79.6 per cent. H_3PO_4 at 0°, when the pressure was found to be 0.636 mm. of mercury.

Conclusions.

1. The solubilities of phosphoric acid and its hydrates were measured with exactness from —16.3° to 42.30° (m. p. of H_3PO_4).
2. The melting point of Joly's hydrate (29.35° ± 0.01) and of orthophosphoric acid (42.30° ± 0.01) were redetermined.
3. A new hydrate, $10H_3PO_4.H_2O$, was discovered.
4. The vapor pressure of a saturated solution of Joly's hydrate at 24.99° ± 0.01 reached 0.85 mm.

[CONTRIBUTIONS FROM THE LABORATORIES OF GENERAL AND PHYSICAL CHEMISTRY OF THE UNIVERSITY OF CHICAGO.]

THE ELECTRICAL CONDUCTIVITY AND VISCOSITY OF CONCENTRATED SOLUTIONS OF ORTHOPHOSPHORIC ACID.

BY ALEXANDER SMITH AND ALAN W. C. MENZIES.

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With increasing concentrations of sulphuric acid, the specific electrical conductivity (at 18°) of an aqueous solution of the acid rises and at 30 per cent. a maximum is attained. As the concentration rises still further, the specific conductivity falls, reaching a minimum at 84 per cent. (the composition of the monohydrate, $H_2SO_4.H_2O$). Beyond this point the conductivity rises to 92 per cent. and finally falls rapidly as 100 per cent. is approached.[1] It will be noted that of the three hydrates revealed by a study of the freezing points of sulphuric acid,[2] namely, those with $4H_2O$, $2H_2O$, and H_2O, only one influences the conductivity. It seemed worth while to learn whether the specific conductivity of phosphoric acid solutions was similarly related to one or both of the hydrates. Kohlrausch and Holborn (p. 157) give the conductivity of phosphoric acid at 18° at concentrations from 10 to 87 per cent. At the time,[3] no measurements had been made beyond the latter concentration. The compositions of the hydrates lie in this unexplored region, namely, the semihydrate ($2H_3PO_4.H_2O$) at 91.58 per cent. and the decihydrate[4] ($10H_3PO_4.H_2O$) at 98.195 per cent.[4]

[1] Kohlrausch and Holborn, *Leitverm. d. Elektrolyte* (1898), p. 156.

[2] Meyerhoffer, *Physikalisch-Chemische Tabellen*, 567.

[3] This was in August, 1908. Phillips (*J. Chem. Soc. Lond.*, **95**, 64 (1909)) has since published a series from 1.4 per cent. to 100 per cent. at 0°. But his series includes only three observations within the region in question, namely, at 92.07, 93.52, and 100.03 per cent., respectively. These three measurements, although they reveal no irregularity in the curve, are not sufficient by themselves to demonstrate the absence of a maximum.

[4] Preceding paper. Smith and Menzies, THIS JOURNAL, **31**, 1186.

Electrical Conductivity of Phosphoric Acid Solutions.—We measured the conductivity at concentrations from 89.7 per cent. to 98.8 per cent. It was inadvisable to make the measurements at 18°, since the semihydrate may crystallize at any temperature below 29.35° (its melting point). We thought it best therefore to choose the temperature 29.30° ± 0.01. Although anhydrous phosphoric acid may crystallize from saturated solutions at temperatures between 29.3° and 42.30° (its melting point), yet it does not readily do so without inoculation. Hence no difficulty was expected, and none was encountered from this source.

The temperature was kept constant by means of the same bath, and was determined with the precautions described in the preceding paper. The Wheatstone's bridge was carefully calibrated and the measurements were made with all the precautions required for accuracy. The conductivity vessel was of U-form, with fixed electrodes. The vessel could be supported on the balance-pan, and the original, most concentrated acid contained in the vessel was diluted by adding successive small quantities of water. The increase in weight was obtained in each case by subtraction. Any dilution of the acid due to absorption of atmospheric moisture was thus taken into account, and the final concentration, determined by analysis, agreed with that calculated from the initial analysis within the limits of the experimental error. The resistance capacity of the vessel was determined by means of normal potassium chloride and saturated sodium chloride solutions. The conductivities assumed for these standardizing solutions were those given by Kohlrausch and Holborn (p. 204). The values found—with N KCl 25.415 (mean of 9 observations), with sat. NaCl 25.416 (mean of 5 observations)—were in excellent agreement.

In the following table, showing the results, the first column (Concn.) shows parts of H_3PO_4 in 100 parts of solution. The second column contains the specific conductivities, in which K = conductivity in 1/ohm, cm.:

