THE ACTION OF YELLOW PHOSPHORUS ON SALT SOLUTIONS OF CERTAIN HEAVY METALS

by

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INTRODUCTION.

The fact that yellow phosphorus is able to precipitate many heavy metals from solutions of their Salts has been known for a considerable period. If a stick of phosphorus is placed in a solution of silver nitrate or of copper sulphate, the phosphorus gradually becomes covered with a deposit of the metal and acids of phosphorus are found in the solution. The action may be represented as follows:

$$P + MX + H_2O \longrightarrow M + HX + P \text{ acids},$$

and continues as long as any free phosphorus remains. The apparent similarity between this action and the displacement of a metal from solutions of its salts by another metal is very marked and has been commented on by more than one investigator. It has even been suggested that phosphorus, which is usually regarded as a typical non-metallic element, does in this case act in the same way as a real metal. There are, indeed, other reactions of phosphorus which point to it being an element of an 'amphoteric' nature, capable of furnishing both negative and positive ions.

It was noticed, however, that in many cases the action between phosphorus and the metallic Salt solution/

solution was more complicated, and other products such as phosphides of the metal were found. The lack of experimental material, particularly of a quantitative nature, suggested the desirability of investigating further this interesting property of yellow phosphorus.

LITERATURE OF THE SUBJECT.

In 1816 Berzelius (Gilbert's Ann. 53, 433) made use of the fact that silver is completely precipitated from a solution of silver sulphate by warming it in presence of yellow phosphorus in order to find the combining weight of phosphorus. Vogel, however, appears to have been the first to investigate the slow reduction of a solution of copper sulphate by yellow phosphorus at the ordinary temperature (J. prakt. Chem. 1836, 8, 109). He stated that the products formed were sulphuric acid, phosphoric acid, metallic copper and a black phosphide of copper. His observations were confirmed by Wöhler (Annalen 1851, 79, 126), who noticed that copper was also precipitated on a copper wire in contact with the phosphorus. Wicke (Annalen 1852, 82, 145) obtained similar results with phosphorus and solutions of silver salts. Böttger (Chem. Zentr. 1878, III, 208) observed that gold and palladium were also precipitated from solutions of their salts by phosphorus at the ordinary temperature. Corne (J. Pharm. Chim. 1882, 6, 123), Philipp (Ber. 1883, 16, 749) and Rosenheim and Pinsker (Ber. 1910, 43, 2003) investigated the action of heating phosphorus with solutions of copper and silver salts and found hypophosphoric acid to be one of the main products. They used fairly concentrated salt solutions and under their/

their conditions of working more complicated reactions appear to take place.

Straub (Z. anorg. Chem. 1903, 35, 460) was the first to study quantitatively the action between yellow phosphorus and solutions of copper sulphate at the ordinary temperature. He found that in all cases a black deposit was first formed, which was gradually covered with a deposit of crystalline copper, while the solution contained sulphuric acid and phosphoric acid, no mention being made of any lower acids of phosphorus. Straub investigated the ratio of amount of copper deposited to total amount of phosphorus which had reacted (i.e. phosphorus as phosphide and phosphoric acid) but did not arrive at any definite value. He concluded that the action must proceed in stages and that the ratio Cu: P was constant only when the reaction was not completed or when atmospheric oxygen was rigorously excluded, in which case he stated that 1 atom of phosphorus precipitated 2 atoms of copper.

Tauchert (Z. anorg. Chem. 1913, 79, 350) also investigated the action of yellow phosphorus on copper salts. He obtained results similar to those of Straub and stated that hypophosphoric acid was also formed. With copper sulphate at least the following four reactions were supposed to take place:

