95. *The Condensed Phosphoric Acids and Their Salts. Part II. Pyrophosphates.*

By C. B. Monk.

The third and the fourth dissociation constant of pyrophosphoric acid at 25° have been estimated from pH measurements on solutions of the sodium salts and the acid, association between the sodium and pyrophosphate ions being taken into consideration. Conductivity measurements of dilute solutions of sodium pyrophosphate at 25° are reported, and corrections applied for hydrolysis and possible ion-associations resulting from hydrolysis.

THREE series of values are given in the literature for the third and the fourth dissociation constant of pyrophosphoric acid. Abbott and Bray (*J. Amer. Chem. Soc.*, 1909, **31**, 729) give $2{\cdot}9 \times 10^{7}$ and $3{\cdot}6 \times 10^{-9}$, respectively, at 18°; Kolthoff and Bosch (*Rec. Trav. chim.*, 1928, **47**, 826) give $2{\cdot}1 \times 10^{-7}$ and $4{\cdot}06 \times 10^{-10}$ at 18°, and Morton (*J.*, 1928, 1401) gives $2{\cdot}1 \times 10^{-7}$ and $1{\cdot}31 \times 10^{-10}$ at 30°. Abbott and Bray's results, which were based on distribution studies of the hydrolysis of pyrophosphate salts, are markedly different from the others because interionic effects were unrecognised at that time and consequently were not included in the calculations. The last two series were averaged from pH measurements ending at rather high concentrations and therefore needed rather large activity corrections. A possible modification in computing the dissociation constants is to take into consideration the extent to which such ions as NaP_2O_7''' and $NaHP_2O_7''$ exist in solution. This approach has been taken in the present paper, the treatment being confined to relatively dilute solutions. The extensive studies which have been made on electrolytes in solution indicate that the 1 : 1 and 1 : 2 valency types of salts show complete or almost complete dissociation. With the higher valency types there is strong evidence to show that this is not the case. As a broad generalisation the extent of association for these cases is of the same order for any particular valency type of salt, and use has been made of this for making minor corrections to the data given here.

The Third Acid Dissociation Constant.—A stock solution of pyrophosphoric acid was prepared from the sodium salt by the ion-exchange method mentioned in Part I (preceding paper). The cell used for the pH measurements contained conductivity water which was kept under a stream of carbon dioxide-free air. Conductivity measurements on some of the water indicated that the amount of carbon dioxide was negligibly small. A convenient amount of the acid stock solution was admitted, followed by suitable amounts of carbonate-free sodium hydroxide. The concentrations are given in the table below.

K_3 for pyrophosphoric acid at 25°.

Concentrations ($\times 10^4$).

	(*a*).	(*b*).	(*c*).		(*a*).	(*b*).	(*c*).
$H_4P_2O_7$	4·16	4·16	4·16	$I \times 10^4$	14·5	16·5	19·1
NaOH	8·99	9·67	10·51	pH	5·78	6·15	6·50
HP_2O_7'''	0·67	1·35	2·19	$K_3 \times 10^7$	2·58	2·72	2·77
$H_2P_2O_7''$	3·49	2·81	1·97				

Ion association between the sodium ions and the pyrophosphate ions is small enough to be ignored in the present case, so the amounts of HP_2O_7''' and $H_2P_2O_7''$ can be obtained from the relations $m = [HP_2O_7'''] + [H_2P_2O_7'']$, and $4m - [NaOH] = [HP_2O_7'''] + 2[H_2P_2O_7'']$, where m is the pyrophosphate molarity. The third acid dissociation constant, K_3, was calculated from the expression

$$\log K_3 = -\text{pH} + \log\{HP_2O_7'''\}/\{H_2P_2O_7''\} + \log f_3/f_2$$

where f_2 and f_3 are the ion-activity coefficients for bi- and ter-valent ions, respectively. The latter were obtained by use of Davies's modified Debye mean ionic-activity coefficient formula (*J.*, 1938, 2093). The results of the calculations are given in the table, and the average of K_3 is $2{\cdot}7 \times 10^{-7}$.

The Fourth Acid Dissociation Constant.—The method used by Kolthoff and by Morton (*locc. cit.*) was employed, *i.e.*, mixing sodium pyrophosphate and hydrochloric acid in 2 : 1 molecular proportions. As for the K_3 measurements, the carbon dioxide present in the water was calculated from conductivity measurements on the same batch of water. Since the solutions were of high pH, the carbon dioxide became converted into bicarbonate and carbonate. The first of these was calculated from the first dissociation constant for carbonic acid, *i.e.*, $4{\cdot}45 \times 10^{-7}$ (Harned and Davis, *J. Amer. Chem. Soc.*, 1943, **65**, 2030), and the carbonate obtained by difference.

