

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

Interaction of Pyrophosphate Ion with Certain Multivalent Cations in Aqueous Solutions¹BY L. B. ROGERS² AND C. A. REYNOLDS³

Introduction

Nearly all metallic cations, with the exception of the alkali metal group, react with aqueous pyrophosphate solutions to form insoluble precipitates. A majority of the precipitates are, however, readily soluble in excess pyrophosphate as a result of complex ion formation. Despite the fact that this behavior has been known for many years, almost nothing is known about the composition of these ions.

Early work on complex pyrophosphate salts was done by a number of investigators,⁴ but they usually analyzed salts which had been dried at elevated temperatures thereby making some of their conclusions doubtful. In general, the analytical methods were inadequate so that investigators had difficulty in duplicating results and were often unable to obtain the compounds reported by their predecessors. Starting in 1915, modern research on complex pyrophosphates was carried out by Rosenheim and his co-workers⁵ who prepared many salts in the dry state. In reporting their results, these investigators assumed that the original metal cation was present in the precipitate as a complex anion. In 1936, Bassett, Bedwell, and Hutchinson⁶ repeated all of the previous work and prepared salts which, for the most part, gave the same analyses as the salts obtained by Rosenheim and his co-workers. However, they presented convincing evidence that, although a complex anion existed in solution, the precipitate was almost always a double salt containing a simple (uncomplexed except by water) metal cation. As a result, it appears that the compositions of complex pyrophosphate ions are, with a few exceptions,⁷ unknown.

Even if complex ions cannot be precipitated for analysis, they can be examined in solution by nu-

merous methods. In the present study, information concerning the ratio of pyrophosphate-to-metal cation was obtained for several representative cations using the conventional techniques of potentiometry, conductivity and polarography.

Experimental Details

Apparatus.—Potentiometric titrations were made using a Beckman Model "G" pH meter in conjunction with a Beckman "1190-E" glass electrode, which had a very small correction for sodium ion, and a Beckman "1170" saturated calomel electrode. Changes in the resistance of a solution during a titration were measured with a conductivity bridge, Model RC-1B, made by Industrial Instruments, Inc., and a conductivity cell having platinized electrodes. All polarographic measurements were made using a polarographic cell containing a calibrated dropping mercury electrode and a salt bridge which connected the polarographic solution to a large calomel electrode used as a reference. All measurements were made with a Leeds and Northrup "Electrochemograph."

No effort was made to thermostat a solution during a titration because it was noted that the temperature did not change more than 3° in that time. On the other hand, the solutions used in the polarographic studies were carefully maintained at 25.0 ± 0.1°.

Kimball "retested" volumetric ware was employed throughout this study.

Reagents and Solutions.—"J. T. Baker Analyzed" chemicals were used without further purification throughout this investigation. Nitrates of the metal cations were employed in the preparation of solutions, and distilled water was used in all cases. The concentration of each standard was generally known within one part per thousand.

Electrolytic procedures using platinum electrodes were employed to standardize the 0.1 M solutions of copper (II),^{8a} cobalt (II),^{8b} cadmium,^{8c} and lead (II).^{8d} Both magnesium^{8e} and zinc^{8f} were precipitated as the double ammonium phosphate and ignited in porous porcelain crucibles to the pyrophosphate. Nickel was determined gravimetrically using dimethylglyoxime^{8g}; aluminum, using ammonia.^{8h} Iron (III) was determined by reduction with stannous chloride and titration with a solution of dichromate using diphenylamine as an indicator.⁸ⁱ

A 0.1 M solution of sodium pyrophosphate was prepared by weighing the salt, Na₄P₂O₇·10H₂O. The solution was standardized by hydrolyzing it to orthophosphate with dilute nitric acid at 90°, precipitating the orthophosphate with magnesia mixture, and igniting the precipitate at 1000°. A solution of sodium pyrophosphate is stable indefinitely at room temperature.^{8j}

A solution of 1% gelatin was made by dissolving Braun-Knecht-Heinman granular gelatin in hot water.

