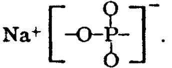
94. *The Condensed Phosphoric Acids and Their Salts. Part I. Metaphosphates.*

By C. W. Davies and C. B. Monk.

The preparations reported in the literature for various sodium metaphosphates have been repeated, and the conductivity of the products has been examined. Evidence is found only for the trimetaphosphate, the tetrametaphosphate, and a colloidal *n*-metaphosphate (Graham's salt). This result is reasonable if the monomeric unit is regarded as the unstable



$Na^+\left[-O-\overset{O}{\underset{O}{P}}-\right]^-.$

The corresponding acids have been obtained from the salts by means of cation-exchange resins. *n*-Metaphosphoric acid is colloidal, and unstable in water; the other two are relatively stable, and very strong acids—the third dissociation constant of the trimeta-acid being comparable with the second dissociation constant of sulphuric acid.

The interaction of the three forms with the calcium ion has been studied by a solubility method.

Condensed phosphate systems have been the subject of much study, and the voluminous literature has recently been reviewed by Yost and Russell ("Systematic Inorganic Chemistry", Prentice-Hall, 1944) and Quimby (*Chem. Reviews*, 1947, **40**, 141). Much of the earlier confusion was resolved by the thermal and *X*-ray studies of Partridge, Hicks, and Smith (*J. Amer. Chem. Soc.*, 1941, **63**, 454) and of Boullé (*Compt. rend.*, 1935, **200**, 658), which have clearly differentiated between a number of solid sodium phosphates. These are tabulated by Quimby, though other metastable forms may yet, of course, be added to the list.

Evidence regarding aqueous solutions, and the ionic species existing in them, is much less satisfactory. Two methods, in the main, have been used: the calculation of molecular weights from freezing-point depressions, and the application of "Ostwald's rule" to approximate conductivity measurements. These have been applied to the sodium salts, with the primary object of determining the valency of the anion. The first method is not entirely convincing, because even in those cases where activity corrections have been applied, there is considerable room for uncertainty as to the extent of complex formation and ion-association in these multivalent electrolytes. Conclusions drawn from Ostwald's rule are equally hazardous. The rule states that the equivalent conductivity of a salt at 25° is less at a dilution of $v = 32$ than at $v = 1024$ litres by $10n$, where n is the valency product of the ions. The rule holds fairly well for a great many salts, but it fails for the orthophosphates, and has never been adequately tested for ions of valency greater than two. In practice, it has been used to support the accepted formulæ of some of the condensed phosphoric acids, but has been disregarded where it does not agree with evidence from other sources.

Our object was to identify more exactly the anions present in aqueous solutions of the various condensed phosphates reported in the literature. First, conductivity measurements were carried out with highly dilute solutions of the sodium salt. These revealed any abnormality in dissociation, furnished evidence, by comparison with Onsager's equation, of the valency of the anion, and further characterised the latter by its mobility. The stability of the salt towards water could also be estimated from the extent, if any, to which the conductivities showed a drift with time. Next, the conductivity of the corresponding acid was measured, and dissociation constants calculated; this further characterised the anion, and also showed to what extent the sodium salt solutions were affected by hydrolysis. Finally, since interest in the condensed phosphates is largely concerned with their power of sequestering calcium in dilute solutions, the extent of complex formation between the anion and calcium ion was determined by a solubility method.

Trimetaphosphates.—*Sodium trimetaphosphate.* Several investigators have prepared a soluble, crystalline metaphosphate for which Yost and Russell accept the formula $Na_3P_3O_9$, on the evidence of freezing-point determinations by Nylèn (*Z. anorg. Chem.*, 1936, **229**, 30). Quimby assigns the same formula to the salt, but apparently with some reserve.

We followed Jones's method of preparation (*Ind. Eng. Chem. Anal.*, 1942, **14**, 536), and confirmed his finding that the salt thus obtained is free from ortho-, pyro-, and "hexameta-" phosphate. The densities of aqueous solutions of the salt were measured and found to be represented, up to $C = 0{\cdot}01$, by the equation $d_{4^\circ}^{25^\circ} = 0{\cdot}99707 + 0{\cdot}0695C$, where C is the equivalent concentration. The conductivities at 25°, for two separate preparations, are tabulated below. Col. 1 gives the number of the preparation, col. 2 the specific conductivity of the solvent water, col. 3 the equivalent concentration, col. 4 its square root, and col. 5 the equivalent conductivity of the salt. The normal solvent correction has been applied, allowance being made for interionic-force effects (Davies, *Trans. Faraday Soc.*, 1929, **25**, 129). The salt is relatively stable in water, for the conductivities of the dilute solutions did not alter perceptibly (that is, to the extent of 1 part in 20,000) over periods of an hour.

Conductivity of sodium trimetaphosphate solutions at 25°.

