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## CONCERNING THE ACIDITY OF SOLUTIONS OF SODIUM METAPHOSPHATES. APPROXIMATE STRENGTH OF MONOMETAPHOSPHORIC ACID. VI

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The acidity of solutions of sodium monometaphosphate, which was prepared by the method of Beans and one of us,<sup>1</sup> was found to diminish when it was recrystallized several times from water. This feeble acid reaction of such solutions of the fused product obtained by heating monosodium orthophosphate has been known since Graham's<sup>2</sup> memorable work. In his report this statement is found concerning the "fused insoluble variety:" "When the preceding insoluble variety, or the biphosphate in any condition, is heated in a platinum crucible to low redness, it undergoes fusion, and on cooling presents itself as a transparent glass, which deliquesces in a damp atmosphere and is highly soluble in water. *But the fused salt has undergone a most extraordinary and permanent change of properties.* The solution has a very feeble acid reaction when compared with crystallized biphosphate." This salt referred to by Graham is classed by J. W. Mellor<sup>3</sup> in a summary as a hexametaphosphate, under which he gives the property of acidity referred to above. G. Tammann<sup>4</sup> believed that Graham's salt was a mixture of three isomeric hexametaphosphates.

The significant fact that the salt prepared by us diminished in acidity when it was recrystallized several times from water indicated that the substance responsible for the acidity was capable of separation and that it existed as an impurity. The source and identity of the acid impurity was therefore sought.

Graham<sup>2</sup> also prepared disodium dihydrogen pyrophosphate by carefully heating monosodium orthophosphate and under properties stated that the solution was acid when no monosodium orthophosphate, detectable by silver nitrate, remained. He found also that the solutions became

<sup>1</sup> Beans and Kiehl, *THIS JOURNAL*, 49, 1878 (1927).

<sup>2</sup> Graham, *Phil. Trans.*, 123, 253 (1833).

<sup>3</sup> Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. II, 1922, p. 870.

<sup>4</sup> Tammann, *J. prakt. Chem.*, [2] 45, 463 (1892).

very acid as the white silver pyrophosphate was precipitated. In consideration of the similar methods of preparation it therefore is not improbable that the acidity of the product of his fused "insoluble variety" was due to the presence of the disodium dihydrogen pyrophosphate. Furthermore, if it is due to the presence of the above pyrophosphate, the "insoluble variety" must also contain it.

Accordingly, some of Graham's "insoluble variety" was prepared from carefully purified monosodium orthophosphate. The substance, in portions, was ground in an agate mortar with distilled water until a large quantity came in contact with the water. From solutions so prepared positive tests were obtained repeatedly for pyrophosphate by the following method of detection developed by Dr. H. P. Coats and one of us:<sup>5</sup> "A thirty-two hundredths molar zinc acetate solution in the presence of one-eighth its volume of glacial acetic acid is sufficiently sensitive to detect six ten-thousandths molar pyrophosphate in the presence of tenth molar ortho- and tenth molar monometaphosphate." Solutions of the sodium monometaphosphate prepared by us also gave positive tests for pyrophosphate.

In addition to the above precipitaton tests for pyrophosphate the changes in acidity of solutions of our recrystallized monometaphosphate were followed by Clark's indicators and color scale. A tenth molar solution of the metaphosphate prepared by crystallization at 450° from fusion gave a hydrogen-ion concentration of  $2.4 \times 10^{-5}$ . After two crystallizations the hydrogen-ion concentration dropped to  $2.5 \times 10^{-6}$ . A third crystallization produced no perceptible change. A fourth crystallization, however, was carried out fractionally. The first portion gave a hydrogen-ion concentration of  $1.6 \times 10^{-6}$  and the second,  $6.3 \times 10^{-7}$  moles per liter in tenth molar solutions. The purifications and measurements were made in conductivity water. The last solution was considered essentially free from pyrophosphate.

To ascertain if heat treatment could cause a change in hydrogen-ion concentration, the following experiments were performed and the hydrogen-ion concentration of tenth molar solutions of substances treated as described in the table was determined. The thrice crystallized sodium monometaphosphate whose tenth molar solution gave a hydrogen-ion concentration of  $2.5 \times 10^{-6}$  moles per liter was used in a comparative way. Measurements were made in conductivity water at 20°.

The results in the table indicate that the heat treatments have produced no significant changes in the acidic nature of the materials. The cause of the acidity of solutions of the various metaphosphates seems not to be due to the formation of polymeric forms whose formation might occur under conditions provided in the above experiments.

<sup>5</sup> Kiehl and Coats, *THIS JOURNAL*, 49, 2180 (1927).

