TABLE III

THERMAL DATA AT 298.16°K.

		$\Delta H^0_{298.16}$, cal./mole	$\Delta S^0_{298.16}$, E. U./mole	$\Delta F^0_{298.16}$, cal./mole
(1)	$2Al + 3S(rh.) + 6O_2 \longrightarrow Al_2(SO_4)_3$	$-820{,}990 \pm 430$	-273.3 ± 0.4	$-739{,}500 \pm 450$
(2)	$2Al + 3S(rh.) + 6H_2 + 9O_2 \longrightarrow Al_2(SO_4)_3 \cdot 6H_2O$	$-1{,}268{,}150 \pm 360$	-552.9 ± 0.8	$-1{,}103{,}300 \pm 430$
(3)	$K + Al + 2S(rh.) + 4O_2 \longrightarrow KAl(SO_4)_2$	$-589{,}170 \pm 310$	-184.4 ± 0.4	$-534{,}190 \pm 330$
(4)	$K + Al + 2S(rh.) + 12H_2 + 10O_2 \longrightarrow KAl(SO_4)_2 \cdot 12H_2O$	$-1{,}447{,}700 \pm 260$	-738.0 ± 2.0	$-1{,}227{,}660 \pm 650$
(5)	$Al_2(SO_4)_3 + 6H_2O(liq.) \longrightarrow Al_2(SO_4)_3 \cdot 6H_2O$	$-37{,}250 \pm 220$	-45.6 ± 0.8	$-23{,}650 \pm 320$
(6)	$KAl(SO_4)_2 + 12H_2O(liq.) \longrightarrow KAl(SO_4)_2 \cdot 12H_2O$	$-38{,}720 \pm 210$	-85.6 ± 2.1	$-13{,}200 \pm 660$
(7)	$^1/_2K_2SO_4 + {}^1/_2Al_2(SO_4)_3 \longrightarrow KAl(SO_4)_2$	$-7{,}340 \pm 230$	-0.7 ± 0.4	$-7{,}130 \pm 260$
(8)	$^1/_2K_2SO_4 + {}^1/_2Al_2(SO_4)_3 + 12H_2O(liq.) \longrightarrow KAl(SO_4)_2 \cdot 12H_2O$	$-46{,}060 \pm 130$	-86.3 ± 2.1	$-20{,}330 \pm 640$

are computed from the relationship $\Delta F^0_{298.16} = \Delta H^0_{298.16} - 298.16\ \Delta S^0_{298.16}$.

Summary

Specific heats of anhydrous aluminum sulfate, aluminum sulfate hexahydrate, anhydrous potassium aluminum sulfate, and potassium aluminum sulfate dodecahydrate, were measured in the temperature range 52 to 298°K. Potassium aluminum sulfate dodecahydrate has a transition at 59.7°K., with a heat of transition of 46.9 cal./mole.

The following molal entropies at 298.16°K. were computed: anhydrous aluminum sulfate, 57.2 ± 0.3; aluminum sulfate hexahydrate, 112.1 ± 0.7; anhydrous potassium aluminum sulfate, 48.9 ± 0.3; and potassium aluminum sulfate dodecahydrate, 164.3 ± 2.0.

Combination of the above entropies with related thermal data yields the free energies of formation from the elements at 298.16°K.: anhydrous aluminum sulfate, −739,500 ± 450; aluminum sulfate hexahydrate, −1,103,300 ± 430; anhydrous potassium aluminum sulfate, −534,190 ± 330; and potassium aluminum sulfate dodecahydrate, −1,227,660 ± 650 cal./mole. Other pertinent thermal data have been calculated.

BERKELEY, CALIFORNIA RECEIVED JANUARY 27, 1945

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KENTUCKY]

A Polarographic Study of Barium Ion Removal by Complex Phosphates[1]

BY J. A. CAMPBELL[2] AND CHARLES SCHENKER[3]

The question of what compounds may be formed by the dehydration of orthophosphoric acid has been actively discussed since metaphosphoric acid was first prepared by Graham in 1833.[4] The existence of many alkali salts of complex phosphates has been claimed, but, in most cases, the supporting evidence is inconclusive, and a survey of the extensive literature seems to lead only to the conclusion that considerable confusion exists throughout the entire field. A review of the more important work has been given by Partridge, Hicks and Smith.[5]

Modern interest in these phosphates was increased by the happy discovery by Hall[6] that one of them, the so-called sodium hexametaphosphate, has the property of binding up alkaline earth ions in such a way as to render them inert to their usual precipitating agents.