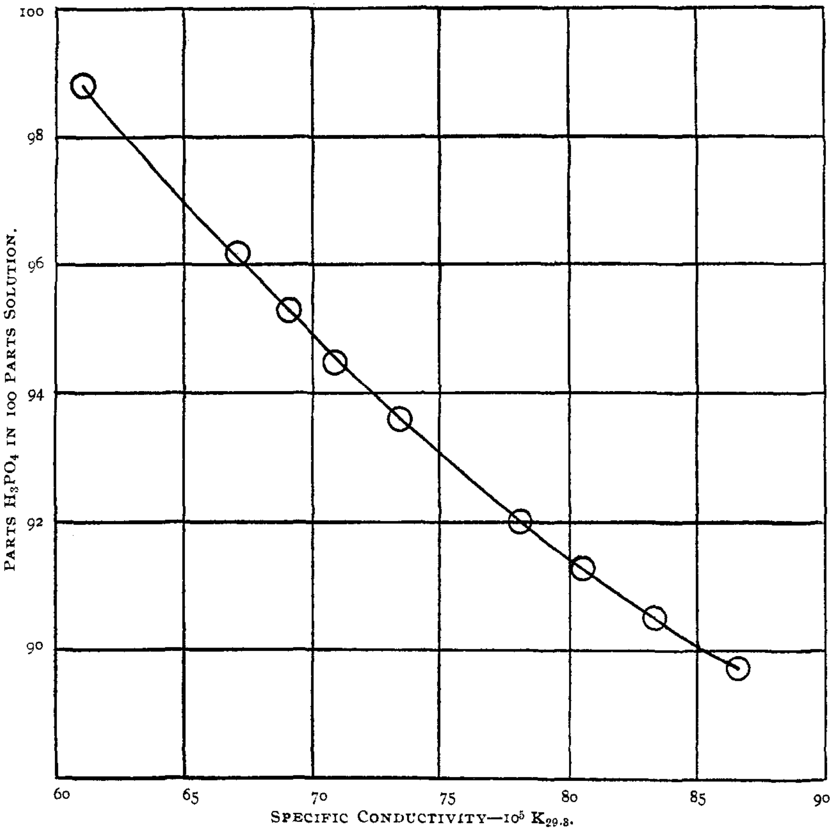
SPECIFIC CONDUCTIVITIES OF ORTHOPHOSPHORIC ACID AT 29.30° ± 0.01.

Concn., per cent. H_3PO_4.	$10^4 \times K_{29.3}$.	Concn., per cent. H_3PO_4.	$10^4 \times K_{29.3}$.
98.8	610.2	92.0	781.5
96.2	670.0	91.2	806.1
95.3	690.2	90.5	833.4
94.5	707.8	89.7	863.9
93.6	732.4		

The error in these measurements may be estimated as follows: The error in the conductivity measurements is less than 1 in 2000. The absolute error in measuring the concentration is less than 1 in 1000, and the relative error therefore much less. Since the conductivities vary, at most, 10 per cent. for one degree change in temperature, and the bath was constant ± 0.005, the relative error from this cause was less than 1 in 2,000. The actual temperature was determined as described in the preceding paper[1] and was accurate to ±0.01°. The error on this account was not more than 1 in 1000. It will be seen that the smallness of the relative error of the observations among themselves would render appreciable even a slight irregularity in the conductivity curve, if such existed.

When the curve given by these measurements is examined (Fig. 2), it will be seen that it shows not the slightest tendency to special flexure at the concentrations corresponding to the compositions of the hydrates. Orthophosphoric acid thus differs markedly from sulphuric acid in this respect.

Fig. 2.



Viscosity of Phosphoric Acid Solutions.—It has been shown by Graham[2] and by many later observers, that the viscosities of

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[1] THIS JOURNAL, **31**, 1185.

[2] *Ann.*, **123**, 90.

mixtures of acids and other substances with water frequently show very pronounced maxima. A single maximum was found by Graham in sulphuric acid (20°) near to the composition $H_2SO_4.H_2O$. The relative viscosities of solutions of phosphoric acid of concentrations from 90.6 and 98.1 per cent. were determined at 25° ± 0.01 with an Ostwald viscosimeter. The measurements were not made with the same accuracy as were those of the conductivity, and the data are therefore omitted here. It is sufficient to say that, when time of outflow was plotted against concentration, the very slight irregularities in the curve were within the experimental error, and no marked flexure occurs within the range of concentrations examined.

THE SIZE OF THE PORES IN PORCELAIN AND OSMOTIC EFFECTS.

BY S. LAWRENCE BIGELOW AND F. E. BARTELL.

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Several methods have been tried in this laboratory to obtain experimental facts bearing upon the question whether or not a membrane, with which osmotic phenomena may be obtained, is or is not a network of capillaries. This article contains the results secured by one of these methods.

In a previous article by one of us[1] it was shown that water passes through collodion, goldbeater's skin, parchment paper and unglazed porcelain membranes at rates conforming to the known formulations for the flow of water through capillary tubes. This was considered as strong, though not conclusive, evidence that these membranes consist of networks of capillaries. It was not possible to estimate the probable diameters of these capillaries, for Poiseuille's formula contains, as one term, the length of the tube. The capillaries in these membranes cannot be considered as perpendicular to the surfaces and so the thickness of the membrane cannot be taken as their length. But Jurin's law furnishes a method for calculating the diameters of such tubes which is independent of their lengths. $a^2 = hr$, where r is the radius of the tube, h is the height to which the liquid ascends due to capillarity, and a^2 is one of the so-called capillary constants. For water at 19°, $a^2 = 14.846$ mm. We may then calculate the radius of a tube if we know the height to which water ascends in it, from the formula, $hr = 14.846$ mm. Furthermore, if water fills a short length of capillary, it will require the hydrostatic pressure of a column of water equal to the height to which water would ascend in such a capillary, to force it out. By measuring the pressure required to force the water out of a membrane saturated with water we can then estimate the radius or diameter of the pores in that membrane.

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[1] THIS JOURNAL, 29, 1675 (1907).