701. *The Mechanism of Electrical Conduction in Fused Phosphoric and Trideuterophosphoric Acids.*

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The conductivity–composition curve of the system H_2O–P_2O_5 has no minimum in the region corresponding to the composition H_3PO_4, the compound being indicated instead by a discontinuous change in slope of the graph. Fused orthophosphoric acid has a high electrical conductivity ($\kappa_{40} = 7{\cdot}68 \times 10^{-2}$ ohm^{-1} cm.$^{-1}$) which decreases slowly during three weeks to an equilibrium value of $6{\cdot}52 \times 10^{-2}$ ohm^{-1} cm.$^{-1}$. Addition of potassium dihydrogen phosphate to the pure acid does not increase its conductivity but diminishes it slightly. These observations can be interpreted in terms of the rapid dissociation of phosphoric acid: $2H_3PO_4 \rightleftharpoons H_4PO_4^+ + H_2PO_4^-$, followed by a slow reaction to give an equilibrium concentration of two further ions: $2H_3PO_4 \rightleftharpoons H_3O^+ + H_3P_2O_7^-$. The ion $H_2PO_4^-$ has so high a mobility that a proton-switch conduction mechanism is implied. Consistent with this, no migration of potassium ions was detected during prolonged electrolysis of a solution of potassium dihydrogen phosphate in anhydrous phosphoric acid, all the current being carried by the dihydrogen phosphate ion. The abnormal mobility can be removed by forming the complex BF_3,H_3PO_4, in which the boron trifluoride molecules occupy positions formerly available for hydrogen bonding and proton jumps (see following paper).

The effects of deuterium substitution were determined by comparing the properties of trideuterophosphoric acid with those of phosphoric acid. As expected, deuteration raised the m. p., density and viscosity, and lowered the refractive index and conductivity. Activation energies were also derived, and the results compared with those obtained on other liquids known to conduct (*a*) by a proton-switch mechanism and (*b*) by normal ionic migration.

No systematic investigation of the conduction properties of anhydrous phosphoric acid has been published though isolated reports suggest that its electrical conductivity is abnormally high for so viscous a liquid. This paper describes the preparation and characterization of pure anhydrous orthophosphoric and trideuterophosphoric acids and the measurement of their conductivity, viscosity, and density over a temperature range of 40°. The results indicate that, even if phosphoric acid were completely dissociated into ions, the average mobility of these ions must be ten times the value for normal ionic mobilities to account for the conductivity. From the way in which the conductivity of the pure acid alters on addition of water or phosphoric oxide, it is concluded that the abnormal mobility is confined primarily to the anion $H_2PO_4^-$ (or $D_2PO_4^-$), implying an apparent migration velocity about twenty times greater than that expected for normal ionic migration. (For comparison, the mobility of the hydrogen ion in water is about six times that of other cations.) These deductions were confirmed by transport measurements and were recently published in a preliminary note.[1] The experimental results are presented in the following section and compared with data in the literature. The results are then interpreted on the basis of a proton-switch conduction mechanism in the fused acids.

Experimental and Results.

The anhydrous acids were prepared in a vacuum line by transferring the stoicheiometric amount of water or heavy water on to a known weight of phosphoric oxide which had been purified by repeated sublimation *in vacuo*.[2] Other apparatus was as described in the preceding paper.[3]

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[1] Greenwood and Thompson, *Proc. Chem. Soc.*, 1959, 352.

[2] *Idem,* " Inorganic Syntheses," Vol. VI, in the press.

[3] *Idem,* preceding paper.

The m. p. of orthophosphoric acid was determined by sealing a sample into a V-tube and slowly crystallizing about four-fifths before decanting the remaining liquid into the second limb. The temperature was then raised slightly so that the crystals started to melt and this fresh liquid used to swill away the viscous film adhering to the crystals after the first decanting. The bulk of the crystals were then remelted and the whole cycle of partial crystallization, decanting, partial melting, and decanting was repeated. The m. p. rose rapidly from an initial value of about 40° for the acid as synthesized to a maximum of 42·35° (lit., 42·35°,[4,5] 42·30° [6]) and this value was not raised by further cycles. By the same technique the m. p. of trideuterophosphoric acid was determined as 46·0°, an increase of $3{\cdot}6_5$°. The only reported value for the trideutero-acid is 38·4°,[7] but this was on an admittedly impure sample and the corresponding figure for orthophosphoric acid, synthesized by the same authors for comparison, was only 40·1°.