Procedures

Resistance Studies.—For titrations in which the metal cation was added to pyrophosphate, 2 ml. of 0.1 M solution of sodium pyrophosphate was pipetted into a beaker and diluted to 500 ml. This solution was titrated with an 0.1 M solution of metal cation from a 5-ml. buret,

(1) Taken from a thesis submitted by C. A. Reynolds to the Department of Chemistry and the Committee on Graduate Study of Stanford University in partial fulfillment of the requirement for the degree of Doctor of Philosophy, July, 1947.

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(4) (a) Persoz, *Ann. Chem. Phys.*, **20**, 315 (1847); (b) Schwarzenberg, *Ann.*, **65**, 133 (1848); (c) Baer, *Pogg. Ann.*, **75**, 152 (1848); (d) Fleitmann and Henneberg, *Ann.*, **65**, 387 (1848); (e) Pahl, *Ofvers. K. Vet. Akad. Forh.*, **30**, 29 (1873).

(5) (a) Rosenheim and Triataphyllides, *Ber.*, **48**, 582 (1915); (b) Rosenheim, Frommer, Glaser and Handler, *Z. anorg. Chem.*, **153**, 126 (1926).

(6) Bassett, Bedwell and Hutchinson, *J. Chem. Soc.*, 1412 (1936).

(7) (a) Stareck, United States Patent 2,250,556 (1941); (b) Kolthoff and Watters, *Ind. Eng. Chem., Anal. Ed.*, **15**, 8 (1943); (c) Pascal, *Compt. rend.*, **146**, 231 (1908); (d) Gilmore, *Ind. Eng. Chem.*, **29**, 584 (1937); (e) Dworzak and Reich-Rohrwig, *Z. anal. Chem.*, **77**, 14 (1929).

(8) (a) W. W. Scott, "Standard Methods of Chemical Analysis," edited by N. H. Furman, D. Van Nostrand Co., Inc., 5th edition, Vol. I, New York, 1939, p. 359; (b) *ibid.*, p. 315; (c) *ibid.*, p. 202; (d) *ibid.*, p. 507; (e) *ibid.*, p. 532; (f) *ibid.*, p. 1058; (g) *ibid.*, p. 619; (h) *ibid.*, p. 8; (i) *ibid.*, p. 473; (j) *ibid.*, p. 689.

(9) Morgan and Swoope, *Ind. Eng. Chem.*, **35**, 821 (1943).

readings being taken at 0.4 ml. intervals with the conductivity bridge. The solution of cation was added until a precipitate was formed and the successive changes in resistance became nearly the same. Then, the procedure was repeated using another sample of pyrophosphate diluted to 750 ml. instead of 500 ml. In the case of copper and zinc, the endpoints for the two titrations did not occur at the same ratio of metal cation to pyrophosphate, so titrations were also made at dilutions of 100, 250, 350, 500, 750 and 1000 ml.

Whenever titrations were made by adding pyrophosphate to a solution of the metal cation the procedure was very similar to that just described. Two ml. of the metal nitrate solution was diluted to 500 ml. and titrated with 0.1 *M* sodium pyrophosphate. Readings were again taken at 0.4 ml. intervals.

Potentiometric Studies.—These titrations were made with a glass electrode which had been cleaned thoroughly with dilute acid, allowed to stand in distilled water for a number of hours, and then calibrated immediately before use by means of a standard potassium acid phthalate buffer at pH 3.90.

As in most precipitation reactions, the problem arose as to how long to wait after the delivery of a portion of solution before recording the potential. It was noted that the pH continued to change for about five minutes after each addition, but that the amount of change after one minute was very small. It appeared that no serious error would be introduced if readings were always taken exactly one minute after the last drop of solution had been added. With the aid of motor stirring, it was possible to reproduce the results of a titration quite easily.

In one set of titrations 25-ml. portions of 0.1 *M* sodium pyrophosphate were diluted to 100 ml. and titrated with 0.1 *M* solutions of metal cation delivered from a 50 ml. buret. Readings were taken at 2-ml. intervals during the major part of each titration and at 1-ml. intervals in regions where equivalence points were expected to produce large changes in potential. The titrations were discontinued when the pH change, upon addition of 2 ml. of solution, was 0.05 pH or less.

