(300°–403°; 35–935 mm.), NH_4I (310°–410°; 48–857 mm.), NH_4Cl (250°–350°; 50–1063 mm.), $N(CH_3)_4Cl$ (190°–233.3°; 120–760 mm.), $N(CH_3)_4I$ (240°–307°; 81–799 mm.), PH_4I (19.2–65.7°; 50–900 mm.), PCl_5(90–167°; 18–919 mm.).

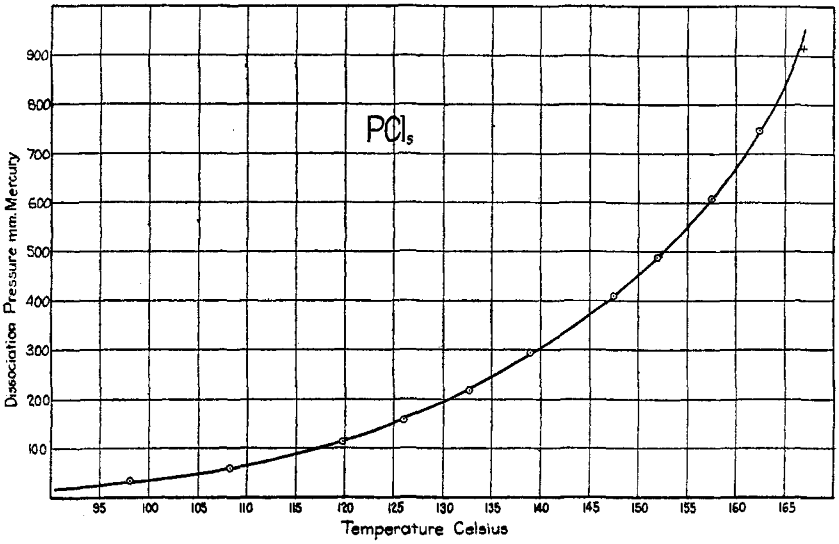

Fig. 7.

2. The measurements on PCl_5 were made with the dynamic isoteniscope; all the others with the static isoteniscope, by means of which the pressure may be determined to ±0.1 mm. A platinum resistance thermometer sensitive to ±0.1° was used.

3. The temperatures at which the various compounds were found to have a dissociation pressure of 760 mm. are: NH_4Br (394.6°), NH_4I (404.9°), NH_4Cl (337.8°), $N(CH_3)_4I$ (305.5°) PH_4I (62.6°), and PCl_5 (162.8°).

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POSITIVE IONS FROM NON-METALLIC ELEMENTS. I. A STUDY OF THE PRECIPITATION OF METALS FROM SOLUTIONS OF THEIR SALTS BY YELLOW PHOSPHORUS.

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Introduction.

It has long been known that yellow phosphorus will precipitate certain metals (Pt, Au, Ag, Hg, Cu) from a solution of the salts of these metals. Berzelius made use of the fact that silver is completely precipitated from its salts by phosphorus to determine the combining weight of phosphorus.[1]

In 1836, Vogel stated that when phosphorus acts on a solution of copper sulfate, there is formed sulfuric acid, phosphoric acid, and phosphide of copper only.[2]

Straub (1903) made a study of this reaction, and found that, in all cases studied by him, phosphoric acid, sulfuric acid, phosphide of copper, and metallic copper were formed. He determined the ratio of the sulfuric acid to the phosphorus in the solution as phosphoric acid at the end of the reaction and found it in several experiments to be as follows: 8.2, 7.6, 7.9, 6.4, 7.4, 7.5 and 8.0; to 1.

From this he concluded that one atom of phosphorus displaces two atoms of copper from solution. (The figures are, however, far nearer to 2.5 Cu to 1 P.) He tried to find a ratio between the copper sulfate and the total phosphorus (*i. e.*, the phosphorus in solution and that combined as phosphide of copper), but his results were so very irregular that he concluded the reaction must proceed by steps, and that no equation could be written to express it.[3]

Christomas,[4] Tauchert,[5] Corne,[6] Granger,[7] and others worked on this or similar reactions of phosphorus. Though all of these workers proposed equations that seemed probable, none were in very close accord with the experimental data. Nor did any of them, so far as we can find, propose any explanation of the mechanism of the reaction.