The refractive index of orthophosphoric acid measured on an Abbé refractometer with Na$_D$ illumination was very sensitive to traces of moisture; $n_D^{20} = 1{\cdot}4503$ (lit., 1·4510,[7] 1·45026 [8]). For trideuterophosphoric acid $n_D^{20} = 1{\cdot}4430$, which is identical with the only published value.[7]

Variation of electrical conductivity with composition at 40·0° was investigated both by adding known weights of water to phosphoric acid and its hemihydrate and also by adding weighed portions of phosphoric oxide to these compounds. Results obtained by the addition of water were reproducible, and detailed measurements in the region of 20 moles % of total P_2O_5 showed no discontinuity or inflexion at the hemihydrate, $H_3PO_4,\frac{1}{2}H_2O$. Addition of phosphoric oxide to these solutions retraced the curve in general but precise results were difficult to obtain because of the slow rate of hydrolysis of the oxide in concentrated acid at 40°. Nevertheless, there was always a definite change in slope at 25 moles % of P_2O_5 (*i.e.*, H_3PO_4) as shown in Fig. 1 which is typical of the many runs made. The lower limb could also be retraced by adding water and again a discontinuity occurred at the composition of the anhydrous acid. Phosphoric acid is therefore not characterized by a minimum in conductivity, and this property cannot be used as a criterion for purity of the acid. The absence of a minimum is also relevant to a discussion of the modes of ionization and the mechanism of conduction in orthophosphoric acid (p. 3490).

The electrical conductivity of anhydrous phosphoric acid, purified by fractional freezing in an apparatus attached directly to the conductivity cell, decreased slowly with time from an initial value characteristic of the pure freshly melted acid to a value characteristic of the slowly attained equilibrium mixture of orthophosphoric acid and higher polyphosphoric acids of the same stoicheiometry $H_4P_2O_7,H_2O$, formed by self dehydration. (This is a second reason why conductivity is not a reliable criterion of purity in this system.) In a typical experiment at 40° on a sample sealed under vacuum into a conductivity cell which was completely immersed in the thermostat bath to eliminate the possibility of slow thermal dehydration, the initial conductivity of $7{\cdot}68 \times 10^{-2}$ ohm^{-1} cm.$^{-1}$ decreased to $6{\cdot}90 \times 10^{-2}$ in 24 hr. and to an equilibrium value of $6{\cdot}52 \times 10^{-2}$ after 21 days. The total decrease was 15% and, at equilibrium, no change

TABLE 1. *Density, viscosity, and conductivity between 25° and 65°* *.

Temp.	d^t_4 (g. cm.$^{-3}$)		η (cP)		$10^2\kappa$ (ohm^{-1} cm.$^{-1}$)		μ (ohm^{-1} cm.^{2} mole^{-1})		$\mu\eta$ (ohm^{-1} cm.^{2} cP. mole^{-1})	
	H_3PO_4	D_3PO_4	H_3PO_4	D_3PO_4	H_3PO_4	D_3PO_4	H_3PO_4	D_3PO_4	H_3PO_4	D_3PO_4
25·0°	1·8683	1·9083	177·5	231·8	4·675	2·818	2·446	1·495	434·1	346·5
30·0	1·8646	1·9042	140·8	182·4	5·589	3·378	2·937	1·791	413·6	326·9
35·0	1·8603	1·9001	112·2	147·8	6·598	3·998	3·475	2·126	389·9	314·2
40·0	1·8568	1·8959	92·69	118·7	7·680	4·632	4·053	2·467	375·8	293·0
45·0	1·8523	1·8922	76·45	95·93	8·836	5·275	4·672	2·815	357·2	270·6
50·0	1·8494	1·8888	64·01	77·44	10·13	5·940	5·366	3·176	343·5	246·0
55·0	1·8458	1·8846	54·83	64·73	11·38	6·558	6·043	3·514	331·3	227·5
60·0	1·8414	(1·8807)	46·11	55·18	12·70	7·261	6·762	3·899	304·6	215·2
65·0	1·8380	(1·8767)	39·64	46·86	14·06	(7·94)	7·495	(4·28)	297·1	(200)

* Values in parentheses were obtained by extrapolation.

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[4] Ross and Jones, *J. Amer. Chem. Soc.*, 1925, **47**, 2165; *Ind. Eng. Chem.*, 1925, **17**, 1081.

[5] Weber and King, " Inorganic Syntheses," Vol. I, 1939, p. 101.

[6] Smith and Menzies, *J. Amer. Chem. Soc.*, 1909, **31**, 1183.

[7] Pannetier and Guenebaut, *Bull. Soc. chim. France*, 1955, 636.