5/

$$5\,CuSO_4 + 4P + 8H_2O = 2H_3PO_4 + P_2Cu_3 + 2Cu + 5H_2SO_4$$

$$4\,CuSO_4 + 4P + 6H_2O = 2H_2PO_3 + P_2Cu_3 + Cu + 4H_2SO_4$$

$$5\,CuSO_4 + 2P + 8H_2O = 2H_3PO_4 + 5Cu + 5H_2SO_4$$

$$4\,CuSO_4 + 2P + 6H_2O = 2H_2PO_3 + 4Cu + 4H_2SO_4$$

A simpler explanation of the action of phosphorus on copper sulphate has been proposed by Bird and Diggs (J. Amer. Chem. Soc. 1914, 36, 1382). According to them there is no essential difference between the metallic and non-metallic elements in respect of their tendency to form positive ions but only in the ease with which they hydrolyse. They suppose that phosphorus goes into solution as P^{+++++} ions, which immediately react with the OH^- of the water to form phosphoric acid. The primary action consists in the transfer of positive charges from the copper ions to the phosphorus,

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

the equation expressing the total reaction being

$$5\,CuSO_4 + 2P + 8H_2O = 5\,Cu + 5H_2SO_4 + 2H_3PO_4\,.$$

In support of their theory Bird and Diggs found that the ratio of copper precipitated to phosphorus oxidised to phosphoric acid was approximately 5 : 2. In obtaining this ratio, however, they did not include the amount of phosphorus present as lower acids, which they found to be present, nor the amount of phosphorus present as phosphide. They did not concern themselves with the method of formation of these products, which they ascribed to secondary reactions.

EXPERIMENTAL.

The phosphorus used throughout the course of this work was purified by warming with caustic soda solution, then with a solution of potassium dichromate and sulphuric acid, and was washed thoroughly. The purified phosphorus was cast into thin sticks and kept under water in the dark.

The action of yellow phosphorus on a large number of salts of different metals was investigated. Metallic looking deposits were obtained when phosphorus sticks were placed in neutral or slightly acid salt solutions of the following metals:-

Gold, Platinum, Palladium, Silver, Mercury and Copper.

In the case of silver and of copper the metal was deposited in a bright crystalline form. No action was observed with salts of metals below copper in the electrochemical series, even after the solutions had remained in contact with the phosphorus for several weeks, so long as the solution was not alkaline. In ammoniacal solution, however, salts of the following metals also gave deposits on phosphorus almost immediately:- Lead, nickel, thallium, and not quite so readily, tin, cobalt, cadmium and zinc.

The behaviour of phosphorus towards metallic salt/

salt solutions is very similar to that of phosphine. The latter, when led into salt solutions of many heavy metals gives black or brown precipitates, which are generally mixtures of metal and metal phosphide (cf. Kulisch, Annalen 1885, <u>231</u>, 327; Moser and Brukl, Z. anorg. Chem. 1922, <u>121</u>, 73; Brukl, Z. anorg. Chem. 1922, <u>125</u>, 252). Salt solutions of the following metals are stated to give precipitates with phosphine:- Gold, platinum, silver, mercury and copper. With salt solutions of metals after copper in the 'potential' series no reaction takes place unless the solution is alkaline. Phosphorus and phosphine, therefore, both react with the same series of metallic salts. Further reference will be made to this point in the discussion of the experimental results.

ACTION OF YELLOW PHOSPHORUS ON SILVER SALTS.

From the preliminary experiments on the action of phosphorus on various metallic salts, the salts most suitable for a more detailed investigation seemed to be those of copper and of silver. As silver salts had not been used previously in any quantitative study it was decided to examine more closely the action of phosphorus on them, and in particular on the nitrate. There is no possibility in this case of the metal being reduced to a lower stage of valency, and silver can be easily and rapidly estimated with accuracy. In order to minimise any oxidising effect due to the free nitric acid formed, concentrations not greater than deci-normal were used as a rule.

When a stick of phosphorus is placed in a deci-normal solution of silver nitrate a black shiny deposit is formed almost immediately on the surface of the phosphorus, which in a short while is entirely covered. The stick of phosphorus on being removed from the solution no longer has its characteristic smell and does not glow in the dark. On remaining in contact with the silver nitrate solution for some hours the black shiny film gradually becomes covered with whitish specks till finally the whole surface is covered/

covered with a coherent deposit of white crystalline silver. The silver deposit gradually grows outwards and eventually the outer position of the deposit loses its bright appearance and becomes grey and spongy. At this stage no more silver is left in the solution. The deposit at the end of the action appears to be almost entirely metallic silver with a very thin darker layer next to the phosphorus.