The Problem.—In spite of the fact that phosphorus is looked upon as a typical non-metallic element, the precipitation of certain metals by it in apparently the same way in which one metal is precipitated by another metal higher in the "potential series" seemed worthy of careful work to determine if the phosphorus reaction is ionic or not. The analogy to such a reaction as zinc displacing copper under similar conditions is very striking. Such reactions are probably always ionic. Apparent exceptions, such as the reduction of ammoniacal solutions of silver by aldehydes, are almost certainly electrolytic also.[8]

Choice of the Metallic Salt.—While silver is precipitated quantitatively, its use is objectionable because of the fact that the only practical salt to use is the nitrate, and nitric acid, even when dilute, will appreciably act on yellow phosphorus. The chlorides of copper and mercury were tried and rejected, because in both cases the "ous" salts are formed and afterwards

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[1] Berzelius, *Gilbert's Ann.*, **53**, 433; *Pogg. Ann.*, **8**, 17.

[2] Vogel, *J. prakt. Chem.*, **8**, 109.

[3] Straub, *Z. anorg. Chem.*, **35**, 460 (1903).

[4] Christomas, *Z. anorg. Chem.*, **41**, 307 (1904).

[5] Tauchert, *Ibid.*, **79**, 350 (1912).

[6] Corne, *J. Pharm. Chim.*, **6**, 323.

[7] Granger, *Compt. rend.*, **122**, 1484 (1897).

[8] Compare Stieglitz, "Analytical Chemistry" (theoretical part), Vol. 1, p. 3.

decomposed. This introduced an unnecessary complication. Sulfuric acid, even when of 5 *N* strength and boiling hot, did not appreciably act on phosphorus; so that all things being considered, copper sulfate seemed the best salt with which to work.[1]

Plan of the Work.—The plan of the work was:

(*a*) To make a complete analysis of solutions after sticks of yellow phosphorus had been left in them for a sufficient time.

(*b*) To determine the equation which represents the reaction, if possible.

(*c*) To make a study of the probable mechanism of the reaction by physical-chemical methods.

Experimental.

Qualitative Results.—1. About 200 cc. of 0.5 *N* copper sulfate was placed in a glass-stoppered Erlenmeyer flask and several small sticks of clean yellow phosphorus were dropped into it. After about a week, the *solution* was analyzed and found to contain:

Copper	None
Phosphoric acid	In large amount
Phosphorous acid	Appreciable
Hypophosphorous acid	Doubtful
Sulfuric acid	In large amount

The *precipitate* was found to be:

(*a*) Chiefly a bright, clean tube of metallic copper surrounding the stick of phosphorus.

(*b*) A thin inside coating of black phosphide of copper, next to the phosphorus.

Many experiments were carried out to determine the effect on the reaction of varying the concentration of the copper sulfate solution, and also the effect of the sulfuric acid formed during the reaction. Greater and less concentrations of acid were studied in order to magnify its effects. The following partial summary of these experiments indicates all the kinds of results which were obtained:

PARTIAL SUMMARY OF QUALITATIVE EXPERIMENTS.

2.	Copper-sulfate, 0.5 *N*, equal vol. conc. H_2SO_4	(At once and after 24 hrs.)	Film copper-phosphide, trace H_3PO_4
3.	Copper-sulfate, diluted H_2SO_4		Same as 2
4.	Copper-sulfate, further dilutions of acid	(After 60 hrs.)	Copper-phosphide, phosphoric acid, trace Cu-salt in sol.
5.	Copper-sulfate, sulfuric acid stronger than *N*		Metallic copper, splotches of phosphide, H_3PO_4, etc.