[8] Tutunzic, Liler, and Kosanovic, *Bull. Soc. chim. Belgrade*, 1955, **20**, 3, 363, 481.

in the conductivity could be detected (1 part in 5000) during 3 days. The time taken to reach equilibrium and the relative concentration of the various species at equilibrium depend on temperature but, as the initial (maximum) rate of change at 40° is only 0·5% per hour, it is possible, by working quickly, to get a moderately accurate set of data on the variation of the " initial " conductivity with temperature. Values so obtained are summarized in col. 6 of Table 1, and these were reproducible to within 2 parts per 1000 on independent samples of orthophosphoric acid synthesized in the vacuum line. An isolated sample was also prepared by dehydrating " AnalaR " syrupy phosphoric acid in a stream of dry air at 100° and subsequently recrystallizing the acid to maximum m. p.; the values obtained were close to those given in Table 1 and are incorporated in Table 2, which also includes the six previously reported determinations of the conductivity. There is general agreement between the values but the published figures are all higher (to varying degrees) than the present values. This discrepancy is not due to the slowly attained equilibrium with polyphosphoric acids, since this decreases rather than increases the conductivities given in Table 1. Indeed, it may well be that the literature values themselves refer to acids which had been molten for some time and that, had the measurements been made on the acids when freshly fused, they would have been even higher than those given in Table 2.

FIG. 1. *Conductivity–composition isotherm for* H_2O–P_2O_5 *at* 40°.

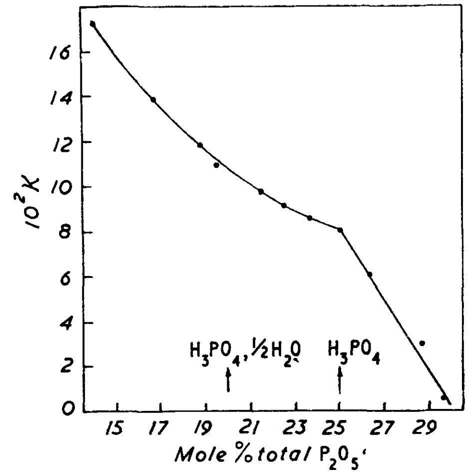

FIG. 2. *Conductivity and fluidity of* H_3PO_4 *and* D_3PO_4.

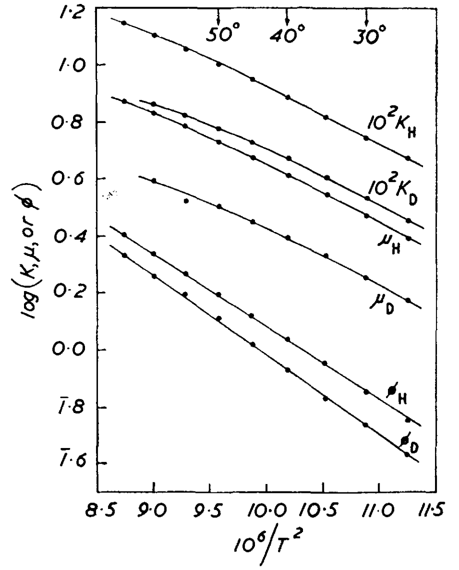

TABLE 2. *Conductivity of phosphoric acid* ($10^2\kappa$, *ohm*$^{-1}$ *cm.*$^{-1}$).

	Present work		
Temp.	Table 1	Dehydr. recryst. " AnalaR "	Other values
0·0°	(1·0) [a]	—	1·406 [b]
25·0	4·675	4·617	4·662—5·041,[c] 5·10,[d] 5·192,[e] 5·66[f]
29·3	5·468	5·413	5·80 [g]
40·0	7·680	7·541	7·845—8·394 [c]

[a] Extrapolated from 25° on Fig. 2. [b] Phillips, *J.*, 1909, **95**, 59. [c] Ref. 8. [d] Topchiev, Paushkin, Vishnyakova, and Kurashov, *Doklady Akad. Nauk, S.S.S.R.*, 1951, **80**, 381. [e] Hetherington, Nichols, and Robinson, *J.*, 1955, 3141. [f] Calculated from the equivalent conductivity, $\lambda_{25} = 3{\cdot}14$, and the number of moles/l. of anhydrous H_3PO_4 (18·02) given in ref. 11. [g] By extrapolation from a value of $6{\cdot}102 \times 10^{-2}$ ohm^{-1} cm.$^{-1}$ for 98·8% H_3PO_4 given by Smith and Menzies, *J. Amer. Chem. Soc.*, 1909, **31**, 1191.

In view of the way in which conductivity varies with composition (Fig. 1), two conclusions are possible: (*a*) the acid used in the present experiments contained an excess of phosphoric oxide, or (*b*) earlier investigators used samples which contained small amounts of water. The sealed-system technique employed in this work for measuring the conductivity of maximum m. p.

acid renders contamination with phosphoric oxide unlikely. On the other hand, it is difficult to avoid the adventitious absorption of moisture when working in open systems with hygroscopic compounds such as phosphoric acid, and our own experience in preliminary experiments confirms that, even during the rapid pouring of phosphoric acid from one vessel to another, sufficient water is absorbed to increase the conductivity appreciably. We conclude that the conductivity values in Table 1 are to be preferred to the published values summarized in Table 2.

