

96. *The Condensed Phosphoric Acids and Their Salts.* *Part III. Polyphosphates, and General Summary.*

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Conductivity measurements on sodium tripolyphosphate ($\text{Na}_5\text{P}_3\text{O}_{10}$) have been made and analysed. The results support the formula. The mobility of the anion, after making an approximate hydrolysis correction, is found to be 109, and the dissociation constant of the $\text{NaP}_3\text{O}_{10}^{4-}$ ion is regarded as being about 0.003.

COMPOUND formation between pyrophosphate and metaphosphate by heat treatment has been the subject of much investigation. Much confusion existed as to the exact number and nature of the compounds formed owing to the difficulty of analysing the products. Because of the industrial importance in water-softening, study of the system has been accelerated in recent years, and thermal analyses, together with microscope methods of examination (Andress and Wüst, *Z. anorg. Chem.*, 1938, **237**, 113; Partridge, Hicks, and Smith, *J. Amer. Chem. Soc.*, 1941, **63**, 454; Morey and Ingerson, *Amer. J. Sci.*, 1944, **242**, 1), have neatly clarified the position. The results show that sodium tripolyphosphate, $\text{Na}_5\text{P}_3\text{O}_{10}$, produced by fusion of equimolecular amounts of sodium pyrophosphate and any of the sodium metaphosphates, is the only stable compound formed by thermal methods. Any other ratios of the constituents produce this compound mixed with the excess component. Confirmation of this has been supplied by polarographic work (Campbell, *J. Amer. Chem. Soc.*, 1947, **69**, 109).

There is the point to consider as to whether or not the tripolyphosphate is polymerised. Freezing-point depressions and application of the Ostwald rule are said to support the simple formula (Bonneman-Bémia, *Ann. Chim.*, 1941, **16**, 395), but, as pointed out in Part I (this vol., p. 413), these methods are open to objection. Bonneman-Bémia (*loc. cit.*) reported a series of conductivity measurements at 25°, but they are much lower than would be expected for this compound. Comparison with the figures which we obtained indicated, as far as can be ascertained, that they were based on the hexahydrate (the product obtained by crystallisation from aqueous solution), instead of on the anhydrous salt.

Sodium Tripolyphosphate.—Calculated amounts of sodium trimetaphosphate and sodium pyrophosphate, prepared as described in Parts I and II, were intimately mixed and heated in a platinum dish in a similar fashion to that described by Jones (*Ind. Eng. Chem. Anal.*, 1942, **14**, 536). Unfortunately, this does not produce a pure compound: Jones's analytical method (*loc. cit.*) indicates that up to 10% of the constituents may be uncombined. According to Quimby (*Chem. Reviews*, 1947, **40**, 141) the compound decomposes as it melts at 622°, recombination depending on the manner of cooling. He considers that a higher degree of combination could be effected by prolonged heating around 500°. However, the analytical methods themselves are not entirely satisfactory; Bell (*Ind. Eng. Chem. Anal.*, 1947, **19**, 97) has given a method which he claims to be better than that of Jones (*loc. cit.*), but the work is still being developed. An attempt at purification was made by dissolving a sample in water and fractionally precipitating

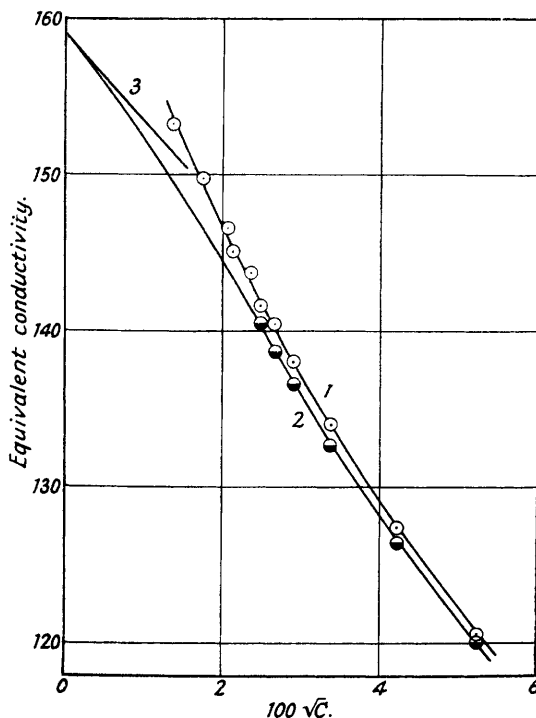
it by alcohol. This, as judged by analysis and by comparison of the conductivity with that of the untreated portion, does not assist in separating the impurities. Campbell (*loc. cit.*) came to a similar conclusion. The slight drift in the resistance readings was corrected as before (Part II). The data are shown in the first table and in the figure. Run 2 was made with the sample obtained by dissolution in water and precipitation with alcohol.