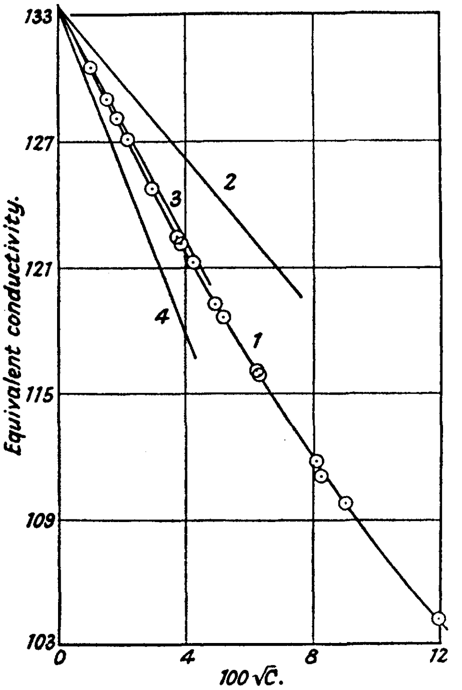
Batch.	$10^6\kappa_{H_2O}$.	10^6C.	$10^4C^{\frac{1}{2}}$.	Λ.	α.	K_3.
1	0·425	117·67	108·5	130·52	0·9985	0·070
2	0·453	243·21	156·0	129·08	0·9970	0·069
		348·24	186·6	128·13	0·9957	0·067
		472·90	217·5	127·15	0·9940	0·063
1	0·44	879·76	296·6	124·74	0·9913	0·071
		1406·1	375·0	122·46	—	—
		2478·2	497·8	119·25	—	—
		3944·5	628·0	115·94	—	—
		6529·0	808·0	111·83	—	—
2	0·25	1484·8	385·3	122·14		
		2724·4	522·0	118·66		
		8172·1	904·0	109·76		
1	0·26	1805·5	424·9	121·28		
		3902·0	624·7	116·01		
		6784·6	823·7	111·04		
		14255	1194	104·19		

The results are shown in Fig. 1, plotted against the square root of the concentration. A linear extrapolation from the most dilute points gives $\Lambda_0 = 133{\cdot}70$, and after deduction of 50·11 for the mobility of the sodium ion (Shedlovsky, *J. Amer. Chem. Soc.*, 1932, **54**, 1411), the mobility of the metaphosphate ion becomes 83·59. Fig. 1 also shows the theoretical limiting slopes, calculated from Onsager's equation, for the possible salts $Na_2P_2O_6$, $Na_3P_3O_9$, and $Na_4P_4O_{12}$. The very close agreement of experiment with the second of these clearly provides strong evidence that the anion is tervalent. There is a small deviation in the concentration range around 0·001N, the experimental points falling slightly below the theoretical line; but this type of deviation is precisely what has been found for other 1-3-valent electrolytes such as potassium ferricyanide and hexamminocobaltic chloride (Hartley and Donaldson, *Trans. Faraday Soc.*, 1937, **33**, 465) and potassium cobalticyanide (James, Ph.D. Thesis, London, 1947), and is explained by the slight degree of ion association to be expected with electrolytes of this valency type.

Only an approximate calculation of the extent of ion association is possible. At the lowest concentrations we can assume that two sodiums per molecule are completely dissociated, and write α for the degree of dissociation of the ion $NaP_3O_9{}''$. At a molar concentration *m*, therefore, we can regard the salt as a mixture of the 1-3-valent electrolyte $3Na^{\cdot}P_3O_9{}'''$, of concentration α*m*, and the 1-2-valent electrolyte $2Na^{\cdot}NaP_3O_9{}''$, of concentration (1 − α)*m*. For the purpose of calculating interionic-force corrections we assume that both salts show the same conductivity in the mixture as they would in pure solutions of the same total ionic strength. We must also assume a value for the mobility of the $NaP_3O_9{}''$ ion, and for this two-thirds of 83·59, *i.e.*, 55·73, has been taken. Onsager's equation may now be used to calculate conductivities for the two forms, and for the molecular conductivity of the salt we obtain :

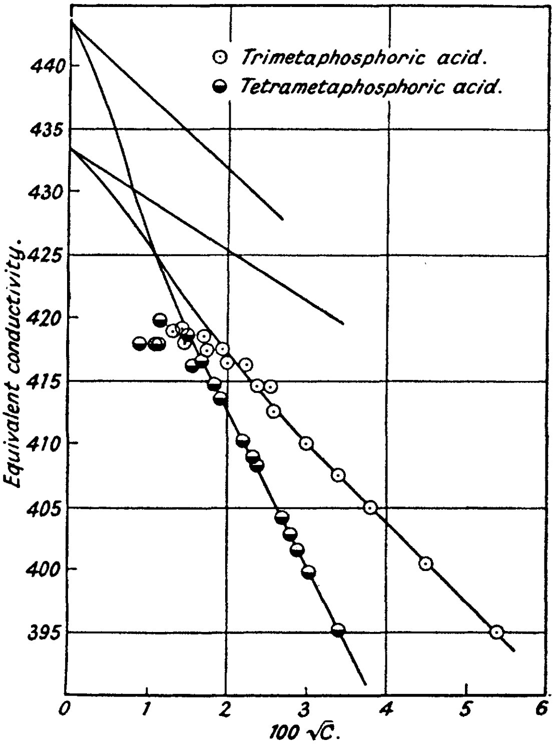
FIG. 1.

Equivalent conductivity of sodium trimetaphosphate at 25°.



1, *Experimental curve.*
2, 3, 4, *Onsager limiting slopes for* 1-2-*valent*, 1-3-*valent and* 1-4-*valent salt, respectively.*

FIG. 2.



$$3\Lambda_{\text{expt.}} = 3\alpha(133{\cdot}70 - 201{\cdot}5\, I^{\frac{1}{2}}) + 2(1 - \alpha)(105{\cdot}84 - 135{\cdot}3\, I^{\frac{1}{2}})$$

where *I*, the ionic strength, is given by $I = \frac{1}{2}[12\alpha m + 6(1 - \alpha)m] = (1 + \alpha)C$. These equations are solved by successive approximations, and the values of α obtained are shown in col. 6 of the above table. The values of the dissociation constant, given in col. 7 of the table, are calculated from the relation

$$K = \frac{\{\mathrm{Na}^{\cdot}\}\{\mathrm{P_3O_9}'''\}}{\{\mathrm{NaP_3O_9}''\}} = \frac{f_1 f_3(2 + \alpha)\alpha m}{f_2(1 - \alpha)}$$

where the ion-activity coefficients, f_1, f_2, f_3 are found from the Debye–Hückel limiting equation $\log f_i = -0{\cdot}509 z_i^2 I^{\frac{1}{2}}$, z_i being the valency of the ion.