In two experiments the deposit was removed from the phosphorus, washed and dried at 110°C. The percentage of silver in the dried deposit was found to be as follows: 99.8%, 99.3%.

The deposit contained a small amount of phosphorus and this was due to the dark layer next to the phosphorus. This thin layer appeared to be a phosphide of silver and was probably the same as the black deposit which was first formed when the phosphorus was placed in the silver nitrate solution. The question of phosphide formation will be considered later on.

The solution from which the silver had been completely deposited was strongly acid and was found to contain

Phosphoric acid,
Phosphorous acid,
Nitric acid,
Slight traces of nitrous acid.

No hypophosphorous acid, hypophosphoric acid or ammonia/

ammonia were detected. The presence of only H_3PO_3 and H_3PO_4 was shown as follows:-

(1) By the action of iodine solution. The two higher acids, H_3PO_3 and H_3PO_4, have no reducing action on iodine. In strongly acid solution only H_3PO_2 is oxidised by iodine; in an alkaline bicarbonate solution only H_3PO_3 reduces iodine (Rupp and Finck, Ber. 1902, 35, 3691; Boyer and Bauzil, J. Pharm. Chim. 1918, 18, 321). With the solutions tested no reducing action on iodine was found to take place in acid solution. In presence of sodium bicarbonate, however, considerable quantities of iodine were reduced.

(2) Hypophosphoric acid may be detected in a mixture of the four acids by means of a solution of guanidine carbonate, with which H_2PO_3 forms a sparingly soluble guanidine hypophosphate; the other acids do not give any precipitate (Rosenheim and Pinsker, Ber. 1910, 43, 2008). No trace of a precipitate with guanidine carbonate was obtained with the solutions examined.

(3) The presence of phosphoric acid was shown by the usual methods, e.g. with magnesia mixture.

The action of phosphorus on other silver salts was examined, viz. on the sulphate, acetate, and phosphate/

phosphate dissolved in phosphoric acid, and the reaction appeared to go in much the same way, phosphorous and phosphoric acids being formed. When phosphorus was placed in an ammoniacal solution of silver nitrate a black deposit was formed at first; after standing for some time a white deposit of silver was formed and the solution contained phosphorous and phosphoric acids. With a solution of silver cyanide in excess of potassium cyanide a black deposit was very slowly formed on the surface of the phosphorus.

The action between phosphorus and silver nitrate dissolved in solvents other than water was observed. Silver nitrate dissolves readily in pyridine, quinoline, aniline and aceto-nitrile. When phosphorus was placed in solutions of silver nitrate, in the first three solvents, a brownish-black precipitate of a phosphide was obtained immediately. The action appeared to take place in solution between dissolved phosphorus and silver salt, and phosphorus was found to dissolve appreciably in these solvents. No crystalline silver was formed. When phosphorus was placed in a solution of silver nitrate in aceto-nitrile the action resembled that which takes place with an aqueous solution, but it proceeded more slowly. Crystalline silver was gradually deposited on the surface of the phosphorus.

QUANTITATIVE EXPERIMENTS WITH SILVER SALTS.

It was decided in the first place to see whether any definite relationship exists between the amount of silver deposited and the total amount of phosphorus oxidised. Solutions of silver nitrate of known concentration were allowed to stand in contact with sticks of phosphorus till all the silver was deposited. The total phosphorus in solution as H_3PO_3 and H_3PO_4 was then estimated by evaporating a known volume of the solution to dryness with aqua regia and determining the phosphoric acid as $Mg_2P_2O_7$. (It was found that evaporation with concentrated nitric acid alone, was not always sufficient to oxidise completely the phosphorous acid: cf. Sieverts, Z. anorg. Chem. 1909, 64, 32). The ratio of number of atoms of silver precipitated to number of atoms of phosphorus oxidised, denoted hereafter as Ag : P, was about 3 : 1, but it was found that the ratio decreased the longer the solution had remained in contact with the phosphorus.

