683. *The Condensed Phosphoric Acids and Their Salts. Part V. Dissociation Constants of Some Tetrametaphosphates.*

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From the conductivities of mixed solutions of bivalent metal chlorides and sodium tetrametaphosphate, the dissociation constants of the resulting MP_4O_{12}'' ions have been calculated. In the case of CaP_4O_{12}'', the solubility of calcium iodate in solutions of sodium tetrametaphosphate confirms the results obtained by the conductivity method.

THE original methods of forming sodium tetrametaphosphate, $Na_4P_4O_{12}$, consisted of heating the oxides of copper and lead with phosphoric acid, followed by exchange with sodium sulphide (Fleitmann and Henneberg, *Annalen*, 1848, **65**, 304). The salt prepared by this tedious method requires extensive purification, resulting in small yields. Such and Tomlinson (Topley, *Quart. Reviews*, 1949, **3**, 345) have now shown, however, that yields exceeding 50% are obtained by hydration of phosphoric oxide with sodium carbonate or hydrogen carbonate solutions at low temperatures. The product is easily purified by cooling a saturated solution made at room temperature. In a similar fashion, by use of water, the corresponding acid may be formed (Audrieth, private communication), with yields of up to 80%. As with the trimetaphosphate, the structure is probably cyclic; a discussion of this, and the evidence for assuming the ion to be quadrivalent, are reviewed elsewhere (Topley, *loc. cit.*; Davies and Monk, *J.*, 1949, 413).

Following the principles used in Part IV (Jones, Monk, and Davies, *J.*, 1949, 2693) to establish the extent of formation of MP_3O_9' ions (where $M^{\cdot\cdot}$ refers to various bivalent cations), we have carried out the same treatment with the tetrametaphosphates. This consisted of adding solutions of metal chlorides, MCl_2, to solutions of sodium tetrametaphosphate, and measuring the specific conductivities of the mixtures. The number of ion-pairs so formed is somewhat greater than in the case of the trimetaphosphates, and for a solution containing c_1 equiv. per l. of sodium tetrametaphosphate and c_2 of MCl_2, if a g.-ions of NaP_4O_{12}''', b g.-ions of MP_4O_{12}'', d g.-mols. of $M_2P_4O_{12}$, and e g.-ions of $NaMP_4O_{12}'$ are present per l., then

$$10^3\kappa(\text{obs.}) = \Lambda_{Na^\cdot}(c_1 - a - e) + 4\Lambda_{P_4O_{12}''''}(c_1/4 - a - b - d - e) + 3\Lambda_{NaP_4O_{12}'''}(a) \\ + 2\Lambda_{M^{\cdot\cdot}}(c_2/2 - b - 2d - e) + \Lambda_{Cl'}(c_2) + 2\Lambda_{MP_4O_{12}''}(b) + \Lambda_{NaMP_4O_{12}'}(e)$$

where κ is the specific conductivity. The same metal chlorides were used as in Part IV (*loc. cit.*), so that no $MCl^\cdot$ ions have to be considered. If the conductivity of the MP_4O_{12}'' ions is taken as one-half of that of the tetrametaphosphate ion, and that of the $NaMP_4O_{12}'$ ions is taken as one-quarter, the above equation reduces to

$$10^3\kappa(\text{obs.}) = \Lambda_{Na_4P_4O_{12}} + \Lambda_{MCl_2} - a(\Lambda_{Na^\cdot} + 1\tfrac{1}{4}\Lambda_{P_4O_{12}''''}) - b(3\Lambda_{P_4O_{12}''''} + 2\Lambda_{M^{\cdot\cdot}}) \\ - 4d(\Lambda_{P_4O_{12}''''} + \Lambda_{M^{\cdot\cdot}}) - e(\Lambda_{Na^\cdot} + 2\Lambda_{M^{\cdot\cdot}} + 3\tfrac{3}{4}\Lambda_{P_4O_{12}''''}) \quad . \quad . \quad (1)$$

If no interaction occurred between the two solutions, we would have, by similar reasoning,

$$10^3\kappa(\text{calc.}) = \Lambda_{Na_4P_4O_{12}}(c_1) + \Lambda_{MCl_2}(c_2) - a_1(\Lambda_{Na^\cdot} + 1\tfrac{1}{4}\Lambda_{P_4O_{12}''''}) \quad . \quad . \quad . \quad (2)$$