Conductivity of sodium tripolyphosphate at 25°.

| Run. | $10^6 \kappa_{\text{H}_2\text{O}}$ | $10^6 C$ | $10^6 C^{\frac{1}{2}}$ | Λ (obs.) | Λ (corr.) | Run. | $10^6 \kappa_{\text{H}_2\text{O}}$ | $10^6 C$ | $10^6 C^{\frac{1}{2}}$ | Λ (obs.) | Λ (corr.) |
|------|------------------------------------|----------|------------------------|------------------|-------------------|------|------------------------------------|----------|------------------------|------------------|-------------------|
| 1 | 0.243 | 452.33 | 2127 | 145.0 | — | 2 | 0.409 | 194.0 | 1393 | 153.1 | — |
| | | 623.63 | 2497 | 141.5 | — | | | 305.1 | 1747 | 149.7 | — |
| | | 910.17 | 2902 | 137.9 | 136.5 | | | 428.2 | 2069 | 146.5 | — |
| | | 1137.7 | 3375 | 133.9 | 132.6 | | | 556.2 | 2358 | 143.5 | 140.4 |
| | | 1776.5 | 4215 | 127.4 | 126.4 | | | 709.8 | 2664 | 140.3 | 138.6 |
| | | 2749.6 | 5244 | 120.6 | 120.1 | | | | | | |

Hydrolysis, the presence of uncombined constituents, and the products of ion-association due to these, preclude any exact treatment of the data. An approximate analysis has been

Equivalent conductivity of sodium tripolyphosphate at 25°.



1, *Experimental curve*; 2, *corrected curve*; 3, *Onsager limiting slope*.

attempted along the following lines. Leaving out of account ion-association due to the by-products, and any change in the conductivity due to uncombined constituents, and only considering the effects of hydrolysis, we may write

$$1000\kappa = 5\Lambda_a[a] + \Lambda_b[b] + 4\Lambda_c[c]$$

where $a = \text{Na}_5\text{P}_3\text{O}_{10}$, $b = \text{NaOH}$, and $c = \text{Na}_4\text{HP}_3\text{O}_{10}$; whence

$$100\Delta\kappa = [\text{OH}'](5\Lambda_a - \Lambda_b - 4\Lambda_c)$$

where $\Delta\kappa$ is the change in the specific conductivity due to hydrolysis. Accordingly $\Lambda_a = \Lambda_{\text{obs.}} + 1000\Delta\kappa/C$, C being the equivalent concentration. The pH of a 1% solution is 9.4 (Bell, *loc. cit.*), so we can take $[\text{OH}'] = 2.5 \times 10^{-5}$ (it will not alter significantly with concentration). The $\Delta\kappa$ values can be deduced by an approximation method. First, the observed conductivity can be taken for Λ_a ; Λ_b is known (Darken and Meier, *J. Amer. Chem. Soc.*, 1942,

