. per liter	Eq. Zr/Eq. Cl	pH
B	89.1	11.2	8.1	3.22
D	136.7	9.0	15	3.50
F	38.5	2.3	17	3.92

Action of Neutral Salts.—The effect of additions of potassium salts upon the pH values of the hydrosols was measured as previously described.[3] All of the potassium salt solutions were adjusted to pH 6.5 ± 0.3 as listed in Table II. The results obtained are plotted in Figs. 1, 2 and 3. It is seen that the pH values were raised in every case, alkaline solutions resulting with citrate, oxalate, malate and tartrate. The order of effectiveness of the anions is, citrate > oxalate > malate > tartrate > glycolate > succinate = malonate = maleinate > propionate = acetate = fumarate = formate > sulfate > chloride = nitrate.

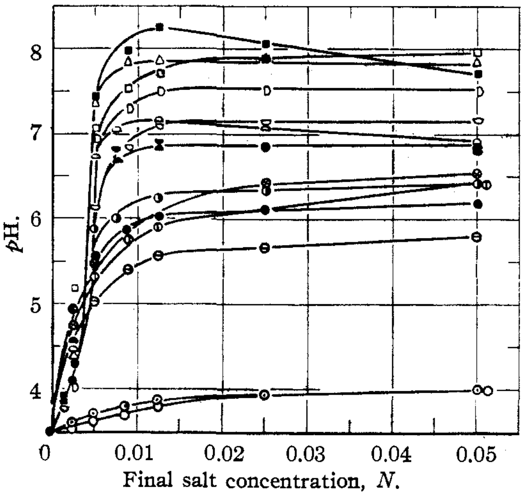

Fig. 2.—Effect of potassium salts on the pH value of Sol D; sol four days old: ⦶, acetate; ⊙, chloride; ■, citrate; ⊖, formate; ◑, fumarate; ◡, glycolate; △, malate; ▾, maleinate; ◠, malonate; ○, nitrate; □, oxalate; ⊗, propionate; ▴, succinate; ●, sulfate; D, tartrate.

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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 R. D. Vartanian, *ibid.*, **57**, 4 (1935).

[2] A. W. Thomas and F. C. von Wicklen, *ibid.*, **56**, 794 (1934).

[3] A. W. Thomas and C. B. Kremer, *ibid.*, **57**, 1821 (1935).

TABLE II

pH VALUES OF 0.1 N POTASSIUM SALT SOLUTIONS

Salt	pH	Salt	pH
Acetate	6.6	Maleinate	6.8
Chloride	6.6	Nitrate	6,4
Citrate	6.8	Oxalate	6.6
Formate	6.5	Propionate	6.6
Fumarate	6.3	Sulfate	6.5
Glycolate	6.5	Tartrate	6.6
Malate	6.3		

In general this is similar to the order found with the other basic metalli-salt hydrosols studied in this Laboratory.[1,2,3] Such an order might be expected from the present incomplete knowledge of the crystalloidal chemistry of zirconium.[4] De Boer,[5] for example, has found the following order for the tendency of anions to become coördinatively bound to zirconium: $OH > F > PO_4 > C_2O_4 > SO_4 > NO_3 > Cl$. Although the OH group seems to be one of the most strongly coördinatively bound (which would indicate difficultly in displacing it), conditions in the experiments performed favored its displacement because the hydroxyl ion concentration in the body of the solution was low while the concentration of the added anion was comparatively high. However, as the hydroxyl ion concentration of the solution increases owing to the displacement of hydroxo groups by the added anion, much greater amounts of salt are required for the reaction to proceed. The equilibria among hydroxo (and ol), hydroxy, aniono, and anion groups accounts for the shape of the curves in Figs. 1–3.

