

RESULTS

Phosphoric acid hemihydrate, prepared by repeated fractional crystallization of "AnalaR" phosphoric acid of appropriate composition, had m. p. $29.30^\circ \pm 0.02^\circ$. Early literature values are 29.35° ,³ 29.32° ,⁴ and 29.25° ⁵ and a recent careful redetermination⁶ also gave 29.25° .

The densities (Table 1) can be fitted by the equation $d_4^t = 1.7747 - 7.80 \times 10^{-4}t$. No determinations referring specifically to the hemihydrate have been published but interpolation of Ross and Jones's⁴ results gives values (compared with ours in parentheses) of 1.7611 (1.7550)

TABLE 1. Density, viscosity, and conductivity of $2\text{H}_3\text{PO}_4 \cdot \text{H}_2\text{O}$.

Temp.	d_4^t (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)
25°	1.7548	70.64	7.008	8.565	604.9
30	1.7506	55.60	8.230	9.840	547.0
35	1.7471	46.73	9.592	11.75	545.0
40	1.7433	39.76	10.99	13.49	536.0
45	1.7396	32.46	12.54	15.44	501.0
50	1.7357	27.57	14.16	17.46	492.5
55	1.7318	23.64	15.85	19.58	463.0
60	1.7279	20.54	17.50	22.20	445.6
65	1.7240	17.87	19.26	23.11	427.4
70	1.7201	15.65	21.21	26.39	414.0

at 25°, 1.750 (1.7433) at 40°, and 1.735 (1.7279) at 60°. Extrapolation of the data of Knowlton and Mounce⁷ to the composition of the hemihydrate gives a value at 25° of 1.7657. The molar volume at 25° is 122.0 ml. which is 1.0 ml. less than the sum of the molar volumes of the components, *i.e.*, the apparent volume occupied by one mole of water when added to two moles of phosphoric acid is 17 rather than 18 ml.

The viscosity of phosphoric acid hemihydrate has not previously been reported. At 25° its value is only 40% of the viscosity of the parent acid but is still 79 times greater than that of water. Values in Table 1 can be fitted by an expression of the type $\eta = \eta_0 \exp(C_\eta/RT^2)$ as shown by the linear plot in the Figure. This implies⁸ that the activation energy of viscous flow is inversely proportional to the temperature in the range studied, the decrease at higher temperatures being related to the decreasing extent of hydrogen bonding. Representative values of the activation energy are presented in Table 2.

TABLE 2. Activation energies for phosphoric acid hemihydrate.

Temp.	E_κ (kcal. mole ⁻¹)	E_μ (kcal. mole ⁻¹)	E_η (kcal. mole ⁻¹)
25°	5.38	5.52	7.07
40	5.13	5.44	6.95
60	4.81	4.94	6.33

The electrical conductivity of phosphoric acid hemihydrate, unlike that of phosphoric acid itself, showed no variation with time and was accurately reproducible in two different cells and on different samples provided these were fractionally crystallized in a closed system attached directly to the conductivity cell. The values found lie between the two published figures for the conductivity; ^{5,9} these refer to 29.3° and are 8.26×10^{-2} and 7.938×10^{-2} compared with the present value of 8.051×10^{-2} ohm⁻¹ cm.⁻¹. At 35° Rabinowitsch⁵ found a value of 9.63×10^{-2} compared with the present 9.592×10^{-2} ohm⁻¹ cm.⁻¹. The Figure shows that the data in Table 1 conform to the relation $\kappa = \kappa_0 \exp(-C_\kappa/RT^2)$ and values of the activation energies at three temperatures are given in Table 2.

The conductivity of the solid is much lower than that of the fused compound and, near the m. p., it tended to drift for some time before equilibrium values were obtained. The results

³ Smith and Menzies, *J. Amer. Chem. Soc.*, 1909, **31**, 1183.

⁴ Ross and Jones, *ibid.*, 1925, **47**, 2165.

⁵ Rabinowitsch, *Z. anorg. Chem.*, 1923, **129**, 60.

⁶ Egan and Wakefield, *J. Phys. Chem.*, 1957, **61**, 1500.