The conductivity of trideuterophosphoric acid also decreased slowly with time to an equilibrium value. Values of the initial conductivity as a function of temperature are set out in Table 1, which indicates that deuteration lowers the specific conductivity to 60% of the value for phosphoric acid itself. The temperature variation of the conductivity of the compounds could not be represented as a linear relation between log κ and $1/T$, and Fig. 2 shows that even the plot of log κ against $1/T^2$ is still slightly curved. This may reflect the changing position of equilibrium between ortho- and poly-phosphoric acids. Approximate activation energies at three temperatures are given in Table 3 and are discussed later.

TABLE 3. *Activation energies of electrical conduction and viscous flow.*

	E_κ (kcal. mole^{-1})		E_μ (kcal. mole^{-1})		E_η (kcal. mole^{-1})	
Temp.	H_3PO_4	D_3PO_4	H_3PO_4	D_3PO_4	H_3PO_4	D_3PO_4
25°	6·0	6·5	6·1	6·5	7·92	8·55
40	5·7	5·3	5·8	5·3	7·54	8·14
60	4·5	4·0	4·6	4·4	7·09	7·66

The viscosity of the two compounds at various temperatures is compared in cols. 4 and 5 of Table 1. There is a very considerable increase on deuteration (30·6% at 25°), but this diminishes to 18·2% at 65° as a result of the greater activation energy of viscous flow in the deutero-compound (see Table 3). Unlike the electrical conductivity, the viscosity showed no detectable change with time over a period of days, so that this property is less sensitive to the presence of small concentrations of polyphosphate anions. Consistent with this, the plot of log ϕ, *i.e.*, $-$ log η, against $1/T^2$ in Fig. 2 was linear for both compounds, the decrease in activation energy with rise in temperature being associated with the decrease in hydrogen bonding as discussed in the preceding paper.[3] The viscosity of trideuterophosphoric acid has not previously been determined, and only two references, giving widely differing values, were found for orthophosphoric acid itself. Simon and Weist [9] report $\eta_{20} = 326{\cdot}0$ cP and $\eta_{50} = 117{\cdot}37$ cP, compared with our values of 220 cP (extrapolated) and 64·01 cP., whereas Tutunzic, Liler, and Kosanovic [8] report values much nearer ours (in parentheses): $\eta_{25} = 164{\cdot}7$—173·3 (177·5), $\eta_{40} = 84{\cdot}88$—88·95 (92·69).

The change in density on passing from phosphoric acid to its deuterium analogue is less spectacular than the corresponding changes in conductivity and viscosity. In fact the change is insufficient to compensate for the greater molecular weight of the deutero-acid, so that there is an increase of 0·93% in the molar volume at 25°. The experimental values in Table 1 lead to the equations

$$H_3PO_4:\ d_4{}^t = 1{\cdot}8876 - 7{\cdot}691 \times 10^4t$$

$$D_3PO_4:\ d_4{}^t = 1{\cdot}9279 - 7{\cdot}873 \times 10^4t$$

The equation for phosphoric acid may be compared with the relation 1·882—7·0 × $10^{-4}t$ derived from the data of Ross and Jones,[10] which gives $d_4{}^{25} = 1{\cdot}866$ (present work 1·8683). Other literature values for $d_4{}^{25}$ are 1·8609 [8] and 1·8224,[10] the latter figure being particularly low. The only published density value for trideuterophosphoric acid [7] refers to acid of very low m. p.: $d_4{}^{20} = 1{\cdot}890$ (present work 1·9119); the value obtained by the same workers for phosphoric acid, however, $d_4{}^{20} = 1{\cdot}873$, agrees well with our value of 1·8729. In short, the published values for the density of the two acids either agree with or are lower than the present values.

Dissolution of potassium dihydrogen phosphate in orthophosphoric acid lowers the specific conductivity of the system indicated in Table 4. This is probably due to the removal of phosphoric acid molecules from the conduction chain when the potassium ion becomes solvated, and more detailed experiments (to be published later) using phosphoric acid hemihydrate as solvent suggest that the solvation number of the potassium is 4.

[9] Simon and Weist, *Z. anorg. Chem.*, 1952, **268**, 301.
[10] Ross and Jones, *Ind. Eng. Chem.*, 1925, **17**, 1170.
[11] Mason and Culvern, *J. Amer. Chem. Soc.*, 1949, **71**, 2387.