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[1] In one experiment phosphorus was permitted to remain in equivalent strengths of copper sulfate and sulfuric acid for about five months without a detectable quantity of phosphorus dissolving in the sulfuric acid, and without any further solution of the phosphorus in the copper sulfate than corresponds to the reactions here given.

6. **Copper-sulfate, 0.5 N, equal vol. acid, N to 0.25 N**	(After 24 hrs.)	**Metallic copper only, H_3PO_4, etc. (same as 1)**
7. Copper-sulfate, acid considerably under 0.25 N	(After 24 hrs.)	Copper, spots of phosphide, H_3PO_4, etc.
8. Copper-sulfate, acid, very dilute	(After 24 hrs.)	Copper-phosphide, little copper, H_3PO_4, etc.
9. **Copper sulfate only, 0.5 N and other moderate dilute sols.**		**Metallic copper only (at first), H_3PO_4, etc. (same as 1)**
10. Copper-sulfate, very dilute sols.		Copper, more or less phosphide, H_3PO_4, etc.
11. **Precip. copper, bright and clean, in distilled water or original sol.**		**Layer of phosphide next to phosphorus increasing with time until no copper remains. No further sol. of P in H_2O**
12. Copper-sulfate, 0.5 N, equal vol. 2.5 N NH_3 sol.	(After 24 hrs.)	Dead black coating, no copper seen. No Cu-salt left in sol.

Quantitative Results. The Determination of the Acids of Phosphorus.—The phosphoric acid was determined as magnesium pyrophosphate. In all cases 10 cc. samples were used. Separate samples were oxidized very thoroughly with hydrogen peroxide and then the phosphoric acid determined as before. The results agreed closely and averaged:

$Mg_2P_2O_7$ before oxidizing.	$Mg_2P_2O_7$ after oxidizing.
0.1106 g.	0.1198 g.
0.4968 milli-mols.	0.5382 milli-mols.

Hence the number of gram atoms of *lower* acids of phosphorus in 10 cc. is $(0.5382 - 0.4968) = 0.0414 \times 2 \times 10^{-3}$. That is, 0.0828 milli-mols of lower acids in each 10 cc. of the solution.

In other samples, after the sulfuric acid had been precipitated as barium sulfate, the clear filtrates were treated with an excess of mercuric chloride to determine the quantity of lower acids of phosphorus. The precipitated calomel weighed 0.0315 g. If we assume the lower acid of phosphorus to be *phosphorous* acid, this corresponds to 0.0669 milli-mols; if, however, we assume the reducing acid to be *hypophosphorous* acid it corresponds to only half as many mols.[1]

A fresh sample, treated with an excess of common salt and mercuric chloride, gave 0.0370 g. of calomel. This corresponds to 0.0783 milli-mols of reducing phosphorous acid.

If we assume that *only* phosphoric acid is formed, we should have enough total acid (sulfuric and phosphoric) in 10 cc. of the solution to neutralize 60 c. of 0.1 N alkali when using methyl-orange as indicator, and 70 cc.

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[1] It is certain that some of the reducing acid was oxidized during the time of precipitating and filtering the barium sulfate.

when using phenolphthalein as indicator. The difference should be 10 cc. and corresponds to one-third of the phosphoric acid present. (This is calculated on the basis of the analysis previously given.)

Three separate samples were titrated with accurately standardized NaOH solution. The results were the same in all to within 0.1 cc. and averaged as follows: with phenolphthalein, 69.5 cc. and with methyl-orange, 58.5 cc. That is, the difference between the titration figures using phenolphthalein as indicator and those using methyl-orange as indicator is 11 cc. whereas we should theoretically expect 10 cc. While this method is far from an exact one, it indicates that about 10% of the total acids of phosphorus present were other than phosphoric. This is in rough agreement with the results found by the calomel method.

The Determination of Sulfuric Acid.—A determination of the sulfuric acid (as barium sulfate) showed that the SO_4 content had not changed; *i. e.*, the sulfuric acid had not been reduced.