In the solutions under consideration, interaction between the sodium ions and the pyrophosphate ions to form NaP_2O_7''', and to a lesser extent $Na_2P_2O_7''$ and $NaHP_2O_7''$, is to be expected. The evidence for the presence of NaP_2O_7''' is, first, that the analogous cases of sodium tetrametaphosphate (Part I, *loc. cit.*) and potassium ferrocyanide (Davies, *J. Amer. Chem. Soc.*, 1937, **59**, 1760) both show this type of association, and for these the dissociation constants of the associated ions are 0·009 and 0·005, respectively. Further evidence was also supplied by the conductivity measurements described later. From the conductivity figures obtained after correction for hydrolysis, an approximate value of 0·002 was obtained for the dissociation constant of the NaP_2O_7''' ion. Accordingly, a dissociation constant of 0·005 was used in the present calculations for the acid dissociation constant. More accurate hydrolysis corrections to the conductivity measurements after the present work was completed justified this chosen value, since the final calculation gave a dissociation constant of 0·0045 for NaP_2O_7'''. In the cases of the other two ions, *i.e.*, $Na_2P_2O_7$ and $NaHP_2O_7$, a value of 0·05 was assumed to be the order of their dissociation constants. This is a round average of the available data. Thus in Part I it was shown that the corresponding sodium trimetaphosphate ion has a value of 0·068, and in addition potassium ferricyanide and hexamminocobaltic chloride have the values of 0·04 and 0·03 respectively (calculated from the data of Hartley and Donaldson, *Trans. Faraday Soc.*, 1937, **33**, 465), while potassium cobalticyanide averages 0·034 (James, Ph.D. Thesis, London, 1947). In any case the concentrations of these two species are quite small, so any uncertainty in the assumed dissociation constant value cannot give rise to serious errors.

The expressions used for calculating the various ionic concentrations are $[HCl] + 2[CO_2] = [HP_2O_7'''] + [HCO_3'] + [NaHP_2O_7'']$ and $m - [HCl] = [P_2O_7''''] + [NaP_2O_7'''] + [Na_2P_2O_7'']$, where the carbon dioxide refers to that present in the water before the addition of sodium pyrophosphate of molarity m and hydrochloric acid of approximately $0·5m$. These two expressions follow from a consideration of the distribution of the hydrogen ions, and from the difference between these concentrations and the total pyrophosphate molarity. In addition the dissociation constant expressions for NaP_2O_7''', $Na_2P_2O_7''$ and $NaHP_2O_7''$ are also required. An approximation method was used, first leaving out of account the intermediate ions, then using the resulting concentrations of P_2O_7'''', HP_2O_7''', and $Na^{\bullet}$ and the ionic strength to find first values of the other species. The activity coefficients were calculated as in the case of K_3. Continuation along these lines led to the constant values shown below. The fourth acid dissociation constant, K_4, was evaluated from

$$\log K_4 = -\mathrm{pH} + \log\{P_2O_7''''\}/\{HP_2O_7'''\} + \log f_4/f_3$$

where f_3 and f_4 are the mean ionic activity coefficients for ter- and quadri-valent ions respectively, calculated as above. The results are shown in the table. The average value of K_4 is $2·4 \pm 0·2 \times 10^{-10}$. A slight drift in these values occurs with increasing ionic strength, which is probably due to the assumed dissociation constant of 0·05 (above) not being quite exact, and to the activity coefficient expression being a little inaccurate in the present case.

K_4 for pyrophosphoric acid at 25°.

Concentrations ($\times 10^4$).