In several instances an unexpected drop in pH was discovered during the titration of a metal cation with pyrophosphate solution. In these instances the initial portion of the titration was repeated using a 5-ml. buret and 0.4-ml. portions of solution. In order to study the reproducibility of the pH drop the results obtained by this process were compared with those obtained when 8 or 10 milliliter portions were added.

Polarography.—Analyses were made on a 50-ml. portion of solution containing 0.1 *M* sodium pyrophosphate, 1.00×10^{-3} *M* reducible ion, a maximum suppressor (about 0.002%), and 1.0 g. of sodium sulfite. The sulfite, which served to remove oxygen, was used only after making certain that it had no influence on the polarographic reaction. The test consisted of comparing runs

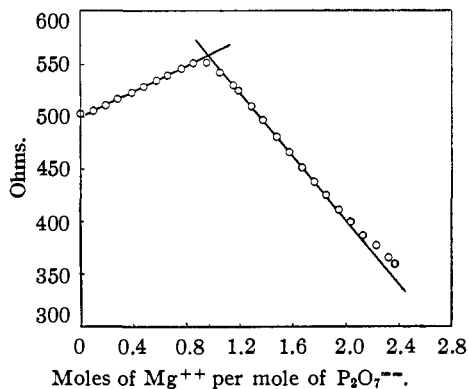


Fig. 1.—Conductometric titration of pyrophosphate with magnesium.

in which sulfite was absent and the oxygen removed by displacement with purified nitrogen with runs in which sulfite was present.

Amperometric titrations were carried out in a manner equivalent to the procedure described by Kolthoff and Lingane.¹⁰ A series of solutions were made up each of which contained a different ratio of cation to pyrophosphate plus the standard amounts of maximum suppressor and sulfite. Complete current-voltage curves were obtained for each solution.

Results

Resistance Studies.—A typical curve for the titration of pyrophosphate with cadmium, cobalt, nickel, and magnesium may be seen in Fig. 1. The peak of resistance in the case of cadmium occurred at a molar ratio of cadmium to pyrophosphate of 0.96, for cobalt at 0.93, for lead at 0.95, for nickel at 0.94, and for magnesium at 0.97. The point at which precipitation began varied with the different metal cations. Cadmium began to precipitate at a ratio of 0.60, cobalt at 1.20, lead at 1.47, and nickel at 1.55. Magnesium did not precipitate at all.

A curve for the titration of pyrophosphate with aluminum is shown in Fig. 2. In this curve, the inflection at 0.51 corresponds to the complex ion $\text{Al}(\text{P}_2\text{O}_7)_2^{--}$, the inflection at 0.96 to the complex $\text{Al}(\text{P}_2\text{O}_7)^-$, and the inflection at 1.33 to the precipitate $\text{Al}_4(\text{P}_2\text{O}_7)_3$. An almost identical curve was found for iron(III).

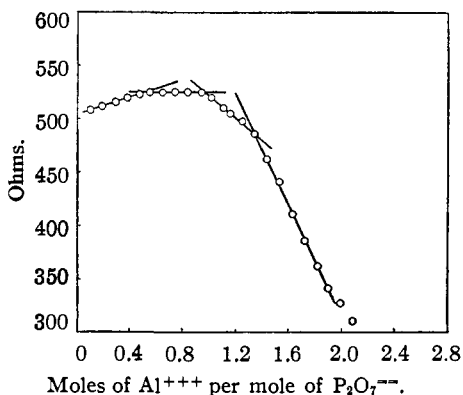


Fig. 2.—Conductometric titration of pyrophosphate with aluminum.

The titrations of pyrophosphate with copper (II) and zinc were exceptional because their peaks of resistance changed with the initial concentration of pyrophosphate. A study of a series of copper titrations is reported in Fig. 3, and it shows that $\text{Cu}(\text{P}_2\text{O}_7)_2^{--}$ is formed in concentrated solutions and $\text{Cu}(\text{P}_2\text{O}_7)^-$ in dilute solutions. A sodium salt of the former was isolated by Bassett, Bedwell and Hutchinson,⁶ but they were unable to isolate a salt of the corresponding zinc complex.