Complex salts of pentavalent phosphorus may be divided into two classes: the polymers of metaphosphates and the polyphosphates, which latter may be looked upon as salts formed from orthophosphoric acid by a degree of dehydration intermediate between that which yields metaphosphoric acid and that which results in pyrophosphoric acid. These substances can also be viewed as a series of compounds formed by molecular addition of pyrophosphates to metaphosphates.

It was the purpose of this work to study the effect of various phosphates on dilute solutions of barium ion. The substances investigated were stoichiometrically equivalent to sodium hexametaphosphate, tetrasodium pyrophosphate, sodium triphosphate, and sodium tetraphosphate, each prepared as hereinafter indicated.

Sodium hexametaphosphate $(NaPO_3)_6$ is the glass obtained by quenching a melt of primary sodium orthophosphate which has been heated above 650° for several hours.

The theory advanced for the binding up of the metallic ion is that the hexametaphosphate ionizes according to the equation

$$(NaPO_3)_6 = 2Na^+ + Na_4P_6O_{18}^{=}$$

The anion can then react with the metallic ion

$$2Ba^{++} + Na_4P_6O_{18}^{=} = Ba_2P_6O_{18}^{=} + 4Na^+$$

The barium is thus sequestered in a complex

---

[1] From a thesis submitted by Charles Schenker in partial fulfillment of the requirements for the degree of Master of Science. Original manuscript received April 20, 1943.

[2] Present address: University of Idaho, Moscow, Idaho.

[3] Present address: Ashland Oil and Refining Company, Ashland, Kentucky.

[4] Graham, *Phil. Trans. Royal Soc.*, **123**, 253 (1833).

[5] Partridge, Hicks and Smith, THIS JOURNAL, **63**, 454 (1941).

[6] Hall, U. S. Patent 1,956,515 (1934), reissue 19,719 (1935).

anion.[7] According to this mechanism, one mole of hexametaphosphate should remove two molecules of divalent metal. The complex forming power of the hexametaphosphate is not, however, limited to the alkaline earths.[8]

The existence of many so-called polyphosphates has been claimed. Only two of these, sodium triphosphate, $Na_5P_3O_{10}$, and sodium tetraphosphate, $Na_6P_4O_{13}$, are of importance now. A thermal study of the system sodium metaphosphate–sodium pyrophosphate made by Parravano and Calcagni[9] failed to reveal any intermediate salts. The more recent work of Partridge, Hicks and Smith[5] has confirmed the existence in the solid state of triphosphate although the sodium tetraphosphate, supposedly prepared by Fleitmann and Henneberg,[10] was found to be in reality a mixture of sodium triphosphate and sodium metaphosphate.

It was thought that a study of the effect of each of these substances on barium ion might give some information on whether they exist in dilute solutions. In the case of all compounds studied, with the exception of the metaphosphate glass, we have, following Partridge, Hicks and Smith, confined ourselves to the crystalline substances formed by slow cooling.

The concentrations of barium ion were determined in the presence of differing amounts of the various phosphates by means of the dropping mercury electrode. Essentially the method was a modification of the so-called amperometric titration technique first employed by Heyrovsky and Berezicky[11] and which has been extensively studied by Kolthoff and his co-workers.[12] This technique consists in setting the voltage at a point above the half wave potential of the ion being precipitated or otherwise being removed and observing the diffusion current as a function of the volume of the removing reagent. Since the diffusion current is directly proportional to the concentration, the current decreases as the titration proceeds and is reduced to zero at the equivalent point. The phosphate concentration at the equivalent point could be determined by extrapolating to zero diffusion current the straight lines of the concn. phosphate *vs.* Ba^{++} diffusion current graphs.

Preliminary experiments showed it was possible to observe a barium wave in the presence of sodium ions. Instead of actually titrating the barium ion with the various phosphates, it was our practice to make up solutions of varying proportions of the two substances and, after degassing with nitrogen, to measure the diffusion current. All reported measurements on the barium diffusion current were made at a potential of -2.0 v. (saturated calomel).

Experimental Methods

Preparation of Materials.—All of the phosphates studied were prepared from reagent grade monosodium orthophosphate monohydrate and disodium orthophosphate dodecahydrate. Following Partridge, Hicks and Smith,[5] sodium metaphosphate was prepared from the former, while anhydrous tetrasodium pyrophosphate was obtained by preliminary heating of the latter salt over a burner followed by heating in platinum to a red heat in an electric muffle.