	(*a*).	(*b*).	(*c*).	(*d*).	(*e*).	(*f*).	(*g*).
$Na_4P_2O_7$	5·23	8·21	8·85	9·00	16·43	16·50	23·40
HCl	2·56	4·11	4·43	4·47	8·22	8·25	11·70
$Na^{\bullet}$	20·37	31·64	34·04	34·60	62·25	62·64	87·71
P_2O_7''''	2·06	3·03	3·28	3·29	5·36	5·25	6·99
NaP_2O_7'''	0·48	0·97	1·11	1·13	2·63	2·72	4·32
$Na_2P_2O_7''$	0·01	0·04	0·04	0·05	0·17	0·17	0·35
HP_2O_7'''	2·59	4·07	4·29	4·36	7·75	7·86	10·86
$NaHP_2O_7''$	0·07	0·15	0·17	0·18	0·50	0·50	0·87
HCO_3'	0·05	0·09	0·03	0·05	0·03	0·09	0·03
CO_3''	—	0·01	—	—	—	0·01	—
$I \times 10^3$	4·21	6·52	7·00	7·11	12·6	12·6	17·7
pH	9·312	9·197	9·201	9·269	9·134	9·125	9·079
$K_4 \times 10^{10}$	2·39	2·62	2·61	2·19	2·25	2·26	2·15

The Conductivity of Sodium Pyrophosphate Solutions at 25°.—Abbott and Bray (*loc. cit.*) measured the conductivity of sodium pyrophosphate solutions at 18°, but these results are based on an obsolete method of determining the cell constant. Other measurements by Watkins and Jones (*J. Amer. Chem. Soc.*, 1915, **37**, 1628) at 25° are expressed in Siemens units. In the present work fresh results are recorded and corrected, as far as possible, for hydrolysis. In addition, corrections have been made for the ion-associations which take place between the products of hydrolysis. Finally, the corrected results have been used to derive the dissociation constant of the ion NaP_2O_7'''. The concentration range $C = 0{\cdot}00045$ to 0·003 was studied. The resistance readings showed a slow drift with time (about 0·1% per hour); so far as possible this was allowed for by taking time measurements and extrapolating back to the time of addition of the stock solution.

Since extensive hydrolysis occurs, and since ion-association amongst the products of hydrolysis must be taken into consideration, complex corrections are necessary to obtain the true conductivities. The equilibria to be taken into account are: $P_2O_7'''' + H_2O \rightleftharpoons HP_2O_7'''$; $2P_2O_7'''' + H_2CO_3 \rightleftharpoons 2HP_2O_7'''$; $P_2O_7'''' + H_2CO_3 \rightleftharpoons HP_2O_7''' + HCO_3'$; $P_2O_7'''' + Na^{\bullet} \rightleftharpoons NaP_2O_7'''$; and $HP_2O_7''' + Na^{\bullet} \rightleftharpoons NaHP_2O_7''$. Letting the concentrations be represented by $a = HCO_3'$, $b = CO_3''$, $d = NaP_2O_7'''$, $e = NaHP_2O_7''$, $y = OH'$, and m the pyrophosphate molarity, we then have

$$K_h = \frac{K_w}{K_4} = \frac{\{OH'\}\{HP_2O_7'''\}}{\{P_2O_7''''\}} = \frac{y(y + a + 2b - e)f_1f_3}{(m - y - a - 2b - d)f_4}$$

In this, K_4, the fourth dissociation constant of pyrophosphoric acid, is $2{\cdot}4 \times 10^{-10}$ (see above), K_w is $1{\cdot}0 \times 10^{-14}$ (Harned and Hamer, *J. Amer. Chem. Soc.*, 1933, **55**, 1924); and f_1, f_3, and f_4 are the ion activity coefficients for uni-, ter-, and quadri-valent ions, respectively, calculated as before. The carbon dioxide was calculated from the specific conductivity of the water. To find the various concentrations, the following procedure was used. First, ion-association corrections were omitted and a preliminary value of y obtained. The resulting value, together with the calculated ionic strength, was then used to calculate first values of a, d, and e, the dissociation constants referred to in connection with the K_4 calculations being used. The difference between the carbon dioxide and a gave the concentration of b. The new ionic strength was used for calculating second approximations, and so on. The constant values eventually obtained are given in Table I.

TABLE I.

Conductivity of sodium pyrophosphate at 25°. [Ion concentrations ($\times 10^5$).]