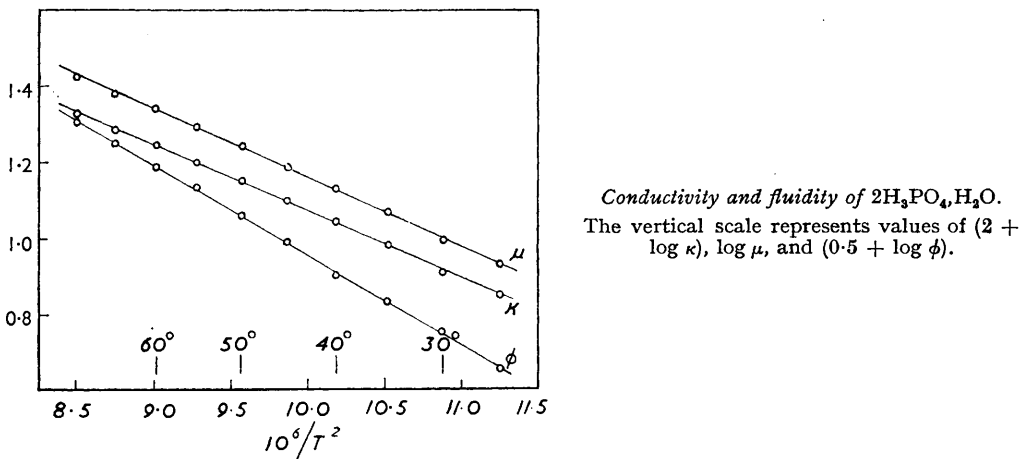
⁷ Knowlton and Mounce, *Ind. Eng. Chem.*, 1921, **13**, 1157.

⁸ Greenwood and Thompson, *J.*, 1959, 3474.

⁹ Smith and Menzies, *J. Amer. Chem. Soc.*, 1909, **31**, 1191.

confirm the premelting increase in conductivity implied by Rabinowitsch's work⁵ and typical values of $10^3\kappa$ ohm⁻¹ cm.⁻¹ (at t°) are 0.97 (19°), 1.22 (21°), 1.63 (23°), 2.36 (25°), and 3.12 (26°). At 25°, *i.e.*, 4.3° below the m. p., the conductivity of the solid was 30 times smaller than that of the supercooled liquid.

Electrolysis of the fused hemihydrate gave hydrogen at the cathode and oxygen at the anode as expected. Transport measurements on solutions of potassium dihydrogen phosphate in the hemihydrate were made by the method previously described.¹ No migration of potassium ion was detected, the entire current being carried by a switch mechanism involving the di-

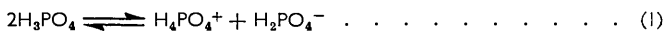


hydrogen phosphate ion. For example, the passage of 740 coulombs (41 mA for 5 hr.) through a 2.66×10^{-2} molar solution of potassium dihydrogen phosphate did not change the potassium ion concentration in any of the three compartments of the transport cell.

DISCUSSION

The transport measurements establish unambiguously that the dihydrogen phosphate ion has an anomalous mobility in the hemihydrate, as it has in the anhydrous acid, but the extent of self-ionization of the solvent cannot be determined without some knowledge of the absolute value of this mobility. It has been argued¹ that a value of 20×10^{-4} cm.² sec.⁻¹ volt⁻¹ should be reasonably close to the actual mobility. Substitution of this and the value of the specific conductivity at 25° into the expression $\kappa = nev$ gives the concentration, *n*, of dihydrogen phosphate ions as 2.20×10^{20} ions per ml. (0.21 molal). As the molar volume of the hemihydrate 2H₃PO₄.H₂O is 122.0 ml., 1 ml. contains 4.94×10^{21} "molecules" of solvent. Hence the degree of ionic dissociation is 4.5%.

The structure of phosphoric acid hemihydrate has not been determined and, although some incomplete X-ray data have been published,¹⁰ no structure for the compound has been suggested. Phosphoric acid itself undergoes ionic dissociation according to eqn. (1).