The interpretation of experimental data collected in titrations of pyrophosphate into solutions containing the metal cation is not as clear-cut as that of the previous set of titrations. A

(10) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, p. 447.

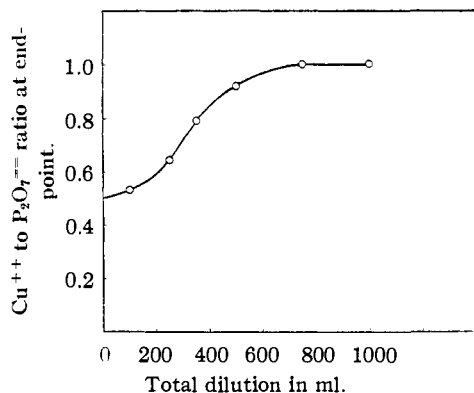


Fig. 3.—Change with dilution in the ratio of pyrophosphate-to-copper at peak resistance in conductometric titrations.

typical plot is shown in Fig. 4. The inflection point at a ratio of 0.5 corresponds to a precipitate of the normal pyrophosphate, $\text{Cu}_2\text{P}_2\text{O}_7$. A similar inflection point was observed for cadmium and zinc which also formed insoluble pyrophosphates, but in the titrations of aluminum, cobalt, nickel, and magnesium, no curve had a definite inflection point at a ratio corresponding to the composition of a similar precipitate. In general, the remaining portion of each curve had an inflection resulting from a complex having a ratio of pyrophosphate-to-cation close to 1.0 or 2.0. However, the exact location of each point was uncertain because the breaks were not sharply defined.

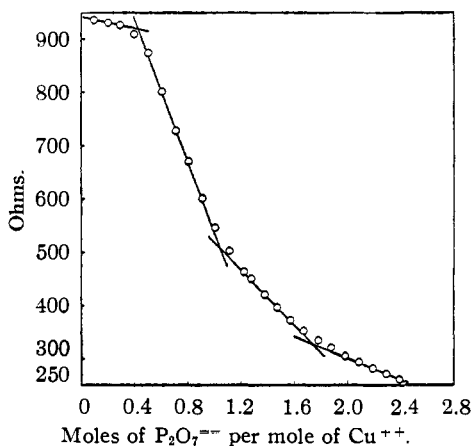


Fig. 4.—Conductometric titration of copper(II) with pyrophosphate.

Potentiometric Studies.—The titrations of pyrophosphate with copper, zinc and cadmium are shown in Fig. 5; the curves for magnesium, nickel, and cobalt in Fig. 6; and the curve for aluminum in Fig. 7. Curves have not been shown for lead and iron (III) because of their similarity to nickel and aluminum, respectively. The jump in pH coincided with the appearance of a precipitate in the titrations of cadmium, cobalt, copper, and zinc and apparently resulted from

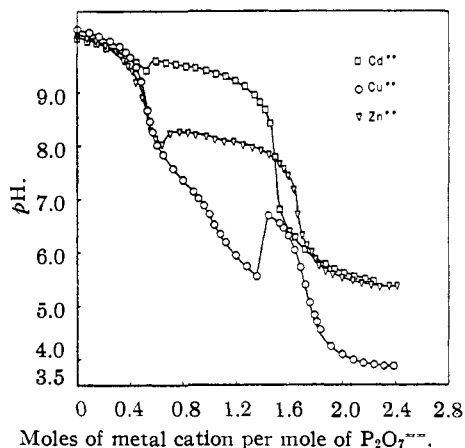


Fig. 5.—Potentiometric titrations of pyrophosphate with cadmium, copper(II), and zinc.

