VIII.—*The Electrical Conductivity of Phosphoric Acid.*

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UNTIL the recent work of Jones, Getman, and Bassett, the only information as to the conductivity of ortho-phosphoric acid was to be found in the few determinations of Arrhenius and the first work of Kohlrausch, who made conductivity measurements of nine strengths of acid at 18°.

In these measurements, no particulars are given as to the method of preparing the acid, except that Jones and Getman state (*Zeitsch. physikal. Chem.*, 1904, **46**, 244) that they obtained it in a "well-crystallised condition" and that the lower concentrations were obtained from the "standardised mother-solution by dilution."

In the present work, the following was the method used to prepare the pure acid. Phosphorus trichloride twice redistilled was mixed very slowly with specially purified water, the flat porcelain dish in which the addition was made being floated on cold water during the operation. It was found that, if the addition was made too rapidly, a discoloration was produced, which at the end of the preparation was seen to be due to a fine powder suspended in the liquid. The phosphorous acid was then heated until it gave no precipitate with silver nitrate. It was then oxidised by cautious addition of pure dilute nitric acid, when an active effervescence ensued. Nitric acid was eventually added in slight excess, and evaporation continued until all this was expelled.

The acid thus prepared was a transparent, colourless substance. Analysis showed the absence of iron, arsenic, lead, cadmium, sulphuric, nitric and hydrochloric acids. Gravimetric analysis showed concordance with the percentage indicated by its specific gravity. The 100 per cent. acid did not crystallise, even on cooling to 0°, but one specimen of 43·26 per cent., after some time, began to crystallise, and on adding a portion of this solution containing crystals to the other high percentage samples, crystals were obtained. These crystals were small and apparently soft, almost gelatinous. They disappeared on gentle heating, and on no other occasion were they formed spontaneously. The 100 per cent. acid does not affect litmus paper, and is without action on sodium carbonate.

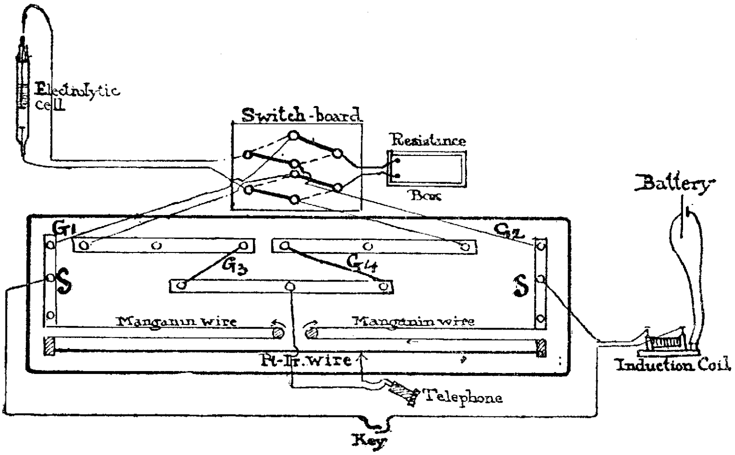
Analysis.—To analyse the acid, the lead oxide gravimetric method used by Watts (*Chem. News*, 1865, **12**, 160) in his density determinations was adopted. Pure lead oxide was prepared from lead nitrate thrice recrystallised, and when thus prepared and protected from organic matter, it could safely be heated in a platinum crucible. The operation consisted in merely adding to a weighed quantity of oxide a weighed quantity of the phosphoric acid solution, and heating until all the water was expelled. It was found difficult at first to obtain successive concordant weighings, but this was found to be due to the method of weighing, the platinum crucible being placed on the bare pan. Two pairs of light blown glass bottles with ground hollow stoppers and without necks were made for the platinum crucibles, so as just to accommodate them, one of each pair being used as a counterpoise, and the other containing the crucible. By this means the glass surface presented on both pans of the balance was equal, and the weighings became concordant.

The pyknometer employed was the bottle-shape, with thermometer stopper and side capillary tube with cap. Sprengel's shape was tried, but the viscosity of the higher strengths of the phosphoric acid made it impracticable in use. To make a specific gravity determination, the acid was run out of the cell into the bottle, which was then transferred to a thermostat with a revolving vane.