The original solution contained 2.5 milli-atoms of copper in 10 cc.; hence, we have very nearly 5 atoms of copper displaced by 2 atoms of phosphorus.[1]

The Formation of Copper Phosphide.—Some of the sticks of phosphorus that were completely covered by a bright coating of metallic copper were removed from the solution and placed in a jar of distilled water. In a few weeks the copper had entirely disappeared and there remained nothing but a mass of phosphide of copper and phosphorus. This convinced us that *the formation of the phosphide of copper is a secondary reaction taking place between the metallic copper and phosphorus*, and not between the sulfate of copper and phosphorus, as was thought by Straub, Tauchert and others.

Probable Reactions.—The quantitative results show that the atomic ratios involved are, in round numbers, 5 of copper to 2 of phosphorus. The simplest equation that will represent this fact is,

$$5\ CuSO_4 + 2P + 8H_2O = 5Cu + 5H_2SO_4 + 2H_3PO_4.^{2}$$

The reaction given above is undoubtedly the essential reaction involved, but this does not tell anything of the nature of the reaction or the role played by phosphorus in it.

The Origin of the Lower Phosphorus Acids.—It is known that yellow phosphorus will reduce phosphoric acid, partly, to phosphorous and hypophosphorous acids. This we believe to be the way in which the *-ous* acids

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[1] $2.5/2(0.4968) = 5/2$.

[2] The ratio of the phosphorus to the sulfuric acid involved in the above reaction is 1 to 7.9. This is about the same as Straub found, but he was so sure that a phosphide was first formed that he interpreted his figures to give *two* atoms of copper to *one* of phosphorus, instead of the far more accurate value of *five* atoms of copper to *two* of phosphorus. The reaction as we have deduced it is given by Tauchert as being one of several reactions that take place more or less simultaneously. He, too, believed that a phosphide of copper was directly formed from the sulfate.

in the analyzed solutions originated. For, if this be correct we should expect to find *less* phosphoric acid than is indicated by the given reaction and *more* total phosphorus in solution than is thus indicated. This is in accord with the figures given on page 1385 and the fact that the quantity of lower acids increases with time. On the whole, the origin of the phosphorous acid is not of very great importance for our investigation.

Physical Chemical Data.

1. It was observed that the metallic copper was formed only on the *surface of the phosphorus, or on the surface of a conductor connected with the stick of phosphorus.* That is, the phosphorus and any *conductor* connected with it becomes *plated* with copper, just as would be the case if iron or zinc were used in place of the phosphorus. In no case did metallic copper form on the surface of the glass beaker or any other *non-conductor* connected with the phosphorus. A piece of platinum wire wrapped around a stick of phosphorus, and extending upwards in the solution, becomes well plated with copper for a distance of several centimeters above the phosphorus.

2. Two side-neck test tubes were joined by means of a piece of rubber tubing; in one was put about 5 cc. of 0.5 *N* copper sulfate and in the other an equal quantity of 0.5 *N* silver nitrate. A piece of phosphorus was put into the *silver nitrate* and joined by means of a platinum wire to the copper sulfate solution. (See Fig. 1.) Both tubes were then filled with magnesium sulfate solution. The wire in the copper sulfate soon became coated with copper, and in about two weeks all copper and silver had been thrown out of solution. A control experiment, in which the platinum wire was used without phosphorus showed no reaction.

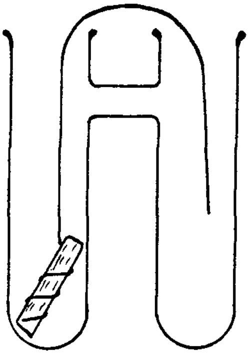

Fig. 1

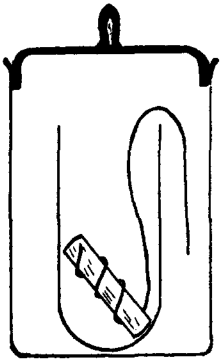

Fig. 2

Similar experiments were performed using a porous alundum cylinder in a glass-stoppered weighing flask. (Fig. 2.) The results were identical with those obtained in the above described experiment, except that the action was much more rapid. A control experiment without the phosphorus gave no precipitate of metal.