Sodium tetrametaphosphate does not fully ionise, and contains NaP_4O_{12}''' ions; this factor has been discussed in Part I (*loc. cit.*), and the amount of this ion-pair, a_1, is markedly different from the real cases, where most of the tetrametaphosphate ions are bound up with the cation $M^{\cdot\cdot}$. In this second expression, the calculated specific conductivity is obtained from the known equivalent conductivity expression for sodium tetrametaphosphate (Part I), *i.e.*,

$$\Lambda = 143{\cdot}80 - 313I^{\frac{1}{2}}$$

and from the Onsager equations for MCl_2 (Part IV, *loc. cit.*), each calculated at I, the actual ionic strengths of the mixed solutions, where $I = \frac{1}{2}(5c_1 + 3c_2 + 4a - 16b - 24d - 20e)$.

Subtraction of equations (1) and (2) enables values of b to be calculated, known or reasonably assumed dissociation constants being used to calculate a, a_1, d, and e. However, this process is very laborious, and advantage may be taken of the fact that the mobilities of the $M^{\cdot\cdot}$ ions are all of the same order; then, using the limiting mobilities of the ions, subtraction of (1) and (2) leads to

$$b = \frac{10^3\{\kappa(\text{calc.}) - \kappa(\text{obs.})\}}{3\Lambda_{P_4O_{12}''''} + 2\Lambda_{M^{\cdot\cdot}}} + \tfrac{1}{2}(a_1 - a) - 1\tfrac{1}{2}d - e$$

The equivalent conductivities of the two ions in this expression can be found from the corresponding Onsager equations,

$$\Lambda_{P_4O_{12}''''} = 93{\cdot}69 - 190{\cdot}8I^{\frac{1}{2}}$$
$$\Lambda_{M^{\cdot\cdot}} = \Lambda^{\circ}_{M^{\cdot\cdot}} - BI^{\frac{1}{2}}$$

where 93·69 is the conductivity at zero concentration of the tetrametaphosphate ion (Part I, *loc. cit.*), and 190·8 is calculated with respect to the sodium ion. B is the theoretical Onsager value for the $M^{\cdot\cdot}$ ion calculated with respect to the chloride ion; the sources of these data have been given in Part IV (*loc. cit.*). For the calculation of a and a_1, the known dissociation constant of NaP_4O_{12}''' is 0·0090 (Part I, *loc. cit.*), while for d, corresponding to the equilibrium $M^{\cdot\cdot} + MP_4O_{12}'' \rightleftharpoons M_2P_4O_{12}$, an assumed value of 0·0020 was used. Some evidence for this was given in Part I, and in addition this value was found to give reasonably constant figures for the dissociation constants of the MP_4O_{12}'' ions over a range of concentrations. To quote further supporting evidence, it may be noted that the value for the similar dissociation stage in calcium ferrocyanide solutions is of the same order, namely, 0·0037 (James, *Trans. Faraday Soc.*, 1949, **45**, 855). The formation of $NaMP_4O_{12}'$ ions results through two reactions, $M^{\cdot\cdot} + NaP_4O_{12}''' \rightleftharpoons MNaP_4O_{12}'$, and $Na^{\cdot} + MP_4O_{12}'' \rightleftharpoons NaMP_4O_{12}'$. For the first of these, by comparison with the results obtained for the 2-3-valent type of dissociation with the trimetaphosphates (Part IV, *loc. cit.*), K was taken as 0·00040, while for the second, a K of 0·20 was used, by analogy with sodium sulphate (Righellato and Davies, *Trans. Faraday Soc.*, 1930, **26**, 592). By continued approximations, constant values of b were obtained, enabling the dissociation constant, K, for the equilibrium $M^{\cdot\cdot} + P_4O_{12}'''' \rightleftharpoons MP_4O_{12}''$ to be calculated from

TABLE I.