The mean value of the dissociation constant is $K = 0{\cdot}068$. The chief uncertainties in the calculation are: (*a*) the value of the intermediate ion's mobility, (*b*) the extent of departure from the limiting Onsager equation at the concentrations studied. If the value 60 is taken in place of 55·73 for the intermediate ion's mobility, the dissociation constant is unchanged, and the constancy is the same as before. The error due to the second cause is more difficult to assess, but the absence below 0·001N of a trend in the K values implies that it is small. The value $K = 0{\cdot}068$ corresponds on Bjerrum's electrostatic theory of ion association to a closest distance of approach of the sodium and trimetaphosphate ions of 8·41 A.

Trimetaphosphoric acid. A stock solution of the acid was prepared by passing a solution of the sodium salt through a column of the cation-exchange resin Amberlite I.R.-100 in the hydrogen form. The conversion into acid was complete to within 0·2%, the limit of sensitivity of the analysis.

The conductivity results are given in the following table in the same form as in the previous table. No solvent correction was deducted when calculating the equivalent conductivity.

Trimetaphosphoric acid does not appear to have been prepared or studied before. It is relatively stable in water, the conductivities showing no change over considerable periods. It is a very strong acid, as is shown by the high conductivities, but the comparison (Fig. 2) of the experimental conductivities with the theoretical Onsager slope indicates that dissociation is not quite complete; the Λ_0 value shown in the figure was obtained by adding 349·82, the mobility of the hydrogen ion (MacInnes, Shedlovsky, and Longsworth, *J. Amer. Chem. Soc.*, 1932, **54**, 2758), to the value found for the anion in the preceding section.

The dissociation constant of the $\mathrm{HP_3O_9}''$ ion has been calculated in exactly the same way as for the sodium salt. The mobility of the intermediate ion has again been assumed to be 55·7; a small error in this value is even less important with the acid than with the sodium salt, since the main result of the association process is the disappearance of a highly mobile hydrogen ion. The measurements at the lowest concentrations have had to be neglected; as is usual when a strong acid is measured in a glass cell, these points are affected by ion-exchange at the glass surface. The K values also show a drift at concentrations greater than $C = 0{\cdot}001$, presumably through the break-down of the limiting Onsager equation. The most probable value over the available range is $K = 0{\cdot}009$, but this may be in error by 20%. This implies that the extent of (immediate) hydrolysis of trimetaphosphates when dissolved in water is negligibly small.

Conductivity of trimetaphosphoric acid solutions at 25°.

Batch.	$10^6\kappa_{\mathrm{H_2O}}$.	10^6C.	$10^5C^{\frac{1}{2}}$.	Λ.	α.	K_3.
1	0·389	208·67	1445	419·10	—	—
		298·26	1727	418·56	0·9556	0·0053
		389·34	1973	417·40	0·9551	0·0067
		506·52	2251	416·16	0·9550	0·0086
		652·87	2555	414·60	0·9536	0·0103
2	0·219	103·50	1142	417·80	—	—
		172·79	1315	418·91	—	—
		219·08	1480	417·91	—	—
		310·32	1762	417·44	—	—
		402·20	2006	416·35	0·9494	0·0061
		570·11	2388	414·57	0·9486	0·0082
3	0·551	670·81	2590	412·52	0·9411	0·0082
		901·30	3002	410·03	0·9365	0·0099
		1158·2	3403	407·62	0·9321	0·0111
3	0·551	1452·4	3811	405·03	—	—
		2052·8	4531	400·39	—	—
		2905·3	5390	394·96	—	—

Interaction of trimetaphosphate ion with calcium ion. The solubility of calcium iodate in sodium trimetaphosphate solutions at 25° is given in the first two columns of the following table; the first shows the molar concentration of the trimetaphosphate solution, and the second the solubility of calcium iodate, in moles per litre, in this solution. The increase in solubility is considerably greater than occurs in sodium or potassium chloride solutions of the same ionic strength, and the simplest explanation of this, which is borne out by the quantitative treatment, is that extensive association occurs between the multivalent ions to give CaP_3O_9'; further interaction between this and other (*e.g.*, calcium) ions is negligible at the concentrations considered.

The quantitative treatment of the results has been carried out in the way described by Wise and Davies (*J.*, 1938, 273). Allowance has to be made for the species $CaIO_3^{\cdot}$, $NaIO_3$, and NaP_3O_9'', and the bases of the calculation are the known dissociation constants of these ($CaIO_3^{\cdot}$, K = 0·13; $NaIO_3$, K = 3·0), the solubility product of calcium iodate, $S_0 = 7·141 \times 10^{-7}$, and Davies's ion-activity coefficient equation (*J.*, 1938, 2093). The results are given in cols. 3—10 of the table, concentrations being in millimols. per litre; the correct values are reached by successive approximations, that of CaP_3O_9' being obtained by difference. Col. 11 gives the ionic strength of the solution, and col. 12 the dissociation constant of CaP_3O_9', calculated from

Solubility of calcium iodate in sodium trimetaphosphate solutions at 25°.