Electrolysis of solutions of potassium dihydrogen phosphate in phosphoric acid and of the acid itself gave hydrogen and oxygen at the electrodes in the ratio 2 : 1. Prolonged electrolysis in a transport cell similar to that described by Hammett and Lowenheim for anhydrous sulphuric acid [12] caused no measurable change in the concentration of potassium ions. For example, passage of 455 coulombs (approx. 13 mA for 10 hr.) through a 0·135m-solution of potassium dihydrogen phosphate in anhydrous phosphoric acid left the concentration of potassium ions in the anode, cathode, and central compartments identical with that of the original solution to within the precision of the analytical methods used (1%). This places an upper limit of 0·002 on the transport number of the potassium ion. In a control experiment on an aqueous solution of potassium dihydrogen phosphate, passage of 189 coulombs (approx. 13 mA for 3·5 hr.) altered the concentration from 1·96 to 1·54 g. of K^+/100 ml. in the anolyte and to 2·38 g. of K^+/100 ml. in the catholyte. These figures correspond to a transport number $t_{K^+} = 0{\cdot}85$ at this concentration. This is consistent with the data of Mason and Culvern [11] who found $\lambda_0(H_2PO_4^-) = 16$; $\lambda_0(K^+)$ being taken to be 76 gives $t_{K^+} = 76/(76 + 16) = 0{\cdot}83$ at infinite dilution. Potassium was determined by precipitation with sodium tetraphenylboron after adjusting the acidity to pH 3 with aqueous sodium hydroxide.

TABLE 4. *Specific conductivity of solutions at* 25°.

Molality of KH_2PO_4	0·00	0·0138	0·0370	0·0687	0·0889	0·0136	0·314
$10^2\kappa$ (ohm^{-1} cm.$^{-1}$)	4·63	4·56	4·38	4·21	4·13	3·93	3·56

DISCUSSION

The self-dissociation of phosphoric acid can be represented by two simultaneous processes. The first is a rapidly attained autoprotolysis equilibrium:

$$2H_3PO_4 \rightleftharpoons H_4PO_4^+ + H_2PO_4^- \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

The second is a slowly attained equilibrium (2) which can be described as an ionic self-dehydration:

$$2H_3PO_4 \rightleftharpoons H_3O^+ + H_3P_2O_7^- \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

The abnormally high electrical conductivity of orthophosphoric acid cannot be explained on the basis of the normal Stokes migration of these ions even if the compound is considered to be completely ionic, since the high viscosity ($\eta_{25} = 177{\cdot}5$ cP) renders any contribution from normal migration negligible. Thus, by using the equations given in the preceding paper,[3] the conductivity can be represented by the expression $\kappa = nev$, where n is now the total number of ions per ml., v their average mobility, and e is the electronic charge ($1{\cdot}59 \times 10^{-19}$ coulomb). If molten orthophosphoric acid is assumed to be completely dissociated according to (1), then $n = 6{\cdot}03 \times 10^{23}/V_M$ ions per ml., where V_M, the molar volume at 25°, is 52·5 ml. The mobility required to give the observed conductivity of $4{\cdot}68 \times 10^{-2}$ ohm^{-1} cm.$^{-1}$ is therefore $2{\cdot}55 \times 10^{-5}$ cm.^{2} sec.$^{-1}$ volt^{-1}. This is ten times greater than the value of $2{\cdot}5 \times 10^{-6}$ obtained on the basis of Walden's rule assuming a similar degree of ionic solvation in water and phosphoric acid and normal ionic migration. In this calculation the dihydrogen phosphate ion has a mobility [11] of $1{\cdot}6 \times 10^{-4}$ cm.^{2} sec.$^{-1}$ volt^{-1} in water, and the mobility of the $P(OH)_4^+$ ion was taken to be similar to that of the ammonium or the sulphate ion, *i.e.*, about 8×10^{-4} cm.^{2} sec.$^{-1}$ volt^{-1}, so that the average ionic mobility is close to 5×10^{-4} cm.^{2} sec.$^{-1}$ volt^{-1} in water ($\eta_{25} = 0{\cdot}894$). This reduces to $2{\cdot}5 \times 10^{-6}$ cm.^{2} sec.$^{-1}$ volt^{-1} when corrected for the viscosity of anhydrous orthophosphoric acid. The tenfold difference between this estimated ionic migration velocity and the minimum possible mobility required to reproduce the observed conductivity cannot be removed by postulating a decrease in ionic solvation and implies some abnormal conduction mechanism. If only one of the ions is abnormal then it must have an effective mobility at least twenty times that of a normal ion. This factor will, of course, be greater if the acid is not completely dissociated; for example, if molten orthophosphoric acid is 10% dissociated according to (1), then one of the ions must be moving

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[12] Hammett and Lowenheim, *J. Amer. Chem. Soc.*, 1934, **56**, 2620.

some 200 times more rapidly than expected to account for the observed conductivity. The abnormal conductance is established conclusively by the transport measurements which indicate no migration of potassium ions during electrolysis of KH_2PO_4, the current being carried entirely by a proton-switch mechanism involving the ions formed by autoprotolysis of the solvent.