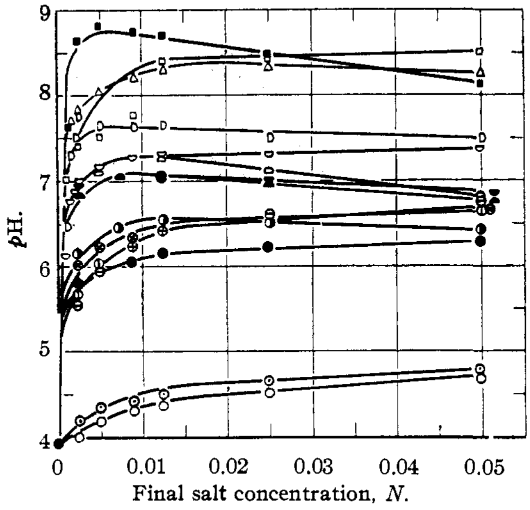

Fig. 3.—Effect of potassium salts on the pH value of Sol F; sol four days old: ⦶, acetate; ⊙, chloride; ■, citrate; ⊖, formate; ◑, fumarate; ⌓, glycolate; △, malate; ▼, maleinate; ⌓, malonate; ○, nitrate; □, oxalate; ⊗, propionate; ▲, succinate; ●, sulfate; D, tartrate.

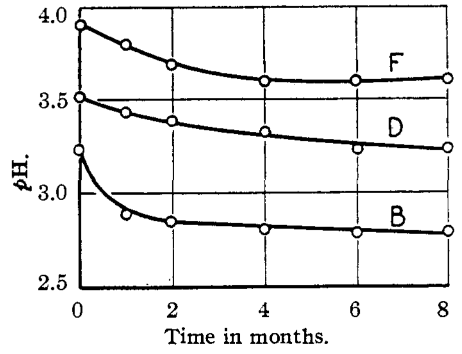

Fig. 4.—Change in pH of sols upon standing at room temperature.

Effect of Aging and Heating.—Representative results of the change in the pH values of basic zirconium chloride hydrosols stored in water-resistant glass bottles at room temperature are given in Fig. 4. It will be noted that the pH values decrease on aging in every case although not so rapidly as reported for basic thorium chloride sols.[3] This decrease is believed to be due to olation, and to a smaller extent oxolation. Olation though not changing the hydrogen ion activity itself, removes the primary hydrolytic

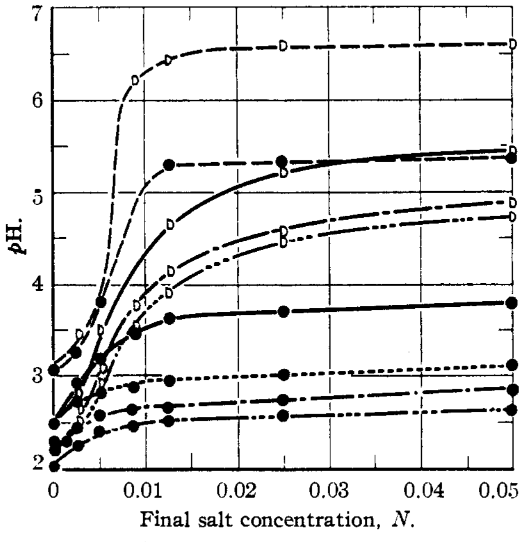

Fig. 5.—The effect of boiling of Sol B upon its reaction to the addition of potassium salts: D, tartrate; ●, sulfate; — — —, not heated; ———, boiled 8 hr.; - - - - - - - -, boiled 96 hr.; — - —, boiled 192 hr.; — - - - - —, boiled 240 hr.

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(4) F. P. Venable, "Zirconium," A. C. S. Monograph, Chemical Catalog Co., New York, 1922.

(5) J. H. de Boer, *Z. anorg. allgem. Chem.*, **165**, 1 (1927).

products favoring further hydrolysis and production of hydrogen ions.

Upon boiling, the *p*H of basic zirconium chloride sols decreases as in the case of other "oxide" sols reported from this Laboratory but, upon standing at room temperature after being boiled, the reaction showed no tendency to reverse. In this respect basic zirconium chloride sols differ from those of aluminum, chromium and thorium. Typical results are given in Table III. Among the group of elements named, zirconium is unique in that the normal ion in crystalloidal solution is a basic one. The stability of the zirconyl radical is well known, powerful coördinators being required to decompose it. The inertness of ignited zirconium oxide to nearly all ordinary reagents also typifies the stability of oxygen bridges between zirconium atoms. For these reasons it is believed that boiling a basic zirconium chloride hydrosol produces a high degree of oxolation.[6] The oxygen bridges thus formed are stable to the acid produced during the boiling and consequently little change in the *p*H values of the sols standing at room temperature would be expected.

In view of the shift of the reactions, hydroxo compounds $\rightleftarrows$ ol complexes $\rightleftarrows$ oxo complexes to the right upon heating, one would expect added neutral salts to exert less *p*H raising effects. A typical series of measurements is plotted in Fig. 5.

