CCCXLI.—*The Electrical Conductivity of Phosphorus Pentachloride.*

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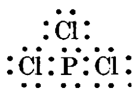
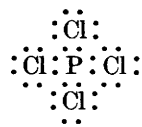
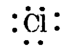
About 2 years ago, one of us (G. W. F. H., *Chem. and Ind.*, 1923, 348) suggested that when phosphorus trichloride (I) combines with chlorine it is probable that the ions (II) and (III) are produced.


(I.)


(II.)


(III.)

In this connexion, using a cell with a constant of about 0·6 and applying an *E.M.F.* of 6 volts, we found that a saturated solution of phosphorus pentachloride in nitrobenzene gave a current of 0·009 amp., a 1·5% solution of hydrogen chloride in nitrobenzene gave 0·0007 amp., phosphorus trichloride introduced into nitrobenzene with no special precautions to exclude moisture gave a just perceptible current, whilst the following gave no current: (1) nitrobenzene; (2) solutions of phosphorus pentachloride in (*a*) ethylene dibromide, (*b*) benzene, (*c*) phosphorus trichloride; (3) hydrogen chloride in ethylene dibromide; (4) hydrogen chloride in phosphorus trichloride.

Plotnikov (*Z. physikal. Chem.*, 1907, **48**, 220) observed that phosphorus pentabromide dissolved in bromine conducted the current, but he states (*Chem. and Ind.*, 1923, 750) that phosphorus is formed at the cathode and combines with the bromine to form pentabromide.

We propose to examine the nature of the ions formed in the case of the pentachloride, and to examine the solution of this substance in nitrobenzene in other respects, and desire to reserve this field of investigation for the present.

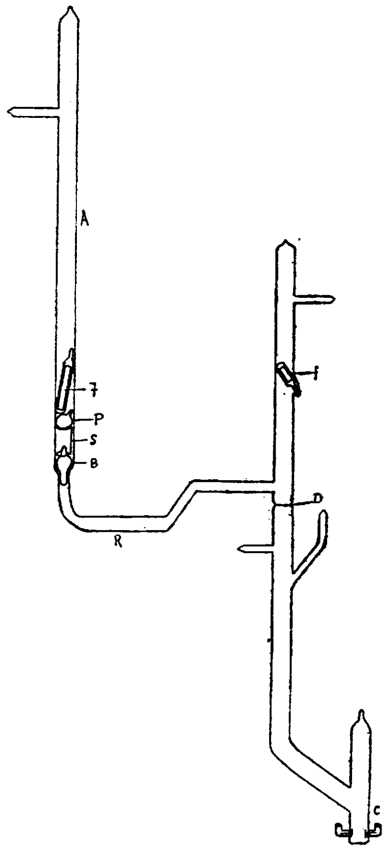
Experimental.

The chlorides of phosphorus were prepared in the following manner. Yellow phosphorus was melted in a stout tube, and water which rose to the surface was removed with filter-paper. The phosphorus was sucked up into a glass syringe, where it was allowed to solidify. The narrow nozzle of the syringe was passed through a rubber stopper into a tube from which dry nitrogen was issuing. Into this tube the phosphorus was discharged. From this tube the phosphorus was distilled in dry atmospheric nitrogen into a receiver. From the latter the phosphorus was run into a second tube, which was then sealed off from the receiver, and from which the phosphorus was again distilled in dry atmospheric nitrogen and collected in bulbs holding 0·5 to 5 g. of phosphorus. These bulbs were then sealed off, cleaned, and introduced into the tube A (see Fig.). The latter was sealed off, filled with dry nitrogen, and the bulb was broken with the help of a magnet acting on F.

Chlorine, prepared from dichromate and hydrochloric acid through which hydrogen chloride had been passed to expel air, was washed and dried and passed over the phosphorus in such quantity as to form the trichloride or the pentachloride. In the latter case, excess chlorine was expelled by dry nitrogen. The inlet and outlet tubes were then sealed, and the cell below the diaphragm was filled with nitrogen and sealed.

For solutions of phosphorus pentachloride in nitrobenzene, the latter was introduced into the cell before sealing. Communication between the tube A and the cell was then made by breaking the diaphragm.

FIG. 1.



P, bulb of phosphorus; F, iron rod sealed up in glass tube; S, frail glass support; B, bulb with spiked top; D, diaphragm; C, conductivity cell; R, reaction chamber; f, similar to F.

The phosphorus had a great tendency to remain liquid after being sealed up in the bulbs, remaining liquid in one bulb for more than 6 months.

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