The shape of the conductivity–composition isotherm gives further information about the anomalously conducting species. In sulphuric acid there is a minimum in conductivity which occurs almost precisely at the composition H_2O,SO_3; [13,14] this establishes that both the HSO_4^- ion (whose concentration is increased by addition of water) and the $H_3SO_4^+$ ion (whose concentration is increased by addition of sulphur trioxide) have very similar mobilities. In the phosphoric acid system, on the other hand, there is no minimum in conductivity (Fig. 1); addition of water to the stoicheiometric acid increases its conductivity, but addition of phosphoric oxide sharply decreases it. As water is a stronger proton-acceptor than phosphoric acid, it removes protons from the $H_4PO_4^+$ ions and thus raises the concentration of dihydrogen phosphate ions according to the scheme:

$$2H_4PO_4^+ + 2H_2O \longrightarrow 2H_3O^+ + 2H_3PO_4 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

$$2H_3PO_4 \rightleftharpoons H_4PO_4^+ + H_2PO_4^- \quad . \; . \; . \; . \; . \; . \; . \quad (4)$$

The overall effect of adding water to phosphoric acid is therefore summarized by equation (5):

$$H_4PO_4^+ + 2H_2O \longrightarrow 2H_3O^+ + H_2PO_4^- \quad . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

The hydroxonium ion, by analogy with its behaviour in the sulphuric acid system,[15] is unlikely to have an abnormal mobility since it is not incorporated into the three-dimensional hydrogen-bonded structure of the liquid. The increase in conductivity is therefore due to the increase in concentration of the dihydrogen phosphate ion, and this ion is thereby established as having an abnormal conductivity in anhydrous phosphoric acid. By contrast, addition of phosphoric oxide to the stoicheiometric acid reduces its conductivity. The reaction here is more complicated because of the intermediate stages involved in the solvolysis of the P_4O_{10} molecule, but the overall reaction can be written

$$P_4O_{10} + 8H_3PO_4 \longrightarrow 6H_4P_2O_7 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

The pyrophosphoric acid will then dissociate to some extent, thus increasing the concentration of $H_4PO_4^+$ ions:

$$H_4P_2O_7 + H_3PO_4 \rightleftharpoons H_4PO_4^+ + H_3P_2O_7^- \quad . \; . \; . \; . \; . \; . \quad (7)$$

The fact that the conductivity decreases sharply with increasing concentration of these ions indicates that neither has any appreciable abnormal mobility. The drop in conductivity is due predominantly to the decrease in concentration of the anomalously conducting dihydrogen phosphate ion which occurs (1) when molecular phosphoric acid is removed from the system by reactions (6) and (7). In its lack of anomalous mobility the $H_3P_2O_7^-$ ion resembles the $HS_2O_7^-$ ion in sulphuric acid.[16] The absence of anomalous mobility for the $P(OH)_4^+$ ion is also readily understandable since, like the NH_4^+ ion, it is symmetrical and has no dipole moment to confer a preferred orientation in the applied electric field. Thus, whether or not the ion is involved in proton switches across hydrogen bonds, it will not contribute to the conductivity since these transfers will occur randomly rather than preferentially in the direction of the field.

The slow decrease in the conductivity of freshly melted phosphoric acid to an equilibrium value receives explanation in terms of eqn. (2) and the known sluggishness of interconversion of the polyphosphoric acids, for removal of molecular phosphoric acid by (2) shifts equilibrium (1) so as to reduce the concentration of the anomalously conducting

[13] Kunzler and Giauque, *J. Amer. Chem. Soc.*, 1952, **74**, 804.
[14] Gillespie, Oubridge, and Solomons, *J.*, 1957, 1804.
[15] Gillespie and Wasif, *J.*, 1953, 221.
[16] *Idem, ibid.*, p. 964.