TABLE III

DECREASE OF *p*H OF HYDROSOLS UPON BOILING

Sol	*p*H before boiling	Hours boiled	*p*H after boiling	*p*H 6 months later[a]
B	3.11	8	2.50	2.45
	2.80	96	2.40	
	2.80	192	2.22	2.22
	2.80	240	2.04	2.09
D	3.50	72	2.50	2.44
F	3.90	72	3.19	3.12
	3.90	120	3.12	
	3.90	190	2.91	
	3.90	240	2.84	
	3.90	288	2.72	

[a] Kept at 25° for six months after cessation of boiling.

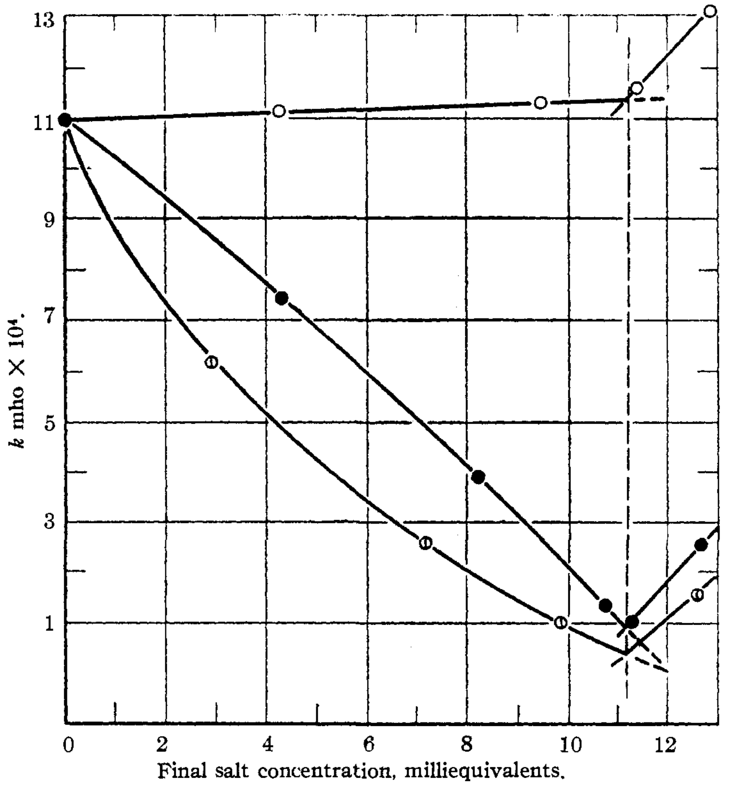

Fig. 6.—The effect of silver salts upon the specific conductivity of Sol B: ◐, silver acetate; ○, silver nitrate; ●, silver sulfate.

Conductance Titrations.—Conductance titrations with silver salts performed by means of a technique previously described[1b,2,3] produced the values plotted in Fig. 6. Here again the silver salt containing the more strongly coördinative binding anion was the more effective in lowering the conductivity. Nitrate shows little or no such tendency and as a result silver nitrate produced an increase in conductivity just as in the case of a basic chromium[2] and of a basic thorium[3] chloride hydrosol. Interpretations of these behaviors have been published.[1b,2,3] Similar curves for "thorium oxide" and "aluminum oxide" hydrosols have been obtained by Pauli.[7]

Summary

The *p*H values of basic zirconium chloride (so-called "zirconium oxide") hydrosols are raised by the addition of potassium salts. The order of effectiveness in general similar to that found with

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[6] x-Ray investigations made by Böhm and Niclassen [*Z. anorg. allgem. Chem.*, **132**, 1 (1924)] upon the gel obtained by ultrafiltration of a freshly prepared basic zirconium nitrate hydrosol showed it to be amorphous. The gel ultrafiltered from such a hydrosol which had been boiled for many hours showed a few bright rings which, considering their location, were probably those of zirconium oxide. After heating the precipitate from an evaporated sol at a higher temperature, the x-ray diagram for zirconium oxide was obtained.