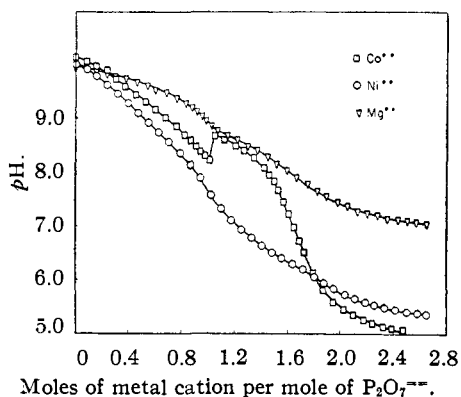


Fig. 6.—Potentiometric titration of pyrophosphate with cobalt, nickel and magnesium.

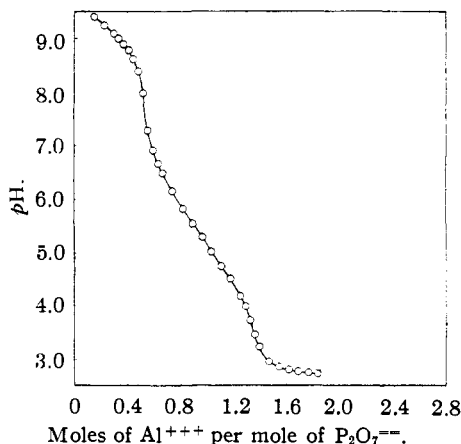


Fig. 7.—Potentiometric titration of pyrophosphate with aluminum.

supersaturation. In the nickel titration, the precipitate appeared at a ratio of 1.5 without any jump in pH. In the titration with magnesium no precipitation occurred.

Groups of curves which are typical of titrations of a metal cation with pyrophosphate are shown in

TABLE I

POLAROGRAPHIC DATA FOR $1.00 \times 10^{-3} M$ REDUCIBLE ION IN $0.10 M$ SODIUM PYROPHOSPHATE AT 25.0°

Ion	$E_{1/2}$ vs. S. C. E.	Diffusion constant	Dissociation constant
$\text{Cu}(\text{P}_2\text{O}_7)_2^{4-}$	-0.40
$\text{Cu}(\text{P}_2\text{O}_7)_2^{3-}$	-1.33	2.49	1.9×10^{-27}
$\text{Fe}(\text{P}_2\text{O}_7)_2^{3-}$	-0.82	1.02
$\text{Pb}(\text{P}_2\text{O}_7)^-$	-0.69	2.57	5.8×10^{-18}

TABLE II

POTENTIOMETRIC STUDIES OF RATIOS OF CATION-TO PYROPHOSPHATE IN PRECIPITATES SHOWING DIFFERENCES RESULTING FROM DIRECTION OF TITRATION

Element	Ratio	
	Cation added to pyrophosphate	Pyrophosphate added to cation
Aluminum	1.33	1.27
Cadmium	1.50	1.73
Cobalt	1.68	1.79
Copper	1.72	1.85
Iron	1.33	1.25
Lead	..	1.67
Magnesium	..	1.52
Nickel	..	1.73
Zinc	1.66	1.82

Figs. 8, 9 and 10. In the titrations of cobalt, lead, magnesium and nickel precipitation occurred at once together with a jump in pH. The slight dips in the curves which appeared immediately thereafter appeared to be real because they could be duplicated. The pronounced dips that were found for cadmium, copper, zinc, aluminum, and iron could also be duplicated readily even when the size of the portion of reagent and the time between additions were varied.

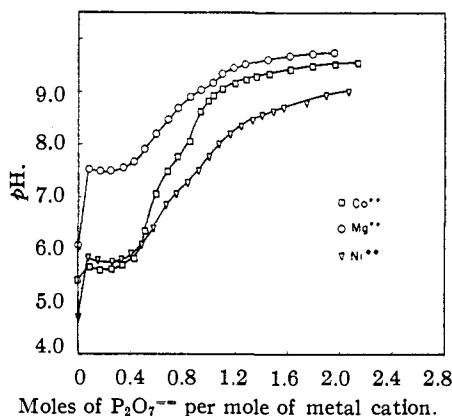


Fig. 8.—Potentiometric titrations of cobalt, magnesium and nickel with pyrophosphate.