dihydrogen phosphate ion. The Kohlrausch mobility of the other three ions is negligible as shown above. The build-up of new species in the melt was confirmed cryoscopically, the m. p. of the acid decreasing steadily by several degrees over a period of days as reaction (2) proceeded. That the process was reversible was demonstrated by crystallizing orthophosphoric acid very slowly from an equilibrium melt. The m. p. was raised to the initial value and the conductivity on remelting had returned to its initial high value; thereafter both m. p. and conductivity fell as before to an equilibrium value, the whole cycle being repeatable indefinitely. There is abundant independent evidence of the presence of the pyrophosphate grouping in anhydrous phosphoric acid,[17,18] and several attempts have been made to determine its concentration quantitatively. Early results from chemical analysis indicated about 6 moles % of polyphosphates,[19] and radio-phosphorus exchange followed by elution from an anion-exchange resin indicated 4 moles % of pyrophosphate.[20] More recent work, using cold hydrolysis and paper chromatography, suggests that stoicheiometric orthophosphoric acid contains 6·3 moles % each of pyrophosphoric acid and "free water,"[21] whereas results obtained by gradient elution supplemented by ascending one- and two-dimensional paper chromatography suggest that the composition of the melt is 86·3 moles % of H_3PO_4, 6·8 moles % each of $H_4P_2O_7$ and H_2O, and 0·03 mole % of $H_5P_3O_{10}$.[22] These figures are entirely consistent with the 15% decrease in the conductivity, which leads to an approximate figure of 7·5 moles % for the concentration of pyrophosphate. The argument is as follows. Let the concentration of dihydrogen phosphate ions in the freshly melted acid be α moles %; then by (1) there will be α moles % of $H_4PO_4^+$ and $(100 - 2\alpha)$ moles % of undissociated H_3PO_4. At equilibrium, let there be β moles % each of $H_4PO_4^+$ and $H_2PO_4^-$ and x moles % each of H_3O^+ and $H_3P_2O_7^-$; the concentration of undissociated H_3PO_4 is then $(100 - 2\beta - 2x)$ moles %. The equilibrium constant K_1 should be independent of the presence of other equilibria, hence

$$K_1 = \frac{[H_4PO_4^+][H_2PO_4^-]}{[H_3PO_4]^2} = \frac{\alpha^2}{(100 - 2\alpha)^2} = \frac{\beta^2}{(100 - 2\beta - 2x)^2} \quad . \quad (8)$$

Taking square roots and cross multiplying, we have $\alpha(100 - 2x) = 100\beta$, so that $2x = 100(1 - \beta/\alpha)$. If the reduction in conductivity is ascribed solely to the decrease in concentration of the dihydrogen phosphate ion, then $\beta/\alpha = 0{\cdot}85$, and substitution of this above gives $x = 7{\cdot}5$ moles %.

It should be possible to detect the gradual formation of 7 moles % of a new species cryoscopically, and this was qualitatively indicated by the steady decrease in the freezing point of anhydrous phosphoric acid when it was kept molten. A quantitative determination of the concentration of pyrophosphate ions requires a knowledge of the cryoscopic constant, k_f, of phosphoric acid. This can be calculated from the heat of fusion, ΔH_f, by means of the relation $k_f = \boldsymbol{R}T_0^2/(m_1\Delta H_f)$, where T_0 is the initial m. p. of pure phosphoric acid, 315·5°K, and m_1 is the number of moles of phosphoric acid per kg., *i.e.*, 10·20. The classical value for the heat of fusion[23] is 2·52 kcal. mole^{-1}, but the more recent value[18] of 3·10 kcal. mole^{-1} is preferred. Hence $k_f = 6{\cdot}26$ deg. mole^{-1} kg. The molal concentration, m_2, of pyrophosphate ions is then $\Delta T/2k_f$, where ΔT is the lowering of the freezing point and the factor 2 arises because the formation of each ion of $H_3P_2O_7^-$ is accompanied by the formation of an H_3O^+ ion which is also cryoscopically active. The equilibrium freezing point of stoicheiometric phosphoric acid was approached several weeks after the initial melting of a given sample and was about 34·6°; ΔT is thus $7{\cdot}7_5$° and $m_2 = 0{\cdot}62$ mole kg.$^{-1}$. Otherwise expressed, each kg. of solution contains 60 g. of $H_3PO_7^-$, 12 g. of

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[20] Higgins and Baldwin, *Analyt. Chem.*, 1955, **27**, 1780.
[21] Huhti and Gartaganis, *Canad. J. Chem.*, 1956, **34**, 785.
[22] Jameson, *J.*, 1959, 752.
[23] Thomsen, *Ber.*, 1874, **7**, 994; N.B.S. Circular 500.

H_3O^+, and 928 g. (9·47 moles) of the monomeric phosphoric species H_3PO_4, $H_4PO_4^+$, and $H_2PO_4^-$, so that the concentration of pyrophosphate is 5·8 moles %. This is in good agreement with the values of 6·3 and 6·8 moles % obtained by chromatography and 7·5 moles % deduced from the slow decease in electrical conductivity, the differences being ascribable to deviations from ideality, to slight changes in the proton-switch mobility in the presence of the new ions, and to the inherent difficulties of chemical and chromatographic analysis for pyrophosphate in the presence of excess of orthophosphate.