The sodium hexametaphosphate was prepared from monosodium orthophosphate monohydrate by heating for three hours in a platinum dish at 750° in an electric muffle. The melt was then rapidly cooled by pouring it on a thick slab of steel. The glassy product was placed immediately in a desiccator.

The sodium triphosphate was prepared by a modification of the directions given by Rudy and Schloesser.[13] Sodium metaphosphate and tetrasodium pyrophosphate, as previously prepared, were mixed in equal molecular proportions and fused in a platinum dish at 800°. The mass was then cooled at 600° for two hours, kept at 400° for one-half hour, raised to 600° for two more hours, and finally brought to room temperature by cooling at the rate of 100° an hour.

Sodium tetraphosphate was prepared by mixing the sodium metaphosphate and tetrasodium pyrophosphate in the proportion of two moles of the former to one mole of the latter and following the same procedure of heating and cooling as for the triphosphate.

The supporting electrolyte, tetramethylammonium bromide was purified by recrystallization from a mixture of alcohol and water.

Apparatus and Technique.—The instrument used was a manually operated Fisher "Electropode." Capillaries were drawn having a drop time between three and five seconds and an $m^{2/3}t^{1/6}$ value of 2.05. Solutions were made in differing proportions, using carbon dioxide-free water. All solutions were prepared immediately before using in order that no reversion to the orthophosphate could occur. The temperature at which all readings were taken was 25°.

Sodium Hexametaphosphate.—An attempt was made to determine whether the polarograph offers any direct evidence regarding the stepwise dissociation of sodium hexametaphosphate, postulated by Smith[7] and also by Treadwell and Leutwyler.[14] Two characteristics of current–voltage curves for complex ions are the shifting of the half-wave potential of the metallic ion as well as a generally observed lowering of the diffusion current. Thus the presence of a very stable $Na_4P_6O_{18}^{=}$ anion in any large amount should affect the polarogram. Using sodium chloride as a reference substance, the polarograms of equivalent concentrations of the various phosphates were observed. No appreciable difference in diffusion currents was observed. These data indicate that no very stable complex ions containing sodium are present, but they do not completely rule out the possibility of their existence.

When varying amounts of sodium hexametaphosphate were added to a known quantity of barium chloride, a flocculent white precipitate was produced which redissolved in an excess of sodium hexametaphosphate. The composition of this precipitate follows from the values of the diffusion current for barium given in Table II. Repeated trials gave an average of 2.9 moles of barium removed for each mole of sodium hexa-

---

[7] Smith, *American Dyestuff Reporter*, June 4, 1934.

[8] Thomson, *Analyst*, **61**, 320 (1936).

[9] Parravano and Calcagni, *Z. anorg. Chem.*, **65**, 1 (1910).

[10] Fleitmann and Henneberg, *Ann.*, **66**, 304 (1848).

[11] Heyrovsky and Berezicky, *Coll. Czech. Chem. Comm.*, **1**, 19 (1929).

[12] Kolthoff and Lingane, "Polarography," Interscience Pub., Inc., New York, N. Y., 1941.

[13] Rudy and Schloesser, *Ber.*, **73B**, 484 (1940).

[14] Treadwell and Leutwyler, *Helv. Chim. Acta*, **21**, 1450 (1938).

TABLE I

DIFFUSION CURRENTS OF SODIUM ION IN DIFFERENT COMPOUNDS

Compound	Molar concn. milli-moles/liter	Diff. current, microamps.	Diffusion current per millimole Na^+
NaCl	6	23.28	3.88
$(NaPO_3)_6$	1	22.12	3.69
$NaPO_3$	4	15.57	3.89
$Na_4P_2O_7$	1	15.57	3.89
$Na_5P_3O_{10}$	1	19.79	3.95
$Na_6P_4O_{13}$	1	21.83	3.64

metaphosphate. To put this in integers, one mole of hexametaphosphate combines with three moles of barium ion to form $Ba_3P_6O_{18}$. It is significant that when this precipitate is redissolved in excess hexametaphosphate, the barium is completely removed so far as can be determined by the polarograph. The barium ion when added to an excess of sodium metaphosphate showed no diffusion current, and the curve for the sodium ion was not affected by the addition of barium. This supports the view that the barium is sequestered in a complex anion. That there are probably two barium atoms in the complex is shown by the fact that when barium ion was titrated into hexametaphosphate the precipitate began to form when two moles of barium were present to one mole of sodium hexametaphosphate, while when the reverse order was followed, the precipitate began to dissolve when the same ratio was reached.