Polarographic Studies.—Preliminary studies in $0.1 M$ sodium pyrophosphate indicated that only copper, lead and iron were readily reduced at a dropping mercury electrode. The copper was reduced in two steps, the others in one. Cadmium gave a flat wave starting at -1.0 v. which did not reach a plateau before hydrogen was evolved at -1.95 volts. The complexes of

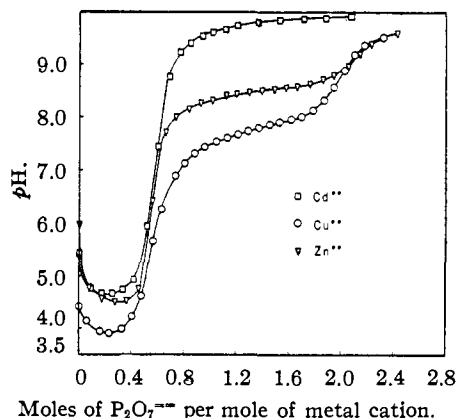


Fig. 9.—Potentiometric titrations of cadmium, copper and zinc with pyrophosphate.

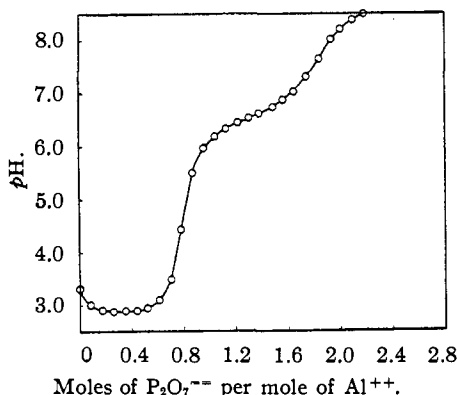


Fig. 10.—Potentiometric titration of aluminum with pyrophosphate.

aluminum, cobalt, magnesium, nickel, and zinc produced waves starting at about -1.85 volts and then fusing with the hydrogen wave.

A maximum was found for the cupric-cuprous reduction and the plumbous-lead reduction. Maximum suppressors such as methyl red, tylose and solutions of electrocapillary-active electrolytes were tried but proved to be less satisfactory than gelatin. The optimum concentration of the latter proved to be about 0.002% . However, the wave for the cupric-cuprous reduction was much smaller than normal and hence unsatisfactory for analysis even without a maximum suppressor present.

A careful study of the form and the height of each wave showed that the cuprous-copper, plumbous-lead and ferric-ferrous steps were reversible.¹¹ No exact data could be obtained for the cupric-cuprous wave because maximum suppressors seriously decreased the diffusion current before the maximum disappeared. In Table I are collected data for half-wave potentials, polarographic diffusion constants¹² and dissociation constants of the complexes involved in the three reversible reductions.

(11) Ref. 10, p. 169.

(12) Lingane, *Ind. Eng. Chem., Anal. Ed.*, **16**, 583 (1943).

Discussion

The data for complex ions found in this investigation can be stated briefly as follows. A complex of the type $M^{II}(P_2O_7)^{2-}$ is formed by cadmium, cobalt, copper, lead, magnesium, nickel and zinc; $M^{III}(P_2O_7)^{-}$ by aluminum and iron; $M^{II}(P_2O_7)^{2-}$ by copper and zinc; $M^{III}(P_2O_7)_2^{--}$ by aluminum and iron. The compositions of the complex ions found in the potentiometric work agreed with those found by conductivity with one exception, *i. e.*, the complex ion $CoP_2O_7^{--}$ was not found by potentiometric titration even though it was readily detectable in the conductometric work.

Information in Table II concerning the composition of precipitates was obtained primarily from potentiometric studies. Aluminum and iron formed precipitates corresponding to $M_4^{III}(P_2O_7)_3$. Divalent ions, on the other hand, did not appear to precipitate as pure compounds, although, if they did, the size of the experimental error did not allow one to select with certainty from $M_5(P_2O_7)_3^{--}$, $M_7(P_2O_7)_4^{--}$ and $M_9(P_2O_7)_5^{--}$. The only exceptions were the titrations of magnesium with pyrophosphate and pyrophosphate with cadmium where the ratio closely corresponded to $M_3(P_2O_7)_2^{--}$. However, even in these cases, mixtures may have formed which by chance had this ratio.