$Na_3P_3O_9$.	$Ca(IO_3)_2$.	$NaIO_3$.	NaP_3O_9''.	$CaIO_3^{\cdot}$.	IO_3'.	$Na^{\cdot}$.	$Ca^{\cdot\cdot}$.	CaP_3O_9'.	P_3O_9'''.	I.	K . 10⁴
0	0·00785	—	—	—	—	—	—	—	—	—	—
0·003353	0·00906	0·04	0·06	0·44	17·64	9·96	6·29	2·33	0·96	0·03221	3·45
0·006677	0·01016	0·09	0·23	0·41	19·81	19·73	5·71	4·04	2·42	0·04477	3·47
0·01332	0·01187	0·19	0·91	0·39	23·16	38·86	5·24	6·24	6·17	0·07439	3·34
0·02005	0·01317	0·30	1·91	0·36	25·68	57·94	5·13	7·68	10·46	0·1070	3·12

the relation $K = f_2f_3[Ca^{\cdot\cdot}][P_3O_9''']/f_1[CaP_3O_9']$. The values are very steady, the mean K being 0·00033. This is a constant of the same order of magnitude as those of the other 2—3-valent complexes so far studied (Davies, *J.*, 1930, 2421; 1945, 463). On Bjerrum's theory it corresponds to a mean ionic diameter of 4·15 A.

Tetrametaphosphates.—The first detailed study of tetrametaphosphates was due to Warschauer (*Z. anorg. Chem.*, 1903, **36**, 137), who based his evidence for a four-fold polymerisation on Ostwald's rule. Yost and Russell quote cryoscopic evidence which they regard as doubtful. The compounds are not mentioned by Quimby.

Sodium tetrametaphosphate. The sodium salt was prepared by Warschauer's method, *via* the copper salt, and purified by several crystallisations from conductivity water. The conductivity results are given below, and are plotted in Fig. 3, which also shows earlier measurements by Warschauer and Tammann. Extrapolation of our results gives a limiting conductivity of 143·80, so that the mobility of the anion is 93·69. The experimental slope is less than that required by Onsager's equation for a 1-5-valent electrolyte; it is somewhat greater than the theoretical slope for a 1-4-valent salt, but this is to be expected since ion-association is considerable in salts with a valency product of four. The extent of ion association has been calculated in the way already described for trimetaphosphate, the effect at the low concentrations studied being attributed to the formation of the ion NaP_4O_{12}''', and the mobility of this being taken as $\frac{3}{4} \times 93·69 = 70·27$. The results are in the last two columns of the table, and the mean value of K, the dissociation constant of the ion NaP_4O_{12}''', is 0·009, corresponding on Bjerrum's theory to a mean ionic diameter of the sodium and tetrametaphosphate ions of 6·40 A. The only dissociation constant available for comparison is the value 0·005 found for potassium ferrocyanide (Davies, *J. Amer. Chem. Soc.*, 1937, **59**, 1760). The value of the dissociation constant, the anion's mobility, and the slope of the conductivity curve all support the quadrivalency assumed for the anion.

Conductivity of sodium tetrametaphosphate solutions at 25°.

Batch.	$10^6\kappa_{H_2O}$.	10^6C.	$10^5C^{\frac{1}{2}}$.	Λ.	a.	K.
1	0·387	244·00	1562	135·97	—	—
		419·40	2048	133·81	0·9665	0·0089
		578·83	2406	131·93	0·9574	0·0090
		779·67	2792	129·85	0·9462	0·0090
		1109·4	3339	127·09	0·934	0·0095
		1436·4	3790	124·85	0·922	0·0096
		2106·8	4590	121·09	(0·908)	(0·0104)
2	0·355	105·37	1027	137·18	—	—
		151·15	1230	136·66	—	—
		223·24	1494	135·65	—	—
		423·55	2058	133·54	0·9621	0·0079
		567·95	2383	131·98	0·9561	0·0086
		807·44	2842	129·69	0·9467	0·0093

Tetrametaphosphoric acid. Stock solutions were prepared from the sodium salt by treatment with Amberlite I.R.-100. Resistance measurements showed no change with time, so this acid, too, is relatively stable in dilute aqueous solution. The conductivities are tabulated below, and plotted in Fig. 2. The figure also shows the theoretical Onsager slope, and it will be seen that dissociation of the acid is not complete. The dissociation constant for the last hydrogen has been calculated, as before, the equation used being

FIG. 3.

Conductivity of sodium tetrametaphosphate at 25°.

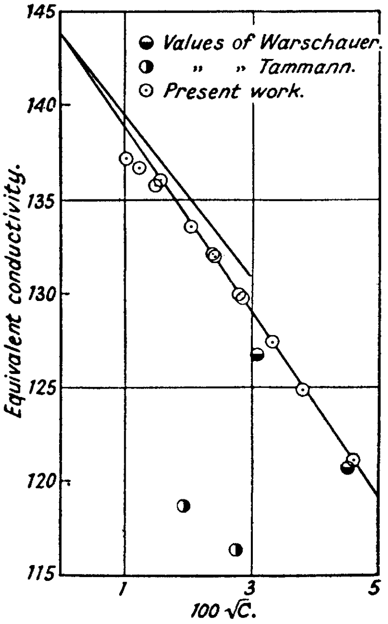
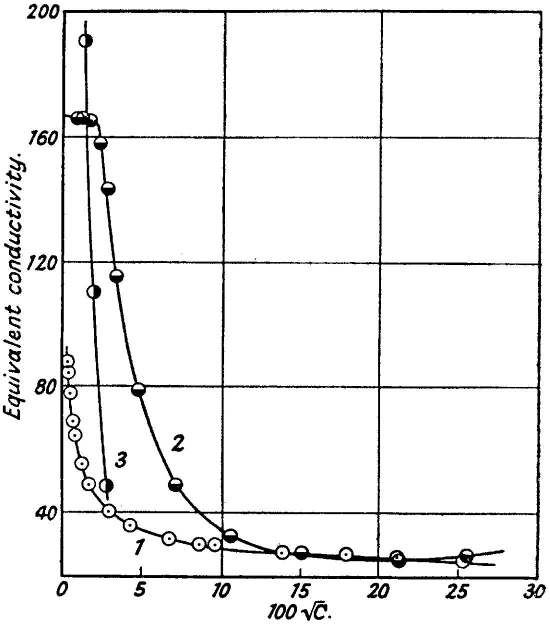


FIG. 4.