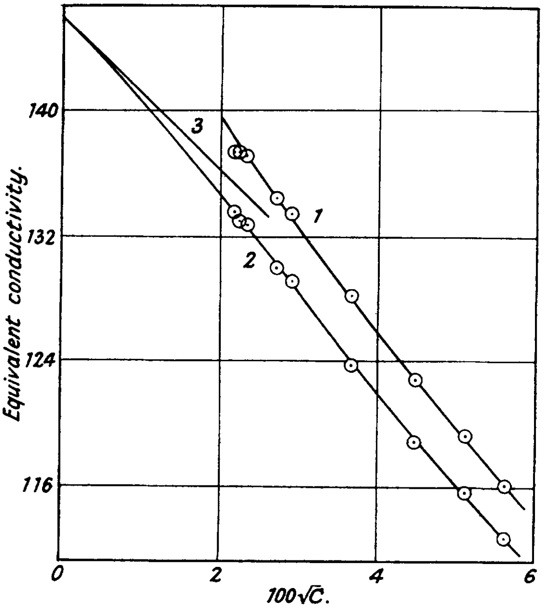
Run............	(*a*).	(*b*).	(*c*).	(*d*).	(*e*).	(*f*).	(*g*).	(*h*).	(*i*).
C	46·13	50·17	54·50	73·35	83·80	133·24	199·99	260·87	316·02
$Na^{\bullet}$	45·7	49·6	53·8	72·2	82·3	129·6	192·4	149·2	300·0
P_2O_7''''	6·22	6·99	7·78	11·08	12·99	21·66	33·07	43·08	51·81
HP_2O_7'''	4·84	4·99	5·18	6·06	6·41	7·99	9·46	10·48	11·22
OH'	4·36	4·69	4·98	5·87	6·30	7·96	9·52	10·62	11·43
NaP_2O_7'''	0·43	0·52	0·62	1·13	1·47	3·51	7·23	11·34	15·58
$NaHP_2O_7''$	0·04	0·04	0·05	0·07	0·08	0·15	0·24	0·32	0·40
HCO_3'	0·39	0·26	0·19	0·18	0·13	0·12	0·12	0·12	0·11
CO_3''	0·06	0·04	0·03	0·04	0·03	0·03	0·03	0·03	0·04
$I \times 10^4$	9·89	10·82	11·80	16·03	18·39	29·40	44·12	57·35	69·17

Corrections to the conductivity measurements were then applied. These were effected by regarding the solutions as mixtures of $Na_4P_2O_7$, $Na_3HP_2O_7$, NaOH, $NaHCO_3$, and Na_2CO_3. That is,

$$\begin{aligned}4m\Lambda_{\text{obs.}} = {} & 4Na_4P_2O_7\Lambda_{Na_4P_2O_7} + 3Na_3HP_2O_7\Lambda_{Na_3HP_2O_7} + 2NaHP_2O_7''\Lambda_{Na_2,NaHP_2O_7} \\ & + 2Na_2CO_3\Lambda_{Na_2CO_3} + NaHCO_3\Lambda_{NaHCO_3} + NaOH\Lambda_{NaOH}\end{aligned}$$

For the conductivity of the sodium hydroxide, Darken and Meier's data (*J. Amer. Chem. Soc.*, 1942, **64**, 621) were taken. Those of $NaHCO_3$ and Na_2CO_3 are given in a further paper (this vol., p. 429). In the case of $Na_3HP_2O_7$, the conductivity was calculated from Abbot and Bray's data (*loc. cit.*), *viz.*, $\Lambda_0 = 102{\cdot}9$ at 18°. The mobility of the sodium ion at this temperature is 43·4 (Davies, "Conductivity of Solutions", Chap. XVII), and is 50·1 at 25° (Shedlovsky, MacInnes, and Longsworth, *J. Amer. Chem. Soc.*, 1932, **54**, 2758). So if a temperature coefficient of 0·022 is used (Davies, *op. cit.*), the resulting Onsager equation for $Na_3HP_2O_7$ at 25° is $\Lambda_0 = 120{\cdot}0 - 190{\cdot}5I^{\frac{1}{2}}$. The equation for the part of this salt which is not fully dissociated can be obtained by the methods used before (cf. sodium trimetaphosphate, Part I), and is $\Lambda = 96{\cdot}7 - 136{\cdot}4I^{\frac{1}{2}}$. The conductivities calculated from these expressions, using the values of I given in Table I, together with the concentrations given in this table, permit the conductivity of sodium pyrophosphate to be calculated from the mixture rule formulated above. The fraction of sodium pyrophosphate which is not fully dissociated has been included with the part which is completely ionised. This is because it is required to evaluate the experimental dissociation constant of the NaP_2O_7''' ion from the corrected conductivity data. The reason for calculating an approximate value of this ion in Table I was to obtain a truer value of I for use in the conductivity equations of the other species, and for calculating the concentrations of these. The corrected conductivity measurements are shown in Table II, and the curve in the figure.