The anomalous drop of pH observed at the beginning of several potentiometric titrations is quite interesting. In the present study cadmium, copper, zinc, iron and aluminum had curves with very pronounced changes in pH while those of cobalt, lead, magnesium and nickel were less pronounced and may not have been real. Extensive studies were made of the first four ions from which it was found that the drop in pH was very reproducible, even when the reagents were mixed at different rates and when the size of the portion of added reagent was changed. Very stable systems appeared to be involved.

Such a change in pH has been found in many studies reported in the literature, but in most cases the change was slight and hence either overlooked or ignored by the authors. The most famous case is that encountered in titrating the second equivalent of orthophosphoric acid with calcium hydroxide. This phenomenon was first discovered by Wendt and Clark¹³ in 1923, and similar results were obtained by Holt, LaMer, and Chown,¹⁴ and by Farnell.¹⁵ Greenwald¹⁶ proposed that a precipitate with a formula $Ca(OH) \cdot CaPO_4$ was formed following the precipitation of $CaHPO_4$, which thereby liberated oxonium ions and lowered the pH .

The potentiometric results obtained in the

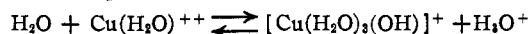
(13) Wendt and Clark, *THIS JOURNAL*, **45**, 881 (1923).

(14) Holt, LaMer and Chown, *J. Biol. Chem.*, **64**, 509 (1925).

(15) Farnell, *J. Soc. Chem. Ind., Trans.*, **45**, 343 (1926).

(16) Greenwald, *THIS JOURNAL*, **66**, 1305 (1944).

present study indicate that a hydroxy-ion existing in an equilibrium such as



is precipitated by pyrophosphate. Because the potentiometric curves did not permit one to assign a definite formula to the precipitate, an amperometric study was made. Fig. 11, a typical curve for the titration of cupric ion with pyrophosphate, unfortunately, did not clarify the question of the composition of the precipitate. A similar study with zinc produced a curve for the "simple" ion very much like the analogous curve for cupric ion, but since the pyrophosphate complex of zinc was not reducible, the corresponding curve could not be drawn for the concentration of the complex ion. Therefore, the composition of the initial precipitate cannot be reported on the basis of these studies.

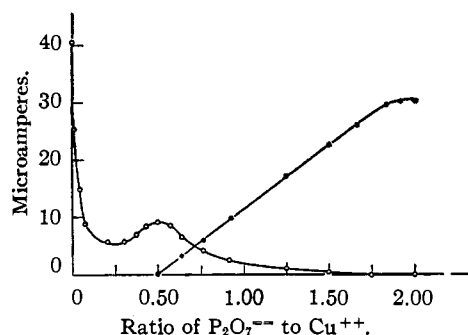


Fig. 11.—Heights of the first and second polarographic waves for copper(II) at different pyrophosphate-to-copper ratios in 0.10 *N* potassium chloride: O, first wave, reduction of "simple" ion; ●, second wave, reduction of complex pyrophosphate ion.

Summary

A study of the ratio of pyrophosphate to coordinating action has been carried out for certain representative cations using resistance and potentiometric titrations together with polarographic data. In most cases only a single complex ion was detected, but copper and zinc each formed two, the more highly coordinated one predominating in concentrated solution, the other, in very dilute solution.

A marked drop in pH which was found in titrating copper(II) with sodium pyrophosphate appears to be due to formation of an insoluble basic salt such as $[Cu(H_2O)_5(OH)]_4P_2O_7$. Aluminum, cadmium and zinc were found to produce equally marked changes in pH which can be explained by assuming that similar precipitates are formed.

Polarographic measurements of half-wave potentials, diffusion constants, and stability constants are given for $1.00 \times 10^{-3} M$ solutions of copper, iron and lead in 0.10 *M* sodium pyrophosphate.

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