1, *Sodium " hexametaphosphate."*
2, *Octadecylamine hydrochloride.*
3, *" Hexametaphosphoric " acid.*

$$\Lambda = 315{\cdot}07 + \alpha(128{\cdot}44 - 14{\cdot}82I^{\frac{1}{2}}) - 226{\cdot}02I^{\frac{1}{2}},$$

where $I = (1{\cdot}5 + \alpha)C$. The values of α and K are shown in the table. The most dilute points had to be neglected, as in the case of trimetaphosphoric acid, but the others give a satisfactory constant with a mean value $K_4 = 0{\cdot}0018$.

Conductivity of tetrametaphosphoric acid solutions at 25°.

Batch.	$10^6\kappa_{H_2O}$.	10^6C.	$10^5C^{\frac{1}{2}}$.	Λ.	α.	K_4.
1	0·379	82·00	907	417·25	—	—
		136·43	1168	419·81	—	—
		190·95	1381	418·95	—	—
		286·90	1694	416·45	—	—
		565·94	2379	408·23	0·8231	0·0018
		837·28	2894	401·38	0·7882	0·0019
2	0·331	232·04	1523	418·55	—	—
		345·87	1860	414·72	0·8536	0·0015
		549·87	2345	408·93	0·8282	0·0018
		794·95	2820	402·73	0·7963	0·0020
3	0·252	126·09	1123	417·81	—	—
		250·42	1583	416·06	—	—
		371·95	1929	413·46	0·8465	0·0015
		489·33	2215	410·26	0·8326	0·0017
		739·90	2720	403·97	0·8023	0·0019
		932·16	3053	399·69	0·7808	0·0020
		1162·2	3409	395·18	0·7579	0·0021

Interaction of tetrametaphosphate ion with calcium ion. The measurements and calculations were made in the same way as for the trimetaphosphate ion, except that here allowance must be made, even at low concentrations, for both stages in the association : $Ca^{\cdot\cdot} + P_4O_{12}'''' \rightleftharpoons CaP_4O_{12}''$; $Ca^{\cdot\cdot} + Ca_2P_4O_{12}'' \rightleftharpoons Ca_2P_4O_{12}$. The two dissociation constants cannot be calculated independently from the measurements, and the less important—that for the first dissociation of calcium tetrametaphosphate—was therefore given the preliminary value $K_1 = 0{\cdot}0037$, which is the value previously found (James, *loc. cit.*) for the comparable salt calcium ferrocyanide. Calculations on this basis gave K_2 values for the second-stage dissociation which altered markedly with concentration. We have therefore proceeded, by trial and error, to determine the two dissociation constants which simultaneously give the best fit for the experimental solubilities. They are: $K_1 = 0{\cdot}0022$ and $K_2 = 1{\cdot}3 \times 10^{-5}$, corresponding on the Bjerrum theory to 3·28 A. for the mean ionic diameter of calcium and tetrametaphosphate ions and 4·00 A. for that of the calcium and calcium–tetrametaphosphate ions. The results are in the following table.

Solubility of calcium iodate in sodium tetrametaphosphate solutions at 25°: $K_1 = 0{\cdot}0022$.

$Na_4P_4O_{12}$.	$Ca(IO_3)_2$.	$NaIO_3$.	NaP_4O_{12}'''.	$CaIO_3^{\cdot}$.	IO_3'.	$Na^{\cdot}$.	$Ca^{\cdot\cdot}$.	CaP_4O_{12}''.	$Ca_2P_4O_{12}$.	P_4O_{12}''''.	I.	$K_2 \times 10^5$.
0	$0{\cdot}00784_5$	—	—	—	—	—	—	—	—	—	—	—
0·003330	$0{\cdot}00996_0$	0·06	0·03	0·39	19·47	13·23	5·10	2·01	1·23	0·07	0·03145	1·2
0·005809	$0{\cdot}01158_0$	0·12	0·16	0·35	22·69	22·96	4·23	3·75	1·63	0·28	0·04183	1·6
0·006932	$0{\cdot}01233_5$	0·15	0·22	0·33	24·19	27·36	3·90	4·63	1·74	0·34	0·04675	1·3
0·007194	$0{\cdot}01255_6$	0·16	0·21	0·33	24·63	28·41	3·79	4·89	1·78	0·32	0·04748	1·1

"*Hexametaphosphates*".—*Sodium* "*hexametaphosphate*". The formula $Na_6(PO_3)_6$ is commonly used for Graham's salt. It rests on doubtful evidence from freezing points, and the dubious preparation of derivatives such as $NaAg_5P_6O_{18}$ and $Na_2Ca_2P_6O_{18}$; the conductivity evidence is conflicting. On the other hand, the amorphous nature of the product, its very large and indefinite solubility in water, and the very high viscosity of its solutions all suggest that it is a high polymer, and Lamm (*Arkiv Kemi, Min. Geol.*, 1944, **17**, *A*, No. 25) has found molecular weights of about 13,000 in the ultra-centrifuge. Our conductivity measurements strongly support the view that the anion is of colloidal dimensions.