Equivalent conductivity of sodium pyrophosphate solutions at 25°.



1, *Experimental curve.* 2, *Corrected curve.* 3, *Limiting Onsager slope.*

Extrapolation of the calculated conductivity curve leads to $\Lambda_0 = 146{\cdot}0$, so the mobility of the pyrophosphate ion is 95·9. The discrepancy between the curve and the theoretical Onsager equation, as discussed in Part I (*loc. cit.*), may be used to estimate the extent of association between sodium and pyrophosphate ions, the process being analogous to that used for sodium tetrametaphosphate. The Onsager equation for the full stage of dissociation is $\Lambda = 146{\cdot}0 - 261{\cdot}0I^{\frac{1}{2}}$. If $\frac{3}{4}$ of 95·9 is taken as the mobility of the NaP_2O_7''' ion, the Onsager equation for the dissociation $Na_4P_2O_7 \rightleftharpoons 3Na^{\cdot} + NaP_2O_7'''$ is $\Lambda = 122{\cdot}0 - 192{\cdot}0I^{\frac{1}{2}}$. So if α is the fraction of sodium pyrophosphate which completely ionises, combination of the two equations leads to

TABLE II.

Conductivity of sodium pyrophosphate at 25° (*corrected data*).

Run.	$10^6\kappa_{H_2O}$.	10^6C.	$10^5C^{\frac{1}{2}}$.	$\Lambda_{obs.}$.	$\Lambda_{Na_4P_2O_7}$.	a.	K.
a	0·480	461·34	2148	137·40	133·65	0·929	0·0043
b	0·382	501·72	2240	137·35	133·06	0·924	0·0043
c	0·311	545·03	2335	137·19	132·78	0·920	0·0044
d	—	733·45	2708	134·50	130·02	0·899	0·0043
e	0·253	838·05	2895	133·52	129·14	0·895	0·0046
f	—	1332·4	3650	128·22	123·80	—	—
g	—	1999·9	4472	122·88	118·94	—	—
h	—	2608·7	5108	119·35	115·74	—	—
i	—	3160·2	5622	116·24	112·82	—	—

$$\Lambda = 91{\cdot}5 \times \alpha(54{\cdot}5 - 117{\cdot}0I^{\frac{1}{2}}) - 144{\cdot}0I^{\frac{1}{2}}$$

The dissociation constant for the equilibrium $NaP_2O_7''' \rightleftharpoons Na + P_2O_7''''$ can thus be obtained from

$$K = \{Na^{\cdot}\}\{P_2O_7''''\}/\{NaP_2O_7'''\} = (3 + \alpha)\alpha m f_{\pm}^{8}/(1 - \alpha)$$

where $\log f_{\pm} = -0{\cdot}509I^{\frac{1}{2}}$. Calculations were confined to the more dilute regions, since, strictly the Onsager equation is only reliable where the difference between Λ_0 and Λ is about 10% of Λ_0. The results are shown in Table II, and the average value of the dissociation constant is about 0·0045, thus substantiating the assumed figure of 0·005 used in the calculations for the fourth acid dissociation constant.

EXPERIMENTAL.

Sodium pyrophosphate was made by fusion, at 1100° in a platinum dish, of " AnalaR " disodium hydrogen phosphate which had been twice recrystallised from conductivity water. The cell used for the pH measurements was a seasoned round-bottomed Pyrex flask. The bung to this contained an entrance tube for the addition of the stock solutions, a tube for the introduction of carbon dioxide-free air, a " Cambridge " glass electrode, and a dipping silver–silver chloride electrode. The last was contained in a potassium chloride liquid-junction tube fitted with a ground-glass cap. The electrode was made by Brown's method (*J. Amer. Chem. Soc.*, 1934, **56**, 646). Temperature control was maintained by an oil-bath at 25° ± 0·01°. The cell was swept out with the washed air before being filled with conductivity water from a stock solution of known value. A " Cambridge " bench-model pH meter was used, and calibrated with suitable buffers (Acree, Hamer, and Pinching, *J. Res. Nat. Bur. Stand.*, 1945, **35**, 47; Manov, De Lollis, and Acree, *ibid.*, 1944, **33**, 287; Manov, De Lollis, Linvall, and Acree, *ibid.*, 1945, **36**, 543). Details concerning the conductivity measurements have been given in Part I.

EDWARD DAVIES CHEMICAL LABORATORIES,
ABERYSTWYTH, WALES.

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