These facts and the analytical data strongly indicate an electrolytic displacement. The phenomena cannot be explained on the theory of a concentration cell, because of the negative results from the control experiments, and also because of the fact that when a platinum wire is wrapped closely around the phosphorus and does not extend out into the solution, both wire and phosphorus become heavily plated with metal.

Explanation of the Phosphorus-Copper Cell.—The qualitative experiments discussed above convinced us that phosphorus and copper really do form a true cell, just as any two metals do. This seems improbable at the first glance because of the position of the two elements in the published "potential series," and of the supposed non-existence of positively charged phosphorus ions. However, we adopted the following as a working hypothesis:

(*a*) The phosphorus goes into solution to an infinitesimal extent as P^{+++++} ions, thus leaving the stick of phosphorus charged negatively. Owing to the exceedingly small solution pressure of phosphorus, the number of such ions would be small relatively to the ions formed in the case of ordinary metals, the latter even being very small.

(*b*) These positively charged phosphorus ions react with the relatively abundant hydroxyl ions (of the water) to form phosphoric acid almost completely. This caused the concentration of the positively charged phosphorus ions to be exceedingly small, *but not zero.*

(*c*) If the negative charge on the stick of phosphorus is neutralized (say, by the Cu^{++} ion), then more phosphorus must go into solution in the effort to re-establish equilibrium. This, in turn, will react with the hydroxyl ions present to form more phosphoric acid and water. This would continue until one of the reacting substances became exhausted, or until the concentration of the hydroxyl ions becomes small in comparison with their usual concentration in water. This would be the case in very strongly acid solution, and this may be the explanation of the fact that phosphorus did not precipitate copper appreciably in very strongly acid solution.

The electromotive force of the phosphorus-copper cell is given by the formula,

$$E = 0.0577\ (1/5 \log P_1/p_1 - 1/2 \log P_2/p_2)$$

where P_1 is the solution pressure of phosphorus, and p_1 the osmotic pressure of the P^{+++++} ion; P_2 the solution pressure of copper, and p_2 the osmotic pressure of the Cu^{++} ion.[1]

The value of P_1 is unknown, and there is reason to believe that the solution pressure of cupric copper is smaller (relatively) than is commonly

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[1] Nernst, "Theoretical Chemistry," pp. 753–759.

supposed. Be this as it may, the solution pressure of phosphorus is certainly even smaller, but p_1 is so very small in comparison with p_2 that we may expect E to be positive; *i. e.*, we may expect phosphorus to be the *negative* electrode with respect to copper, just as iron would be. The reason however, is different; for in the case of iron it is due to a larger solution pressure and in the case of phosphorus to a smaller *osmotic* pressure.

The above hypothesis looks upon phosphorus *as playing the same role as do metals while passing into solution* from the solid form.

A phosphorus sulfate (analogous to the zinc sulfate in a Daniell cell) is not formed because phosphorus functions so weakly as a base that such a salt, if formed, would be immediately hydrolyzed, just as the chlorides of phosphorus are known to be.

If the hypothesis outlined above be tentatively accepted, the reaction between phosphorus and copper sulfate becomes easy to explain; it is simply an interchange of ionic charges, which might be expressed thus:

$$5Cu^{++} + 2P = 5\ Cu + 2P^{+++++}$$

in the same sense that we write

$$3Cu^{++} + 2Al = 3Cu + 2Al^{+++},$$

or

$$Cu^{++} + Zn = Cu + Zn^{++}$$

The equation which expresses the reaction between phosphorus and copper sulfate would be

$$5CuSO_4 + 2P + 10H_2O = 5Cu + 2H_3PO_4 + 5H_2SO_4 + 2H_2O.$$

Or, so far as concerns the formation of phosphoric acid it would be

$$2P^{+++++} + 10(OH)^- = 2P(OH)_5 = 2H_3PO_4 + 2H_2O.$$[1]

Measurement of the E. M. F. of the Phosphorus-Copper Cell.—In order to further test the above explanation of the reaction, cells were made consisting of a copper electrode immersed in 0.5 *N* copper sulfate and a phosphorus electrode immersed in various solutions, including those from which all copper had been precipitated by phosphorus.