When sodium dihydrogen phosphate is fused, and then rapidly cooled, the "hexametaphosphate" produced is always contaminated, according to Jones (*Ind. Eng. Chem. Anal.*, 1942, **14**, 536), with a small amount of trimetaphosphate. This is probably because the reaction "hexametaphosphate" $\rightleftharpoons$ trimetaphosphate, which occurs at 625°, has time to proceed appreciably before the equilibrium is frozen. We removed the trimetaphosphate, and analysed our product, by the procedures suggested by Jones. The materials for which conductivity measurements are reported were shown in this way to be at least 99·92% pure. Other batches of fused material, used without further treatment, contained up to 10% or more of impurity, and gave conductivities that were the higher the greater the percentage impurity; this agrees with Jones's conclusions, since the trimetaphosphate has the higher conductivity of the two salts.

The densities at 25° of solutions of the pure product were determined, and may be expressed, up to an equivalent concentration $C = 0{\cdot}35$, by the equation $d_{4^{\circ}}^{25^{\circ}} = 0{\cdot}99707 + 0{\cdot}078C$. The conductivities are tabulated herewith, and are plotted against the square-root of the equivalent concentration in Fig. 4, curve 1. In the more concentrated solutions, hydrolysis caused a slow drift in the resistance readings, and we have extrapolated back to zero time to correct, as far as possible, for this effect.

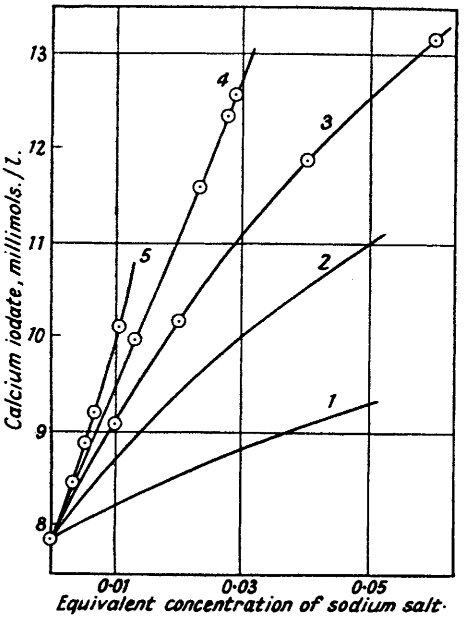
Conductivity of sodium "hexametaphosphate" solutions at 25°.

Batch.	$10^6\kappa_{H_2O}$.	10^4C.	$10^4C^{\frac{1}{2}}$.	Λ.	Batch.	$10^6\kappa_{H_2O}$.	10^4C.	$10^4C^{\frac{1}{2}}$.	Λ.
1	0·389	0·05641	23·8	87·8	1	0·457	2·7671	166·4	48·67
		0·10084	31·8	84·3			6·2650	250·3	42·57
		0·15195	39·0	80·8			8·7527	295·4	40·41
		0·22507	46·6	77·4			13·768	371·1	37·64
2	0·491	0·18911	43·5	81·3			18·988	435·8	35·88
		0·33125	57·6	73·0	1	0·519	8·8683	297·8	40·59
		0·43471	65·9	68·3			24·519	495·2	34·46
		0·57536	75·9	65·3			46·007	678·3	31·49
1	0·295	0·59768	77·3	64·05			74·602	863·7	29·73
		0·95087	97·5	59·30	2	0·480	92·287	960·7	29·83
		1·4687	121·2	55·10			192·42	1387	27·57
		2·0159	142·0	52·19			322·49	1796	26·56
		2·6882	163·9	49·71			443·13	2105	25·56
							640·44	2531	24·81

The conductivity curve is quite unlike that of a normal salt, and the slope in the most dilute solutions is far greater than would be expected even for a 1-6-valent salt. To provide a comparison with a colloidal electrolyte, the results of Ralston, Hoerr, and Hoffman (*J. Amer. Chem. Soc.*, **1942**, **64**, 97) for octadecylamine hydrochloride at 60° are shown in curve 2. The similarity of the two curves will be evident.

Quimby points out that the ultracentrifuge results need not necessarily mean the linkage of a large number of PO_3 units through chemical bonds, since the loose association of numerous $(PO_3)_6$ units to form a micelle would lead to the same result. There seems little reason to expect such a micelle formation, but to test the point we pushed our conductivity measurements to the utmost practicable dilution. If the micellar explanation were correct, a " critical concentration for micelles " should exist at which a reversible dissociation into the simple hexameric units would occur. Such a critical concentration is clearly shown by octadecylamine hydrochloride at about $C^{\frac{1}{2}} = 0{\cdot}02$. For the " hexametaphosphate " there is no evidence for such a transition even at $C = 5 \times 10^{-6}$, which is the order of concentration in which it is employed in the " threshold " treatment of waters. Although this does not preclude the possibility of a critical concentration occurring at a still higher dilution, we can at least state that there is no evidence of the existence of units of ordinary molecular size at any attainable concentration, and that there remain, therefore, no experimental grounds for the hypothesis that a hexameric form of phosphoric acid exists.

FIG. 5.



Solubility at 25° of calcium iodate in solutions of: 1, *Sodium chloride*; 2, *sodium sulphate*; 3, *trimetaphosphate*; 4, *tetrametaphosphate*; 5, " *hexametaphosphate*."

" *Hexametaphosphoric acid* ". This was prepared, like the other acids, by ion exchange in an Amberlite column. The product was too unstable to give accurate conductivity data; the resistance readings decreased by about 1·5% in ten minutes. Three approximate measurements are shown in Fig. 4, and suggest that the acid has a conductivity curve similar to that found for the sodium salt.