Data for the dissociation constants of MP_4O_{12}'' *at 25°.*

10^4c_1.	10^4c_2.	10^5a_1.	10^6a.	10^4b.	10^6d.	10^7e.	$10^4\kappa$(calc.).	$10^4\kappa$(obs.).	10^3I.	10^6K.
				$M^{\cdot\cdot}$ = Calcium.						
9·2256	4·3470	1·52	3·1	1·796	2·6	8·4	1·7817	1·1195	1·469	3·8
9·1336	6·9597	1·47	1·0	2·038	8·4	9·6	2·1067	1·3231	1·580	4·0
8·7892	8·5685	1·35	0·5	1·969	13·5	9·0	2·2614	1·4793	1·733	3·8
8·7432	11·0498	1·36	0·3	1·918	20·0	8·4	2·5641	1·7727	2·059	4·0
8·9008	4·5777	1·43	2·2	1·845	2·5	8·2	1·1732	1·0917	1·389	3·4
				$M^{\cdot\cdot}$ = Barium.						
7·7656	7·6986	1·06	1·2	1·655	9·0	8·2	2·0495	1·3878	1·651	9·9
7·8460	4·9811	1·11	2·2	1·531	3·8	9·3	1·7051	1·1154	1·421	10·2
7·9776	4·6163	1·16	2·7	1·494	3·1	7·5	1·6730	1·1015	1·436	10·7
7·9080	6·7705	1·12	1·5	1·644	7·2	8·2	1·9470	1·2986	1·577	10·9
7·9228	2·5012	1·12	5·6	1·004	0·7	5·0	1·3783	1·0028	1·518	10·0
				$M^{\cdot\cdot}$ = Magnesium.						
7·6728	5·2934	1·08	1·5	1·597	5·3	6·6	1·6718	1·0828	1·359	7·2
7·7124	3·4232	1·10	3·3	1·334	1·6	5·6	1·4449	0·9676	1·336	6·8
7·4112	5·5160	1·01	1·2	1·567	5·9	6·9	1·6658	1·0829	1·343	7·1
7·4544	3·6087	1·04	2·6	1·375	1·9	5·5	1·4372	0·9451	1·267	6·3
7·7536	1·6834	1·06	6·6	0·747	0·2	2·4	1·2275	0·9636	1·559	6·3
				$M^{\cdot\cdot}$ = Manganese.						
8·3728	3·2255	1·28	3·4	1·535	0·5	5·5	1·5174	0·9762	1·331	1·6
14·3280	17·7524	3·04	0·5	3·070	44·2	18·0	3·9594	2·7154	3·239	2·6
14·4160	11·9963	3·23	0·6	3·296	23·0	20·7	3·3165	2·0864	2·474	1·6
14·4920	7·0338	3·37	3·9	3·143	2·9	37·0	2·7424	1·6541	2·077	1·4
				$M^{\cdot\cdot}$ = Nickel.						
7·9364	3·0472	1·13	4·6	1·153	1·4	6·0	1·4252	1·0131	1·478	10·9
7·8908	4·4446	1·13	2·7	1·423	3·6	6·5	1·5952	1·0756	1·441	11·9
13·6768	11·6334	2·88	3·3	2·791	22·1	25·0	3·1757	2·1161	2·629	12·3
13·7460	8·0705	2·51	5·9	2·639	9·8	22·8	2·7597	1·8038	2·372	11·0
7·9776	1·5876	1·12	7·5	0·666	0·3	5·1	1·2428	1·0077	1·662	10·4

$$K = \frac{\{M^{\cdot\cdot}\}\{P_4O_{12}''''\}}{\{MP_4O_{12}''\}} = \frac{(c_2/2 - b - 2d - e)(c_1/4 - a - b - d - e)f_1f_2}{bf_3}$$

where the ion activity coefficients f_1, f_2, and f_3 are found from the Debye–Huckel limiting equation, $-\log f_i = 0{\cdot}509 z_i^2 I^{\frac{1}{2}}$, z_i being the ion valency (this was also used in calculating a, a_1, d, and e). The results of these calculations are given in Table I.

Solubility Measurements.—In Part I (*loc. cit.*) the dissociation constant of CaP_4O_{12}'', as determined from the solubility of calcium iodate in solutions of sodium tetrametaphosphate, was given as $1{\cdot}3 \times 10^{-5}$. These calculations did not take into account ion-association between $Na^{\cdot}$ and CaP_4O_{12}'' ions, and between $Ca^{\cdot\cdot}$ and NaP_4O_{12}''' ions. Some of the older data have therefore been recalculated, these effects being taken into account by using the dissociation constants mentioned earlier in this paper, *i.e.*, 0·20 and 0·0004, respectively. In addition, fresh solubility measurements have been made with the sodium tetrametaphosphate used in the conductivity work (the previous ones were made with samples prepared from the copper salt and sodium sulphide, as described in Part I, *loc. cit.*). To obtain reasonably constant values for the dissociation constant of CaP_4O_{12}'', it was found necessary to use a K of 0·0025 for $Ca_2P_4O_{12}$, as compared with 0·0020 in the conductivity measurements. The calculations are given in Table II, the method previously described (Part I, *loc. cit.*) being used; points (b) and (c) are recalculated from the older data. The average result of $4{\cdot}8 \times 10^{-6}$ compares favourably with $3{\cdot}8 \times 10^{-6}$ obtained by the conductivity method.