The precise extent of the autoprotolysis (1) cannot be determined from the present results, but an indication of the degree of self-dissociation comes from the absolute value of the specific conductivity if a reasonable value for the proton-switch mobility can be arrived at. In water at 25°, the H_3O^+ ion has a total mobility of $36{\cdot}3 \times 10^{-4}$ cm.^{2} sec.$^{-1}$ volt^{-1}; some of this will be contributed by the normal ionic migration velocity of the ion, and if this is taken to be the same as that of the potassium or the ammonium ion, *viz.*, $7{\cdot}6 \times 10^{-4}$ cm.^{2} sec.$^{-1}$ volt^{-1}, then the proton-switch mobility is approximately $28{\cdot}7 \times 10^{-4}$ cm.^{2} sec.$^{-1}$ volt^{-1}. Similarly, the total mobility of the OH^- ion, $20{\cdot}6 \times 10^{-4}$ cm.^{2} sec.^{1} volt^{-1}, can be considered as comprising a normal component, say, $6{\cdot}2 \times 10^{-4}$ cm.^{2} sec.$^{-1}$ volt^{-1} by comparison with the fluoride ion, and a proton-switch component of approximately $14{\cdot}4 \times 10^{-4}$ cm.^{2} sec.$^{-1}$ volt^{-1}. In sulphuric acid, because of the higher viscosity, the contribution from normal migration to the total mobility of the $H_3SO_4^+$ and HSO_4^- ions is only about 3%,[24] and as the observed mobility of the HSO_4^- ion [15] is $15{\cdot}6 \times 10^{-4}$ cm.^{2} sec.$^{-1}$ volt^{-1}, the proton-switch mobility in this medium is approximately $15{\cdot}1 \times 10^{-4}$ cm.^{2} sec.$^{-1}$ volt^{-1}. This is very similar to the anomalous part of the mobility of the hydroxyl ion but somewhat less than that of the hydroxonium ion in water. It therefore seems reasonable to assume a proton-switch mobility in phosphoric acid of the order of 20×10^{-4} cm.^{2} sec.$^{-1}$ volt^{-1}. Substitution of this and the initial conductivity into the expression $\kappa = nev$ gives $1{\cdot}47 \times 10^{20}$ as the number of $H_2PO_4^-$ ions per ml. As there is the same concentration of $H_4PO_4^+$ ions, the total number of ions/ml. in the freshly melted acid is $2{\cdot}94 \times 10^{20}$. Complete dissociation according to (1) would afford $6{\cdot}03 \times 10^{23}/52{\cdot}5$ ions per ml. as shown above. Hence the degree of dissociation is 2·56%, and the initial concentration of each of the ionic species 0·13 m. This leads to an autoprotolysis constant ($K_{ap} = [H_4PO_4^+][H_2PO_4^-]$) of $1{\cdot}7 \times 10^{-2}$ mole^2 kg.$^{-2}$ at 25°, a figure which can be compared with $K_{ap}(H_2SO_4) = 2{\cdot}9 \times 10^{-4}$, and $K_{ap}(H_2O) = 1{\cdot}01 \times 10^{-14}$ mole^2 kg.$^{-2}$. In short, if the proton-switch mobility in anhydrous phosphoric acid is similar to that in sulphuric acid and in water, then the initial concentration of ions in phosphoric acid is about 8 times higher than in sulphuric acid and is greater than the ionic concentration in pure water by a factor of $1{\cdot}3 \times 10^6$.

The general conduction characteristics of trideuterophosphoric acid are similar to those of orthophosphoric acid, and specific differences have already been mentioned under Experimental and Results. Unlike sulphuric acid, in which deuterium substitution surprisingly leaves the activation energies of conduction and viscous flow virtually unchanged,[3] deuteration of phosphoric acid has a marked influence, particularly on the viscosity. There is insufficient information to deduce the rate-determining step of the proton-switch process from these changes, or to apportion the decrease in conductivity on deuteration between the decrease in degree of self-dissociation and the decrease in switch mobility. The effect of the slow equilibrium (2) is also a complicating factor in the analysis. However, it is clear that deuterium substitution diminishes the reduced conductivity ($\mu\eta$ in Table 1) by 20% at 25° and 30% at 60° implying, as expected for a proton-switch conductor, that the conductivity is not viscosity-controlled. This contrasts with the behaviour of the boron trifluoride adducts of these acids which are discussed in the following paper; in these, conduction occurs by normal ionic migration, and the reduced conductivity is independent of temperature and is insensitive to deuterium substitution.

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[24] Gillespie and Wasif, *J.*, 1953, 209.