TABLE I  
 EXPERIMENTAL DATA

Expt.	Material treated	Treatment	$C_{H^+} \times 10^6$
1	$\text{NaH}_2\text{PO}_4$	Heated carefully, fused and crystd. at $450^\circ$	24.0
2	$\text{NaH}_2\text{PO}_4$	Heated carefully, held in fused state 14 hours and then crystd. at $450^\circ$	24.0
3	$\text{NaH}_2\text{PO}_4$	Heated carefully to $400^\circ$ until meta was formed without fusion	24.0
4	$\text{NaH}_2\text{PO}_4$	Heated carefully to fusion and quenched	40.0
5	Metaphosphate prepared in Expt. 1	Recrystallized twice	2.5
6	Purified salt of Expt. 5	Held 18 hours $450^\circ$	1.6
7	Purified salt of Expt. 5	Fused and quenched	2.5

The feeble acid nature of the solutions is doubtless due to disodium dihydrogen pyrophosphate which is formed during the preparation. A study of the dissociation pressure of monosodium orthophosphate was made by Wallace<sup>6</sup> and one of us in which the dissociation pressure of monosodium orthophosphate to disodium dihydrogen pyrophosphate was found to be much below that of disodium dihydrogen pyrophosphate to metaphosphate at lower temperatures. The formation of disodium dihydrogen pyrophosphate would no doubt occur in considerable amount in the beginning and it would be retained in the molten mass in spite of the prolonged heating.

From tests outlined above it seems that the acidity of solutions of "Graham's salt" and other sodium metaphosphate prepared from monosodium orthophosphate by heating without recrystallization from water is due to disodium dihydrogen pyrophosphate.

**Approximate Strength of Monometaphosphoric Acid.**—If it is logical and sound to consider the acidity or alkalinity resulting from hydrolysis of an aqueous solution of a normal salt as a measure of the strength of the acid or base, it is of interest to note the relative position assumed by monometaphosphoric acid when hydrogen-ion concentration measurements in solutions of its sodium and ammonium salts are compared to the position determined for other acids by similar measurements in solutions of their carefully purified sodium and ammonium salts. By use of indicators and Clark and Lubs' color chart, the hydrogen-ion concentration in moles per liter for tenth molar solutions of the salts are:<sup>7</sup> ammonium monometaphosphate  $1.6 \times 10^{-6}$ , sodium monometaphosphate  $6.3 \times 10^{-7}$ , ammonium chloride  $1.6 \times 10^{-5}$ , sodium chloride,  $1 \times 10^{-5}$ , ammonium nitrate  $6 \times 10^{-6}$  and sodium nitrate  $4 \times 10^{-6}$ . The hydrogen-ion concentrations of solutions of the monometaphosphates are much lower than those of the two well-known strong acids. When it is compared, moreover,

<sup>6</sup> Kiehl and Wallace, *THIS JOURNAL*, 49, 375 (1927).

<sup>7</sup> Kiehl and Hill, *ibid.*, 49, 123 (1927).

with sodium acetate, whose hydrogen-ion concentration is  $3.2 \times 10^{-8}$  in a tenth molar solution, it would assume a position much nearer the strong nitric acid than the weak acetic acid. Such an approximation would place it near sulfuric acid but below it.

### Summary

1. The presence of disodium dihydrogen pyrophosphate is given as an explanation for the acidity of solutions of "Graham's salt" and solutions of other sodium metaphosphates prepared by heating monosodium orthophosphate when they are not purified by repeated crystallizations from water.

2. The monometaphosphoric acid is near but below sulfuric acid with respect to its activity.

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## CALCIUM NITRATE. III. HEATS OF HYDRATION AND OF SOLUTION OF THE BINARY SYSTEM CALCIUM NITRATE-WATER

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By means of well-known thermodynamic principles, heats of hydration of salts can be calculated from vapor pressure-temperature data. The system calcium nitrate-water lends itself admirably to an investigation of these relationships since the salt crystallizes from water in four forms—the tetrahydrate, the trihydrate, the dihydrate and the anhydride, according to the concentration of the solution and other conditions. In a previous article,<sup>1</sup> a temperature-composition diagram was presented showing that each of these crystalline forms can exist in a metastable equilibrium with what is ordinarily called a supersaturated solution. In reality they are saturated solutions of the metastable crystals. In a second article,<sup>2</sup> temperature-vapor pressure data for the mixture of crystals of this system were presented. It was shown that equilibrium vapor pressures could be measured not only for the stable eutectic mixtures tetrahydrate-trihydrate, trihydrate-dihydrate, and dihydrate-anhydride, but also for the metastable eutectic mixtures tetrahydrate-dihydrate and tetrahydrate-anhydride.

Fragmentary data are given in "International Critical Tables" for the experimental heats of this system. In order to compare the heats calculated from vapor pressure measurements with experimental data, it seemed advisable to make accurate heat measurements for the reactions

<sup>1</sup> Ewing, Krey, Law and Lang, THIS JOURNAL, 49, 1958 (1927).

<sup>2</sup> Ewing, *ibid.*, 49, 1963 (1927).