TABLE II

EFFECT OF $(NaPO_3)_6$ ON $BaCl_2$ SOLUTIONS

CONCN. OF $BaCl_2$: 2×10^{-3} MOLAR

Concn. $(NaPO_3)_6$, milli-moles/liter	Diff. current Ba^{++}, microamp.	Concn. Ba^{++}, milli-moles/liter
0.000	12.80	2.00
.202	8.91	1.39
.404	5.38	0.84
.606	1.75	0.27

It is interesting to note that a solution of the sodium metaphosphate that was prepared by slow cooling of a melt of the orthophosphate had no effect on the diffusion current of the barium ion.

Tetrasodium Pyrophosphate.—In Table III are shown the results which were obtained with tetrasodium pyrophosphate. Upon adding the pyrophosphate to the barium ion a white, non-redissolving precipitate was formed. The polarograph showed that one mole of tetrasodium pyrophosphate removed 1.98 moles of barium. That the precipitate is barium pyrophosphate is, of course, well known and the result serves as a check on the other determinations.

TABLE III

EFFECT OF $Na_4P_2O_7$, $Na_5P_3O_{10}$, AND $Na_6P_4O_{13}$ ON $BaCl_2$ SOLUTIONS

Concentration of barium chloride, 2×10^{-3} mole per liter; i_d (Ba)$^{++}$ = diffusion current of barium ion in microamp.; concentrations in milli-moles per liter.

Concn. of phosphate	$Na_4P_2O_7$		$Na_5P_3O_{10}$		$Na_6P_4O_{13}$	
	$i_{d(Ba)^{++}}$	$C_{Ba^{++}}$	$i_{d(Ba)^{++}}$	$C_{Ba^{++}}$	$i_{d(Ba)^{++}}$	$C_{Ba^{++}}$
0.00	12.80	2.00	12.80	2.00	12.80	2.00
.20	10.19	1.60	9.60	1.50	9.75	1.52
.40	7.91	1.21	6.40	1.00	6.69	1.04
.60	5.24	0.822	3.11	0.478	3.49	0.546

Sodium Triphosphate.—The polarograph showed that one mole of sodium triphosphate removed 2.5 moles of barium ion in the form of a precipitate. The removal of 2.5 moles of barium is in accord with the reaction $2P_3O_{10}(-5) + 5Ba^{++} = Ba_5(P_3O_{10})_2$. Since Parravano and Calcagni[9] believed sodium triphosphate to be only an equimolecular mixture of sodium metaphosphate and tetrasodium pyrophosphate, a mixture of this proportion of our products was tested. As might be expected, it removed two moles of barium ion, because only the pyrophosphate in such a mixture is effective.

Additional evidence for the existence of sodium triphosphate is furnished by the fact that the precipitate is soluble in an excess of this substance. Titrations indicated that one mole of barium was present in the complex, probably resulting in a salt, $Na_3BaP_3O_{10}$. The mixture of slowly cooled sodium metaphosphate and tetrasodium pyrophosphate formed no complex with barium.

Sodium Tetraphosphate.—Experiments performed with a slow-cooled melt stoichiometrically equivalent to sodium tetraphosphate, $Na_6P_4O_{13}$, showed that one mole of this substance removed 2.4 moles of barium ion. If the precipitate which formed had been $Ba_3P_4O_{13}$, as would be expected, one mole of tetraphosphate would have removed three moles of barium ion. An equimolecular mixture of slow-cooled sodium metaphosphate and sodium triphosphate was found to remove 2.5 moles of barium ion. This was the expected result, since only the triphosphate is effective.

Summary

1. A study of the effect of various complex phosphates on the barium ion has been made, using the polarograph.

2. Sodium hexametaphosphate forms a compound of the composition $Ba_3(PO_3)_6$, which dissolves in excess hexametaphosphate, probably forming $Na_2(Ba_2P_6O_{18})$.

3. Tetrasodium pyrophosphate precipitates barium pyrophosphate.

4. Evidence has been found indicating the existence in solution of a compound $Na_5P_3O_{10}$ which will react with barium to form insoluble $Ba_5(P_3O_{10})_2$ and probably soluble $Na_3(BaP_3O_{10})$.

5. In agreement with the work of Partridge, Hicks and Smith, the slow cooling of a melt corresponding to the composition $Na_6P_4O_{13}$ has been shown to result in a mixture of sodium triphosphate and sodium metaphosphate.

LEXINGTON, KY.

RECEIVED JANUARY 15, 1945