[7] Wo. Pauli and E. Valkó, "Elektrochemie der Kolloide," Verlag Julius Springer, Vienna, 1929, pp. 552, 554.

other hydrosols is citrate > oxalate > malate > tartrate > glycolate > succinate = malonate = maleinate > propionate = acetate = fumarate = formate > sulfate > chloride = nitrate, the first named markedly increasing the *p*H value while the last named exerted very slight effect. This effect is ascribed to displacement of coördinatively bound OH groups by the anion of the added salt, the anion then becoming coördinatively bound to zirconium atoms in the micelle. Dialyzed basic zirconium chloride sols become more acid upon standing at room temperature although not so rapidly as basic thorium chloride sols. The decrease in *p*H is hastened by heating and the reactions show no sign of reversal after six months of storage at 25°. In the latter respect, basic zirconium hydrosols differ from those of thorium. As in the cases of other basic metalli-salt hydrosols, the heated sols are less responsive, in so far as *p*H changes, to the action of added neutral salts.

It may be said that "zirconium oxide" hydrosols show a very strong tendency to oxolate.

By application of the ideas which Werner and Pfeiffer suggested for crystalloid basic salts, and assuming that the micelles in basic zirconium chloride hydrosols are polyolated and/or oxolated structures, their behaviors can be readily interpreted.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

The Extraction of Germanium and Gallium from Germanite. I. The Removal of Germanium by the Distillation of Germanous Sulfide

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Germanite is a sulfide ore containing chiefly copper, iron, arsenic, germanium, zinc, lead, gallium, and aluminum as well as minute amounts of several other elements. It was discovered in 1920 at Tsumeb, South West Africa, by Schneiderhöhn.[2] An analysis by Pufahl[3] showed the presence of germanium, and further analyses by Kriesel,[4] Lunt,[5] and Thomas and Pugh[6] not only verified the germanium but, in addition, showed gallium to be present in appreciable quantities.

Several methods of extraction of germanium from germanite have been reported[7] in which the ore is either roasted or subjected to oxidation with a mixture of nitric and sulfuric acids, leading eventually to the separation of the germanium from aqueous solutions containing the other elements of the ore. The procedures are tedious and require the handling of relatively large quantities of solutions. Patnode and Work[8] chlorinated the ore at 350° and then fractionally distilled the anhydrous chlorides produced. The fraction containing the germanium was hydrolyzed to precipitate the dioxide. After this product had been dissolved in hydrochloric acid, germanium tetrachloride was distilled from the solution in the presence of chlorine, according to the very useful method of Buchanan.[9]

In the present paper, a process is reported for the complete removal of germanium from germanite as germanous sulfide in the vapor phase. The method eliminates the handling of large volumes of solutions, the distillation of liquids, and leaves a residue from which the gallium can be removed very readily. The simplicity of the process will be evident from a description of the operations required for the removal of germanous sulfide.

Operation I.—Finely ground germanite is heated in a stream of dry, oxygen-free, nitrogen gas at 800° with the removal of arsenious sulfide and sulfur.

Operation II.—Ammonia gas is passed over the residue from (I) at 825° whereby the germanic sulfide of the ore is reduced to germanous sulfide, which, in turn, distils from the ore mass to collect in cooler regions of the apparatus. If the arsenious sulfide is completely removed in (I), germanous sulfide is the only substance to leave the ore in (II).

For the preliminary experiments, we are greatly indebted to the late Professor Charles James of

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(1) Present address: University of Chicago, Chicago, Illinois.

(2) Schneiderhöhn, *Metall u. Erz*, **17**, 364 (1920).

(3) Pufahl, *ibid.*, **19**, 324 (1922).

(4) Kriesel, *ibid.*, **20**, 257 (1923); *Chem. Ztg.* **48**, 961 (1923).

(5) Lunt, *S. African J. Sci.*, **20**, 157 (1923).

(6) Thomas and Pugh, *J. Chem. Soc.*, **125**, 816 (1924).

(7) Keil, *Z. anorg. allgem. Chem.*, **152**, 101 (1926); Dede and Russ, *Ber.*, **61**, 2451 (1928); and Pugh, *J. Chem. Soc.*, 2540 (1929).

(8) Patnode and Work, *Ind. Eng. Chem.*, **23**, 204 (1931).

(9) Buchanan, *ibid.*, **8**, 585 (1916); *cf.* Müller, THIS JOURNAL, **43**, 1088 (1921); Dennis and Papish, *ibid.*, **43**, 2131 (1921); Dennis and Johnson, *ibid.*, **45**, 1380 (1923).