The Water.—The water used throughout the experiments was distilled by a modification, devised by Manley, of the apparatus described by Jones andMackay (*Zeitsch. physikal. Chem.*, 1897, **22**, 237). Ordinary tap-water is boiled in a conical copper flask, and the steam passed through a second flask, which contains acid permanganate. This flask is also heated by a small flame. The steam then passes into a third flask, which contains acid permanganate, and on leaving this, the steam is condensed in a block-tin condenser. There is also a trap which prevents regurgitation.

The Bridge.—The bridge employed was made expressly by the author for the work. Profiting by the experience of Veley and Manley (*Phil. Trans.*, 1898, **191**, *A*, 365) in their measurements of the conductivity of nitric acid, a bridge was made in some respects similar to the one used by them, but instead of the bridge wire being two metres in length, only half a metre of specially drawn platino-iridium wire is used. The whole metre did not seem necessary, as the resistances are always arranged so as to bring the slider contact near the middle of the bridge, and additional delicacy is secured by adding to the main wire at each end a thin wire of manganin alloy mounted parallel to the main wire, which, on each side starting from the same brass clamp as the main wire, is continued to the middle of the bridge; there it makes a turn on a fixed ebonite drum, and returns to a brass clamp similar to the one used for the platino-iridium wire, and mounted on the same slab of ebonite, but air-insulated from it. This is connected with the first copper strap at each end by a short piece of copper wire. The bridge-end resistance is therefore due to the combined effects of the contacts of the brass clamps, the brass clamps themselves, the thin manganin wires and their contacts, together with the short pieces of connecting wires to the first copper straps. This

FIG. 1.



has the result of making the effective wire-length greater for the relation:

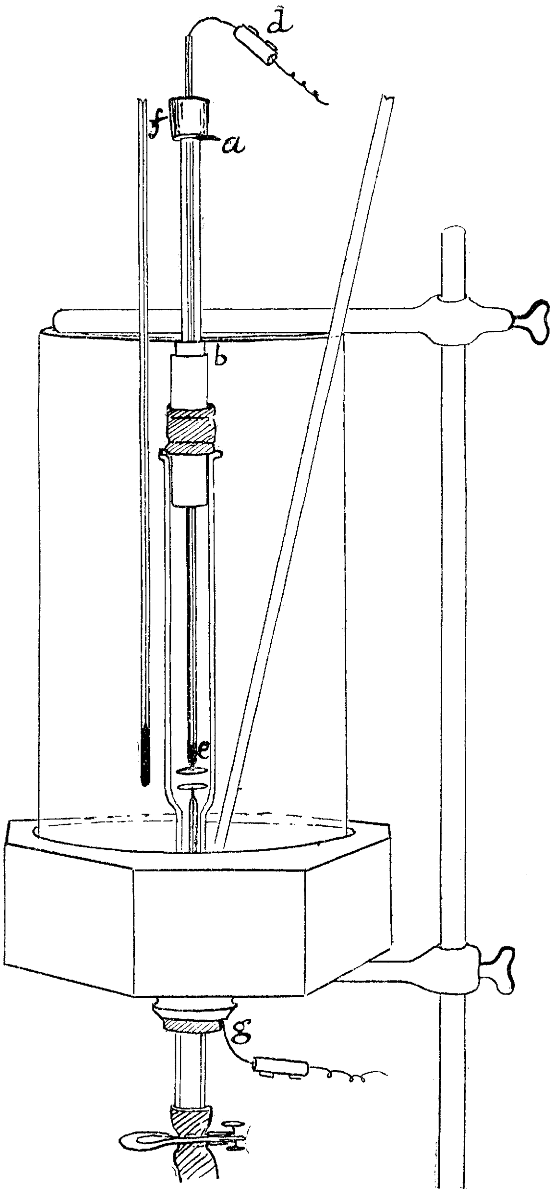
$$\frac{P}{Q}=\frac{1+(x_1-x_2)}{1-(x_1-x_2)},$$

where 1 is the effective length of the bridge wire.