Attempts were made to study the barium salt by utilising the solubility of barium iodate, but $Ba_2P_4O_{12}$ proved to be too insoluble—this might prove to be useful in analysing mixtures of the metaphosphates.

The average dissociation constants, all $\times 10^6$, are: calcium, 4·3; barium, 10·3; magnesium, 6·7; manganese, 1·8; and nickel, 11·3. These correspond on Bjerrum's electrostatic theory of ion association to the following values for the closest approach of the $M^{\cdot\cdot}$ and tetrametaphosphate ion: Ca, 3·6; Ba, 3·9; Mg, 3·8; Mn, 3·3; Ni, 3·95 A.

TABLE II.

Solubility data for the dissociation constant of CaP_4O_{12}'' *at* 25°.

(Concentrations are in millimols. or mg.-ions per l.)

	(a).	(b).	(c).	(d).	(e.)	(f).
$Ca(IO_3)_2$	11·23	11·58	11·92	12·56	14·45	17·67
$Na_4P_4O_{12}$	5·21	5·81	6·27	7·19	9·93	14·70
$Ca^{\cdot\cdot}$	4·31	4·14	3·98	3·73	3·11	2·43
IO_3'	21·99	22·70	23·37	24·64	28·36	34·68
$Na^{\cdot}$	20·50	22·79	24·57	28·07	38·52	56·38
$CaIO_3^{\cdot}$	0·36	0·34	0·34	0·32	0·30	0·25
$NaIO_3$	0·11	0·12	0·13	0·16	0·24	0·41
$NaCaP_4O_{12}'$	0·20	0·27	0·31	0·42	0·73	1·38
NaP_4O_{12}'''	0·03	0·06	0·07	0·11	0·23	0·63
P_4O_{12}''''	0·06	0·09	0·12	0·16	0·30	0·64
CaP_4O_{12}''	3·48	3·90	4·25	4·91	7·03	10·49
$Ca_2P_4O_{12}$	1·44	1·49	1·52	1·59	1·64	1·56
$10^3 I$	37·74	40·12	42·03	45·78	57·67	80·14
$10^6 K$	4·2	5·1	5·7	5·6	4·6	3·4

In Part IV (*loc. cit.*) a comparison was drawn for calcium, barium, and magnesium, between the dissociation constants of the hydroxides, where the order is that of the unhydrated cation, *i.e.*, Ba > Ca > Mg (which is similar to that found where chelation occurs such as in the malonates and oxalates), and the nitrates and iodates, where the energy of solvation is greater than the electrostatic forces of attraction, so that the order of the dissociation constants is that of the hydrated cations, *i.e.*, Mg > Ca > Ba. It was pointed out that with the 2-3-valent trimetaphosphates the stronger electrostatic forces cause the dissociation constants to be between the above orders, *i.e.*, Mg > Ba > Ca, the electrostatic forces partly overcoming the forces of hydration. With the 2-4-valent tetrametaphosphates studied in the present paper, this effect is even greater, so we now find the order to be Ba > Mg > Ca. With ions of even higher valency-products we should therefore expect to get back to the order of the hydroxides and chelated compounds.

Experimental.—Sodium tetrametaphosphate, $Na_4P_4O_{12},4H_2O$, was made by low-temperature hydration of phosphoric oxide by sodium carbonate, and was given to us by Messrs. Albright and Wilson, Ltd. It was recrystallised by cooling a saturated solution made at room temperature in conductivity water. Conductivity measurements on this agreed well with those reported in Part I, where the salt was prepared by an older method. " AnalaR " chlorides were used, and duplicate gravimetric analyses *via* silver chloride were ±0·03% or better in all cases. The conductivity measurements were made with the equipment used for previous work (Davies, *J.*, 1937, 432; Part I, *loc. cit.*). The solubility measurements were followed with the apparatus used by Wise and Davies (*J.*, 1938, 273).

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