The apparatus used is illustrated by Fig. 3. The copper electrode was of the usual type, and the phosphorus electrode consisted of a glass tube into one end of which a platinum wire was sealed, and the tube filled with melted phosphorus. There was in all cases at least 3 cm. and usually 5 cm. of phosphorus below the end of the wire. This work had to be done carefully, as the least leak gave, virtually, a platinum instead of a phos-

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[1] An analogous reaction where a positive ion passes into solution and immediately reacts with negative ions already present to yield a negative ion, is seen in the case of silver dissolving in potassium cyanide solution; our measurements showed that the undissolved silver is charged negatively while the solution is taking place.

phorus electrode.[1] Out of more than a dozen of such electrodes only three showed appreciable leaks. These were discarded.

The measurements were made by means of a high resistance potentiometer, a sensitive galvanometer of the D'Arsonval type, and a standard Weston cell.

Experiments were made at temperatures ranging from 0° to the melting point of phosphorus; and with samples of phosphorus that were new and colorless as well as with some that had been in the laboratory for many years.

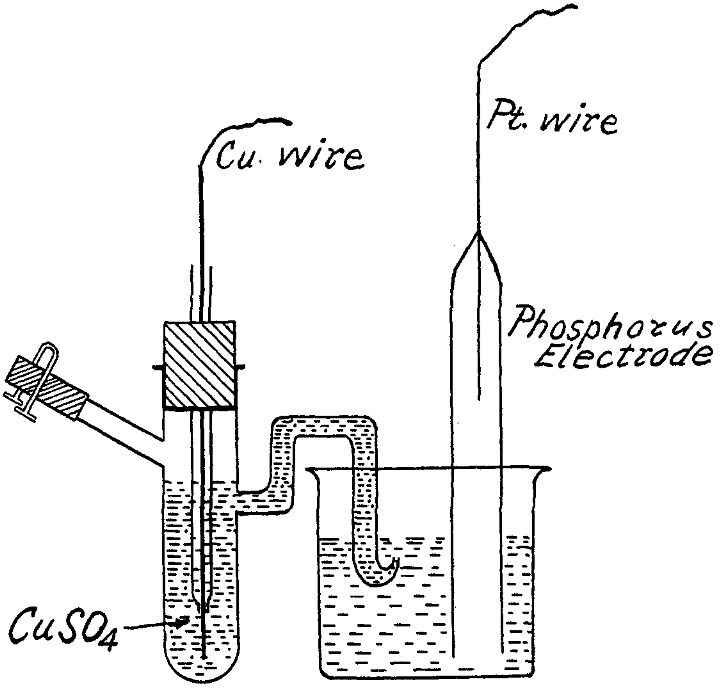

Fig. 3.

Readings were made during a period of more than four months, using new and old electrodes, some having been exposed to diffused daylight till the color had changed to a red-brown. *In all cases the phosphorus was negative to copper*, and the E. M. F. was about 0.35 volt. It is believed that the true value is somewhat higher, and that the irregularities are due, for the most part, to a very small leakage. The very small conductivity of phosphorus makes important a leakage that is ordinarily negligible.

Little or no difference was to be found between immersing the phos-

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[1] It is easy to know if there is a bad leak, as the platinum electrode is *positive* to the copper, *i. e.*, the polarity of the cell is reversed.

phorus in sulfuric acid of concentrations varying from 0.000001 N to 5 N. There was also little difference between distilled water and solutions of magnesium sulfate, sodium sulfate, or that from which the copper had been precipitated by phosphorus.

Values of E. M. F. of the Phosphorus-Copper Cell, Using Various Samples of Phosphorus and Various Solutions in which to Immerse it. Readings Extending Over a Period of Four Months.