The copper straps S, S (Fig. 1) are 12 mm. square in section, and are supported by being set at each end in a groove cut in a plate of ebonite 12 mm. thick, set on its side, this ebonite plate in turn being supported at each of its ends by slotted boxwood supports. Pieces of waxed paper just under each end prevent the ebonite from actually touching the board. Extremely satisfactory insulation is thus secured. Binding screws are soldered to the copper straps. The arrangement of these can be seen by referring to Fig. 1.

The slider and tapper combined is a simple rocker. Underneath two parallel lengths of brass tube, which are soldered to the heartshaped end pieces, are two boxwood cones, also fastened to the end pieces with a wide slot in them, and these slots enable the slider to be drawn by the cord passing round the hand wheel at one end, along the plain glass tube fixed to the wooden base and parallel to the half metre scale. An ebonite arm carrying a brass binding screw, on to the underside of which is soldered a small piece of platinum wire, constitutes the tapping arrangement, and a small cord brings the tapper on to the wire by moving it through the very small arc through which it "rocks," by means of a lever at one end of the cord which also serves to keep the contact. When this cord is released, the weight of the slider "rocks" it back, and contact is broken, whilst the projecting brass piece then lies flat on the scale. This brass flap is pierced by a small mica window, which has a line scratched across its centre underneath,

FIG. 2.



so that through the hole the position of the slider on the scale can be easily read from the position of the scratched line in relation to the lines of the scale. The thin wire from the binding screw of the slider is connected with the middle of the bridge, and in this circuit the telephone is placed. The platino-iridium wire was carefully calibrated and found to be uniform, and to have a mean resistance of 0·0001455 ohm per mm.

The total resistance of the main wire, the manganin wire, and all connexions was calculated by Carey Foster's method, and found to be 0·5546 ohm. This, in terms of the platinum-iridium wire, made an effective length of $\frac{0{\cdot}5546}{0{\cdot}0001455} = 3812$ mm., so that the bridge was equivalent in delicacy to one of 3·8 metres in length, without the difficulties attending the stretching of such a length of wire.

This can best be realised by the alteration in the usual formula for the ordinary metre bridge: $\frac{P}{Q} = \frac{1000 + (x_1 - x_2)}{1000 - (x_1 - x_2)}$, the formula for the present bridge being $\frac{P}{Q} = \frac{3812 + (x_1 - x_2)}{3812 - (x_1 - x_2)}$.

The Electrolytic Cell.—Two forms were tried, but the U-form was relinquished in favour of the straight one, shown in position in the bath (Fig. 2). This has one fixed and one movable electrode. The platinum wire from the fixed electrode, which is made of stout platinum sheet, passes downwards and is fused through the glass, and thence through the cork, *g*, by the side of the glass tube used for emptying the cell, to the binding screw. The wire from the movable electrode is fused into a tube closed at its lower end and containing a little mercury. The connecting wire, amalgamated at its lower end, passed in at the top of this tube, where the binding screw *d* is seen, and dips into the mercury at *e*. This tube works smoothly in a slightly larger one, *ab*, fixed at *b*. When the inner tube is lifted up, a steel rod is inserted between the upper end of the fixed outer tube and a brass disk, seen edgewise at *a* and fastened to the cork *f*, which serves as a handle for raising the electrode. In the illustration, the electrodes are in the closed position. The length of the steel rod is therefore equivalent to the mean distance between the electrodes.

After calibration, the electrodes were coated with platinum-black by the electrolysis of platinum tetrachloride as recommended by Kohlrausch.

The results obtained are collected in the table on page 64.

Percentage concentration.	Equivalents per litre.	Specific resistance.	$K_0^0 \times 10^4$. Specific conductivity.	Molecular conductivity.	Dissociation values.
1·4	0·43	71·435	140·0	97·50	40·63
2·87	0·89	39·484	253·3	85·20	35·50
5·28	1·66	23·553	424·5	76·60	31·92
16·09	5·37	12·401	806·4	44·91	18·71
22·60	7·96	9·978	1002·2	38·32	15·97
30·71	11·20	7·803	1281·6	34·43	14·35
33·75	12·53	7·266	1376·3	32·94	13·72
36·08	13·58	6·938	1441·3	31·83	13·26
38·49	14·71	6·853	1459·2	29·77	12·40
43·26	17·03	6·704	1491·6	26·28	10·95
48·90	19·91	6·921	1444·9	21·77	9·07
52·83	22·06	7·272	1375·0	18·70	7·79
53·22	22·27	7·391	1353·1	18·23	7·60
65·72	29·92	9·779	1022·6	10·30	4·29
71·29	33·76	12·697	787·6	7·00	2·92
74·99	36·45	16·430	607·6	4·99	2·08
79·21	39·69	21·366	468·0	3·54	1·48
82·22	42·08	24·670	405·5	2·89	1·20
92·07	50·42	45·388	220·3	1·31	0·55
93·52	51·73	57·518	173·9	1·01	0·42
100·03	57·69	71·134	140·6	0·73	0·30