64, 621), and for Λ_c , the conductivity of sodium pyrophosphate may be taken as a reasonable basis (Part II). These give results leading to $\Lambda_0 = 154$ for $\text{Na}_5\text{P}_3\text{O}_{10}$, thus giving 104 as the mobility of the anion. As a second approximation we can take 4/5 of this for the mobility of the $\text{HP}_3\text{O}_{10}''''$ ion, and, using the Onsager equation, derive truer values of Λ_c at each concentration, thereby obtaining a second value of Λ_0 for $\text{Na}_5\text{P}_3\text{O}_{10}$. Continuation along these lines eventually leads to constant figures, giving $\Lambda_0 = 159.0$ for $\text{Na}_5\text{P}_3\text{O}_{10}$. The corrected figures are given in the table and plotted in the graph. The theoretical Onsager equation based on the assumption that this is a 1 : 5-valent salt is $\Lambda = 159.0 - 323I^{1/2}$. The slope corresponding to this is shown in the graph and approximates to that of the corrected conductivity curve. If the substance were polymerised we would expect a much greater discrepancy between the two slopes. Furthermore, if it were heavily polymerised we would expect the corrected and experimental curves to be much lower in value, as found in the case of sodium "hexametaphosphate". The mobility of the $\text{P}_3\text{O}_{10}''''$ ion is 109, as compared with 95.9 for the $\text{P}_2\text{O}_7''''$ ion (Part II); this therefore follows the general rule that the higher the valency of the anion, the higher the mobility.

As discussed in the other Parts of this series, the discrepancy between the corrected curve and the theoretical Onsager curve may be used to calculate the extent of ion-association. Taking $\frac{4}{5}$ of 109 for the mobility of the $\text{NaP}_3\text{O}_{10}''''$ ion, the Onsager equation for this stage of the dissociation is $\Lambda = 137.3 - 252I^{1/2}$, so if α is the fraction which fully dissociates, we have

$$\Lambda = 109.8 - \alpha(49.0 - 121I^{1/2}) - 202I^{1/2}$$

The treatment is necessarily approximate because of the restrictions mentioned earlier, so it is not worth while making detailed calculations for the dissociation constant. One point only has been considered, *i.e.*, for $\Lambda_{(\text{obs.})} = 140.3$, for which a K value of 0.0027 is obtained. There are no other salts with which to compare this at present, although it is of the order expected for a 1 : 5-valent type.

Tetrapolyphosphate.—Earlier claims for the preparation of sodium tetrapolyphosphate, $\text{Na}_6\text{P}_4\text{O}_{13}$, by fusion methods (Fleitmann and Henneberg, *Annalen*, 1848, 65, 304) can no longer be accepted in view of the work of Partridge, *et al.* (*loc. cit.*). This does not preclude the possibility, however, of preparing the tetrapolyphosphate in aqueous solution. Hatch (U.S.P. 2,365,190; Dec. 19, 1944) and Bell (*Ind. Eng. Chem.*, 1947, 39, 137) have shown that tripolyphosphate is the first product of hydrolysis when sodium trimetaphosphate is treated with 1% sodium hydroxide solution at 100°. It may therefore be suggested that sodium tetrametaphosphate, the existence of which was confirmed in Part I, may give rise in an analogous way to tetrapolyphosphate when subjected to alkaline hydrolysis. The major difficulty in investigating this lies in the chemical analysis, the limitations of which were referred to earlier.

Summary of Results.—The new data obtained in this series of papers are collected below.

Mobilities at 25° of complex phosphate ions.

| | | | | | |
|----------------|------|-----------|-------------|--------|-----------|
| | Ion. | Trimeta-. | Tetrameta-. | Pyro-. | Tripoly-. |
| Mobility | | 83.59 | 93.69 | 95.9 | 109 |

Dissociation constants of the acids and their sodium and calcium salts.

| | | | | | | |
|------------------|--------|----------|--------------------------|----------------|---------------------------|----------|
| | Acid. | Na salt. | Ca salt. | | Acid. | Na salt. |
| Trimeta- | 0.0083 | 0.068 | 0.00033 | Pyro- | $K_3 2.7 \times 10^{-7}$ | — |
| Tetrameta- | 0.0018 | 0.009 | $K_1 0.0022$ | Tripoly- | $K_4 2.4 \times 10^{-10}$ | 0.0045 |
| | | | $K_2 1.3 \times 10^{-5}$ | | — | 0.003 |

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