Contradictory reports have been published about the strength of this acid. Treadwell and Leutwyler (*Helv. Chim. Acta*, **1938**, **21**, **1450**) state that two hydrogens (out of six) are strong, Salih (*Bull. Soc. chim.*, 1936, **3**, **1391**) that four are strong, while Rudy and Schlosser (*Ber.*, **1940**, **73**, 484) report that " all six hydrogens " ionise freely. The colloidal nature of the acid would account for the apparent strength varying with the concentration range studied, and this, together with the unstable nature of the acid, probably explains the conflicting results.

Interaction of " hexametaphosphate " with calcium ion. The solubilities of calcium iodate in sodium " hexametaphosphate " solutions are given below, and the collected solubility data are shown in Fig. 5. The " hexametaphosphate " results show an upward curvature; there is no basis for a quantitative treatment.

Solubility of calcium iodate in sodium " hexametaphosphate " solutions at 25°.

" Hexametaphosphate " (g.-equiv./l.)	0	0·003776	0·005455	0·006958	0·01065
$Ca(IO_3)_2$ (g.-mol./l.)	0·00784	0·00853	0·00886	0·00919	0·0101

Dimetaphosphates.—The preparation of sodium dimetaphosphate has been reported by Pascal and Rechid (*Compt. rend.*, **1933**, **196**, 828), but the freezing-point evidence for the dimeric formula is not convincing. Travers and Chu (*ibid.*, **1934**, **198**, 2100) gave an alternative method of preparation, and we have followed this method. The product, after several crystallisations from water–alcohol mixtures, gave the following conductivity results.

Equivalent conductivity at 25° of " sodium dimetaphosphate ".

10^6C	505·3	773·4	970·8	1290
$10^5C^{\frac{1}{2}}$.	2248	2781	3116	3592
Λ	126·75	125·15	124·25	122·83

When plotted, these points give a straight line which extrapolates to $\Lambda_0 = 133{\cdot}5$. This would imply an unusually high mobility, 83·4, for the bivalent ion, and, moreover, the slope of the line is far greater than that predicted by Onsager's equation for a 1-2-valent salt. On comparing this curve with that for sodium trimetaphosphate, we find that the points fall on the curve with an error of not more than 0·1%, and we conclude that it is the trimetaphosphate which is prepared by Travers and Chu's method, and probably also, in a contaminated form, by that of Pascal and Rechid.

Monometaphosphates.—Work has been published by Beans and Kiehl (*J. Amer. Chem. Soc.*, 1927, **49**, 1878) on what is termed sodium monometaphosphate. This is discussed by Yost and Russell, who conclude that the salt is the trimetaphosphate, possibly contaminated with " hexametaphosphate ". This would be in keeping with the conductivity figures of Kiehl and Hill (*ibid.*, p. 123), which lie approximately midway between our results for the two salts. We have prepared a sample of Kiehl's salt, and submitted it to Jones's analytical procedure (*loc. cit.*). This also showed the product to be a mixture of sodium trimeta- and " hexameta "-phosphates, confirming Yost and Russell's suggestion.

The other claim to have prepared a monometaphosphate is that of Pascal (*Bull. Soc. chim.*, 1923, **33**, 1611), who obtained his product by the interaction of an ethyl phosphoric ester with sodium ethoxide. The evidence for a monomeric formula came from freezing-point measurements, but these could not be confirmed by Nylèn (*loc. cit.*), whose freezing points are almost identical with those for the trimetaphosphate. We followed the method of preparation given by Pascal, and obtained for our product the conductivities given in the following table.

Equivalent conductivity at 25° of Pascal's " monometaphosphate ".

10^6C	312·7	580·9	1036·5	1569·5	2280·4
$10^5C^{\frac{1}{2}}$	1768	2410	3220	3962	4776
Λ	127·0	125·85	122·7	119·8	116·7

These points fall on a line almost parallel with our results for sodium trimetaphosphate, but about 2 units lower. It is likely therefore that this product also is mainly trimetaphosphate, possibly contaminated with orthophosphate; but all that can be said with certainty is that the conductivity results offer no support for the hypothesis that this method of preparation yields a monomeric (or dimeric) metaphosphate.

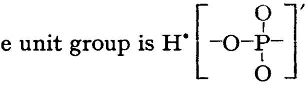
" *Metaphosphoric acid* ". The conductivity was examined of the product obtained by heating orthophosphoric acid at 400° for 5 hours. The results are tabulated herewith.

Conductivity at 25° of " ordinary " metaphosphoric acid.

10^6C	412·1	1032	1654	2161	3112
$10^4C^{\frac{1}{2}}$	203	321	407	465	558
Λ	280·6	257·9	247·9	242·1	233·7

These figures do not correspond with any of the pure acids we have studied. They fall about midway between the curve for the " hexameta "-acid and those for the tri- and the tetra-acid. It might be possible to account for them by postulating a new, semi-strong, polybasic acid; but a much more probable explanation, which is in accord with Rechid's freezing-point data (*Compt. rend.*, 1934, **198**, 860), is that the product is a mixture.

Conclusions.

Yost and Russell, in their review of the literature on metaphosphates, conclude that if $(HPO_3)_n$ is written as a general formula for the metaphosphoric acids, there is evidence for the existence of the individuals in which n has the values 2, 3, 4, 6, and, possibly, 1; other writers, *e.g.*, Ephraim (" Inorganic Chemistry ", transl. by Thorne, 1926, 623), add 5, 8, 10, and 14 to the probable values of n. In our study of the soluble products of a variety of preparative methods, we have been able to identity only $H_3P_3O_9$, $H_4P_4O_{12}$, and a colloidal metaphosphoric acid (the former " hexametaphosphoric " acid) in which the value of n appears to be greater than 100 (cf. Lamm, *loc. cit.*). We conclude that the monomer is not stable, but tends to give polymers in which the unit group is  $\mathrm{H}^{\bullet}\left[\begin{array}{c}\mathrm{O}\\ | \\ -\mathrm{O}-\mathrm{P}- \\ | \\ \mathrm{O}\end{array}\right]'$; such polymers may be closed rings of three units (the relatively stable trimetaphosphates), or of four units (the tetrametaphosphates, with a more limited range of stability), or may be very long chains of colloidal dimensions. In addition to these, there are the insoluble metaphosphates which we have not examined, and which presumably have continuous structures such as are found in the silicates.