In Fig. 3 are shown the curves for the conductivities of various acids as compared with phosphoric acid.

Summary of Conclusions.

1. Pure phosphoric acid is obtained by hydrating re-distilled phosphorus trichloride slowly, keeping the temperature of the reaction low, heating to expel hydrochloric acid, and oxidising with pure dilute nitric acid.

2. The most trustworthy means of analysis of phosphoric acid are:
   a. by the usual magnesium method, which is capable of great accuracy.
   b. by heating the solution with pure lead monoxide in a platinum crucible until all the water has been expelled.

3. A very accurate form of Wheatstone bridge can be made by an air-line of platinum-iridium wire of half a metre in length, the "bridge-ends" being lengthened by a subsidiary wire of manganin alloy running parallel to the main wire to the middle of the bridge and back again. The slider is most convenient when mounted to run between the scale and the wire, and capable of rocking through a small arc from scale to wire.

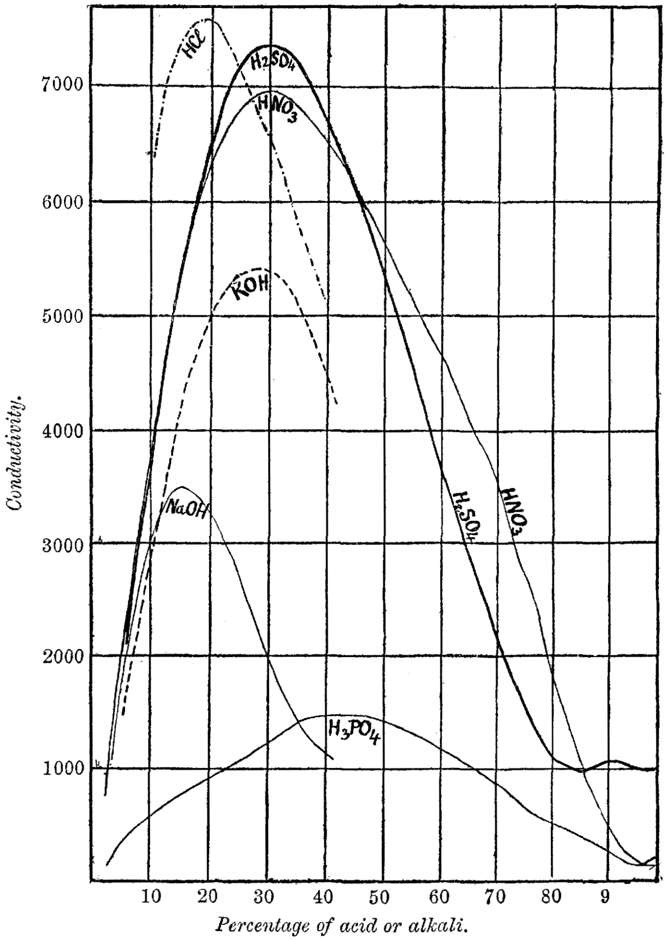
4. The conductivity measurements seem to bear out the theory of indicators regarding the ionisation of the hydrogen atoms in the molecule of phosphoric acid.

5. The conductivity of phosphoric acid increases with the concentration from 1·4 per cent. to about 38 per cent.; thence to 44 per cent.

it increases more slowly; it then decreases slowly to about 50 per cent., after which the decrease is as rapid as the former rise.

The author gratefully acknowledges the help continually received

FIG. 3.



Conductivities of common mineral acids and alkalis compared.

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