Accordingly, experiments were made to determine the ratio Ag : P both before and after complete precipitation of the silver. Sticks of phosphorus were placed in solutions of silver nitrate, and portions were withdrawn at intervals for the determination of the amount of silver salt still in solution and of/

TABLE I.

	Time in hours.	gram-atoms of Ag / litre	gram-atoms of P / litre	Ratio Ag : P.
	0	0.1008	0	
	19	.0729	0.00588	4.74 : 1
Expt	48	.02445	.01810	4.22
1.	55	.01042	.02207	4.10
	61	0	.02836	3.56
	77	0	.03048	3.31
	97	0	.03317	3.04
	0	0.1000	0	
	24	.0810	0.00367	5.18 : 1
Expt	48	.0296	.0156	4.51
2.	54	.0154	.0197	4.29
	59.2	.0025	.0236	4.13
	72.2	0	.0303	3.29
	78	0	.0311	3.22

of phosphorus acids in the solution. The silver was determined in one portion by Volhard's method. In another portion the total phosphoric acid was determined gravimetrically as $Mg_2P_2O_7$, after evaporating the solution to dryness with aqua regia. In later experiments this somewhat lengthy method was replaced by the more convenient volumetric method of Wilkie (J. Soc. Chem. Ind. 1910, 29, 794). The phosphoric acid is precipitated under given conditions as silver phosphate by means of a standard solution of silver nitrate, the excess of silver nitrate being titrated with thiocyanate solution after filtering. It was found that phosphoric acid could be rapidly estimated by this method with an accuracy sufficient for the purpose. The error was less than 0.5%.

The results of two experiments with deci-normal solutions of silver nitrate are shown in Table 1.

It will be seen that the ratio Ag : P decreases with the time; and that phosphorus is oxidised, although more slowly, even after all the silver has been deposited. No special precautions were taken in these experiments to exclude atmospheric oxygen. That the increasing oxidation of the phosphorus with the time was not due to this cause, was shown by the following experiments.

Sticks of phosphorus were placed in deci-normal solutions of silver nitrate in two flasks. In the first/

TABLE 2.

	Expt. 1. Air bubbled in.			Expt. 2. Air excluded.		
Time in hours.	gram-atoms of Ag per litre	gram-atoms of P per litre	Ratio Ag : P	gram-atoms of Ag per litre.	gram-atoms of P per litre	Ratio Ag : P.
0	0.1000	0		0.1000	0	
16.5	.0888	0.00204	5.49 : 1	.0880	0.00243	4.93 : 1
24	.0790	.00428	4.90	.0772	.00470	4.85
41	.0392	.01419	4.29	.0376	.01472	4.24
65	.0004	.02686	3.71	0	.02826	3.54

first flask air was bubbled through the solution throughout the experiment, while in the second the solution was kept stirred in an atmosphere of hydrogen. Portions of the solution were withdrawn at intervals and analysed as before. The results are shown in Table 2. In both cases the ratio Ag : P decreases at about the same rate.

In another experiment known quantities of silver nitrate solution were sealed up with a few small pieces of phosphorus in small flasks. After sufficient time had elapsed to allow all the silver to be deposited, the flasks were opened after varying intervals of time and the total phosphorus acids determined in the solution. The values of Ag : P obtained, shown in Table 3, were again found to decrease with the time the solution had remained in contact with the phosphorus. In the last two experiments of Table 3 the solution of silver nitrate was boiled, cooled, and sealed up with phosphorus in an atmosphere of pure nitrogen. In this case the first stage of the reaction, viz. the formation of the black deposit, appeared to be slower than usual. Eventually, however, the reaction appeared to go in the usual manner.

Experiments were also made in which solutions of silver sulphate were used, in order to avoid the formation of free nitric acid, although the absence of any considerable quantity of nitrous acid in the experiments/

TABLE 3.