EXPERIMENTAL.

The equipment used for the conductivity measurements, and the conductivity-water still, were similar to those described in earlier papers (cf. Davies, *J.*, 1937, 432). Measurements were made at frequencies of 1000 and 2500 cycles, and a cathode-ray oscillograph showed that the oscillator was producing a good sine wave. The cell used for the more concentrated solutions was standardised by means of Jones and Bradshaw's 0·01D-potassium chloride solution, and had a constant of 0·13103 ± 0·03%. For more dilute solutions a Hartley–Barrett cell (constant : 0·045960 ± 0·02%) was standardised against potassium chloride solutions of concentrations below 0·001N, using the interpolation formula $\Lambda = 149{\cdot}92 - 93{\cdot}85C^{\frac{1}{2}} + 50C$ (Davies, *loc. cit.*).

The solubility measurements were made in the manner described in previous papers (*J.*, 1935, 1416; 1938, 273).

Sodium Trimetaphosphate.—Sodium dihydrogen phosphate was prepared in the following manner. A slight excess of " AnalaR " phosphoric acid was added to a concentrated solution of " AnalaR " disodium phosphate in distilled water. Crystallisation was induced by addition of alcohol and cooling in a refrigerator. The crystals were recrystallised twice in a similar manner, being filtered each time on to a sintered-glass filter and washed with dilute aqueous alcohol. The trimetaphosphate was formed by Jones's method (*loc. cit.*), the samples being heated in a platinum crucible in an electric furnace.

Sodium Tetrametaphosphate.—Pure cupric oxide was heated in a platinum dish with 5% excess of "AnalaR" phosphoric acid according to Warschauer's method (*loc. cit.*). The cupric tetrametaphosphate was ground to a powder and a slight excess of " AnalaR " sodium sulphide solution stirred with it, and the resulting cupric sulphide filtered off on a sintered-glass crucible. The sodium salt was precipitated from the filtrate by adding alcohol and cooling. Recrystallisations were effected first from distilled water and alcohol, traces of sulphur being filtered off by means of a fine paper, and finally two recrystallisations were made from conductivity water and pure alcohol. The first sample was recrystallised five times and the second eight times. The crystals were dried over phosphoric oxide in a vacuum, and the water content found, at the time of taking a sample for conductivity, by ignition in a platinum crucible.

Sodium " Hexametaphosphate ".—Sodium dihydrogen phosphate, prepared as above, was fused at 900° in a platinum dish in a gas muffle furnace, and then cooled rapidly by ice-water. The product was dissolved in water, and the solution slowly added to a solution of " AnalaR " silver nitrate with rapid stirring. The coagulum of silver " hexametaphosphate " was filtered on to a sintered-glass funnel and well washed with water. It was then suspended in about a litre of water, stirred mechanically, and an excess of " AnalaR " sodium chloride solution added. After the silver chloride had been filtered off, alcohol was added slowly with vigorous stirring, until about 20% was present. Slow addition of the alcohol is important, otherwise no separation occurs. The " hexametaphosphate " separated out in globules of viscous liquid which rapidly collected at the bottom of the beaker. The supernatant liquor was decanted off, the coagulum washed several time with 10% aqueous alcohol, and then redissolved in distilled water. Separation was carried out three times more by addition of alcohol, the last two being from solution in conductivity water. The oil was partially dehydrated by transference to a platinum dish and application of a vacuum pump for 5 hours. After a final drying in a vacuum over phosphoric oxide, it was obtained as a porous brittle glass containing about 9% of water. The exact amount was determined each time by ignition of samples. Analysis for other forms of phosphate by Jones's method (*loc. cit.*) indicated that not more than 0·08% of these were present.

Tri-, Tetra-, and " Hexa "-metaphosphoric Acids.—A column of Amberlite I.R-100 of approximately 40 g. dry weight (about four times that required) was formed in a 1-cm. hard-glass tube. After hydrogenation with acid, it was washed with distilled water and then with conductivity water. Tests showed that the specific conductivity of the water only rose to 2 or 3 gemmhos. This meant a negligible error in the conductivity measurements on the acid, since only a small amount of the stock solutions of these were used. About 1·5 g. of the sodium salt in about 400 ml. of conductivity water were passed through this column, the rate being adjusted so that the operation took about an hour. The resulting stock solutions were tested for sodium by means of zinc uranyl acetate (Vogel, " Quantitative Inorganic Analysis "), and comparison with a blank test on the reagent indicated that the conversion was complete to within 0·2%, the blank being equivalent to this amount. The concentrations of the stock solutions were found by weighing out portions, hydrolysing by nitric acid (Jones, *loc. cit.*), and carrying out a double precipitation as magnesium ammonium phosphate (Vogel, *op. cit.*). The ignition to magnesium pyrophosphate at 1100° was effected on sintered-porcelain crucibles. Duplicate estimations were made on each sample. For the trimetaphosphoric acid these agreed to within 0·05%, 0·2%, and 0·03% for the three runs respectively, for the tetrametaphosphoric acid to within 0·1%, 0·03%, and 0·02%, and within 0·1% for the " hexametaphosphoric " acid.

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