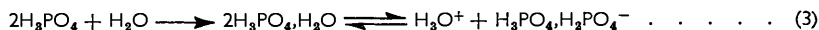
Addition of water to the system removes a proton from the phosphoric acidium cation thus forming a hydroxonium ion and liberating a molecule of phosphoric acid. When an equimolar quantity of water has been added the reaction can be represented as (2), although



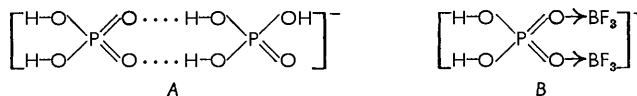
the monohydrate does not exist as a separate solid phase. When only a hemimolar quantity of water has been added, the liberated molecule of phosphoric acid can solvate

¹⁰ Smith, Brown, and Lehr, *J. Amer. Chem. Soc.*, 1955, **77**, 2728.

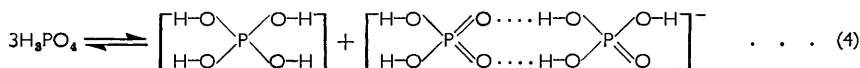
the dihydrogen phosphate ion as shown in (3), and this is the suggested mode of ionic dissociation of this compound.



The stability of the monohydrate thus arises from the ability of the phosphoric acid molecule to form hydrogen bonds to both the phosphoryl oxygen atoms of the dihydrogen phosphate ion, the structure of the anion being shown in *A*. Such a structure would



facilitate proton switches since a proton added to the free phosphoryl oxygen atom could, in effect, be liberated at the other end of the ion. The structure is similar to that postulated for the anion of the boron trifluoride complex of phosphoric acid, *B*, the removal of the hydrogen bridges effectively suppressing the proton-switch conduction mechanism in this compound.¹¹ It is probable that the dihydrogen phosphate ion is solvated in the anhydrous acid also and that the dissociation equilibrium (1) is more accurately represented by (4). The formation of a hemihydrate rather than a monohydrate in the system is thereby explained.



On the basis of eqn. (3) as the autoprotolysis equilibrium it can be seen that the formation of each anomalously conducting anion is accompanied by one hydroxonium ion. As the estimated concentration of the anion in the melt at 25° is 0.21 molal, the autoprotolysis constant is $K_{\text{ap}}(2\text{H}_3\text{PO}_4 \cdot \text{H}_2\text{O}) \simeq 4.4 \times 10^{-2} \text{ mole}^2 \text{ kg.}^{-2}$. This is slightly larger than the value obtained similarly for the parent acid,¹ $K_{\text{ap}}(\text{H}_3\text{PO}_4) \simeq 1.7 \times 10^{-2} \text{ mole}^2 \text{ kg.}^{-2}$.

The reduction in conductivity which occurs on addition of potassium dihydrogen phosphate to the molten hemihydrate may be due to the removal of phosphoric acid molecules from the conduction chains by solvation of the potassium ions. To test this hypothesis, other potassium salts were investigated in the range 0—0.2 molal. Potassium sulphate and dipotassium hydrogen phosphate both lowered the conductivity of the solvent, these salts being chosen because (*a*) they were anhydrous, (*b*) they contained twice as many potassium ions per ml. as potassium dihydrogen phosphate, and (*c*) their anions were similar in size and shape to the dihydrogen phosphate ion. Potassium perchlorate was insoluble. The rate of decrease of conductivity as a function of molality was the same for both salts and was more than twice as great as for potassium dihydrogen phosphate. The decrease per potassium ion is rather less for this solute because of the compensating effect of simultaneously adding the anomalously conducting dihydrogen phosphate ion. In fact, at concentrations below 0.03 molal there were indications that addition of potassium dihydrogen phosphate to the hemihydrate did not lower the conductivity of the system. There is clearly considerable scope for extensive cryoscopic and ion-transference experiments in this solvent; it can readily be obtained pure, melts at a convenient temperature, and, unlike phosphoric acid itself, has an accurately reproducible *m. p.* and conductivity, neither of which vary with time due to secondary equilibria.

We thank the University of Nottingham for a Research Scholarship (to A. T.).

THE UNIVERSITY, NOTTINGHAM.

[Received, June 10th, 1959.]

¹¹ Greenwood and Thompson, *J.*, 1959, 3493.