Expt.	Time in days.	gram-atoms of Ag precipitated	gram-atoms of P oxidised.	Ratio Ag : P.
1	6	0.00250	0.000717	3.49 : 1
2	9	.00250	.000807	3.10 : 1
3	14	.00250	.000865	2.89 : 1
4	7	.002765	.000857	3.23 : 1
5	17	002765	.001197	2.31 : 1

TABLE 4.

Time in hours.	gram-atoms of Ag/litre	gram-atoms of P/litre	Ratio Ag : P.
0	0.0486	0	
22.5	.0308	0.00400	4.45 : 1
28.5	.0170	.00787	4.02
47.5	.0010	.01313	3.62

experiments already mentioned showed that the oxidising effect of the free nitric acid produced was very small. Table 4 shows the results obtained in one experiment. The same decrease in the value of Ag : P takes place.

An experiment was made to see whether the ratio Ag : P was greater than 5 : 1 when the reaction had proceeded for a very short time only. A $\frac{N}{2}$ solution of silver nitrate was allowed to remain in contact with phosphorus sticks and portions were removed for analysis before a third of the total silver had been used up. The following results were obtained:

TABLE 5.

Gram atoms of Ag used up per litre.	Gram atoms of P per litre.	Ratio Ag : P.
0.1060	0.01871	5.66 : 1
0.1555	0.03053	5.09 : 1

In the early stages of the reaction more silver appears to be deposited than corresponds to a ratio of 5 : 1.

All these experiments to find a relationship between the amount of silver precipitated and the amount of phosphorus oxidised, show that the ratio Ag : P varies from a value of over 5 : 1 , when the action has proceeded for a short time only, to a value of about 3.6 : 1 at the point corresponding to complete precipitation of the silver, after which a further/

[To face p. 16.]