Phosphorus electrode immersed in the solution from which the copper had been precipitated by phosphorus:

0.296, 0.296, 0.306, 0.308, 0.319.

Phosphorus immersed in distilled water. (No reading at first instant, but in a few minutes giving the following values. Two different electrodes were used at different times.)

0.275; 0.335.

In 0.000001 N sulfuric acid; 0.380.

In 0.001 N sulfuric acid; 0.334, 0.330.

All other recorded values are given below. Various electrodes and solutions were used, as already stated.

0.301
0.330
0.324
0.302
0.257
0.300
0.330
0.280
0.320
0.310
0.347
0.355
0.370
0.344
0.405
0.340
0.372
0.354
0.398
0.350
0.340
0.399
0.430
0.430
0.382
0.387
0.374
0.340
0.360
0.330
0.343
0.320
0.383
0.361
0.409
0.414
0.370
0.365
0.374
0.400
0.400
0.450

It will be noted that the latter values are on the whole markedly higher than those first taken. This is believed to be due to the greater care taken to prevent electrical leaks, particularly by carefully drying and greasing the outside of the tube containing the phosphorus electrode.

These values include all measurements made, except in those few cases in which actual leaks were found, in which case the reading was reversed, just as for a copper-platinum cell. With a poorly made cell the readings were in the above direction, but low. For the sake of completeness, all of the latter readings are given below; they were made with different solutions at different times.

0.170, 0.174, 0.106, 0.193, 0.203, 0.036, 0.020, 0.030, 0.141.

Some Precautions to be Noted in Measuring the E. M. F. of the Phosphorus-Copper Cell.

1. Owing to the very high resistance of phosphorus it is necessary to use a high resistance potentiometer and a sensitive galvanometer.

2. Care must be taken to secure a balance as quickly as possible, because experience shows that the cell is easily polarized, *i. e.*, if we draw current from it for an appreciable time the voltage drops, or if the current passes the other way it rises. Using storage cells it was found possible to "charge" the phosphorus electrode till an E. M. F. of nearly a volt was obtained, and by reversing the current the E. M. F. fell to about 0.1 volt. It slowly recovered its normal condition in both cases, however.

3. It should be remembered that very small electrical leaks (of a kind not usually important) are fatal to good results.

Conclusion.

This work, and some other not yet completed, seems to sustain our conclusion in a very definite manner. We, therefore feel, justified in saying that in displacing certain metals from their salts, phosphorus first passes into solution as a positively charged ion, in the same way as do the metallic elements. We further believe that the chief distinction between the so-called non-metallic elements and the metallic elements depends upon their tendency to hydrolyze and the subsequent ionization of this product, rather upon their ability to form positive ions.[1]

Note.

In order to see whether or not the above is a general reaction of the non-metallic elements, and to throw light upon the electrochemical character of their oxygen acids, experiments are now being conducted with the following: vanadium, arsenic, antimony, bismuth, sulfur, selenium, chromium, molybdenum, tellurium, tungsten, iodine, carbon, silicon and boron. Cells like Fig. 2 are being used and there have been obtained precipitates of metallic silver on a pure gold wire in contact with *amorphous carbon, amorphous boron, crystalline silicon, antimony and arsenic,* immersed in 0.01 *N* silver nitrate solution—one solution only being used inside and outside the porous thimble. Check solutions with silver nitrate and nitric acid but without the non-metallic element have shown no precipitates. Carbon yields carbonic acid; the others have not yet been analyzed.

The reactions of *solutions of phosphorus* in various solvents in contact with solutions of salts are also being studied in light of the above results.

An effort is being made to obtain a comparable potential series of all elements and to determine if those elements (both metallic and non-metallic), which exhibit different valences occupy more than one position in the series.

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[1] See the note which follows. Also, for an excellent discussion of the part played by positive ions in reduction and oxidation reactions, as well as a discussion of certain ions that are little known, see "Qualitative Chemical Analysis," Vol. I, by Julius Stieglitz.