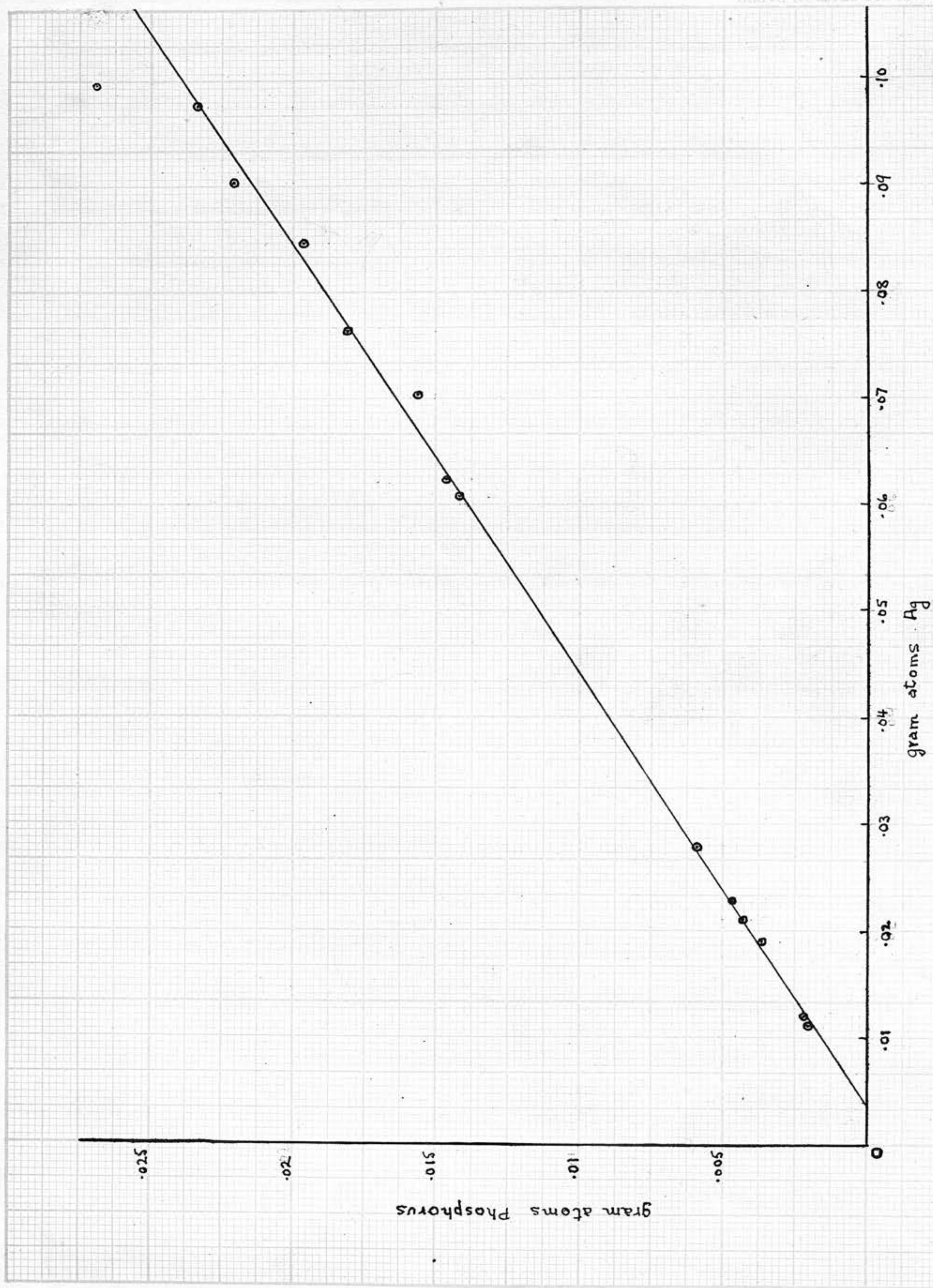

FIG. 1.

further slow oxidation of the phosphorus occurs. No appreciable oxidation of the phosphorus takes place by the atmospheric oxygen or by the oxy-acid set free from the metallic salt, and the necessary oxygen must come from decomposition of the water.

If, however, the values of silver precipitated and phosphorus oxidised before complete precipitation of the silver (obtained from the foregoing experiments with $\frac{N}{10}$ Ag NO_3), are plotted against one another, the points so obtained are found to lie approximately on a straight line corresponding to a constant ratio Ag : P of 4.04 : 1 (Fig. 1). The line does not pass through the zero of coordinates but cuts the Ag axis. This shows that there is a small period at the beginning of the reaction when the ratio Ag : P is much higher than 4 : 1 , but after a certain time the main reaction taking place corresponds approximately to 1 atom of phosphorus oxidised for every 4 atoms of silver precipitated. If the ratio Ag : P is calculated by taking, instead of the values of total silver precipitated and total phosphorus oxidised from the beginning of the reaction, the differences between subsequent values and the first value in each experiment, a much more constant ratio Ag : P is obtained, as shown in the last column of Table 6. The average for all the experiments (neglecting the two shown in brackets, which are obtained from small differences/

TABLE 6.

Relation between Ag deposited and total P oxidised.

Number of Experiment	gram atoms of Ag precipitated per litre = a	gram atoms of P oxidised per litre = b	Ratio Ag : P $= \frac{a}{b} : 1$	Ag : P (calculated described in $= \frac{a - a_o}{b - b_o}$:
1 (Table 1)	0.02787 (=a_o)	0.00588 (=b_o)	4.74	
	.0764	.01810	4.22	4.0
	.0904	.02207	4.10	3.9
2 (Table 1)	.0190 (=a_o)	.00367 (=b_o)	5.18	
	.0704	.0156	4.51	4.3
	.0846	.0197	4.29	4.1
	.0975	.0236	4.13	3.9
1 (Table 2)	.0112 (=a_o)	.00204 (=b_o)	5.49	
	.0210	.00428	4.91	(4.4)
	.0608	.01419	4.29	4.1
	.0996	.02686	3.70	3.6
2 (Table 2)	.0120 (=a_o)	.00243 (=b_o)	4.94	
	.0228	.00470	4.85	(4.8)
	.0624	.01472	4.24	4.1
Table 5	.1060 (=a_o)	.01871 (=b_o)	5.66	
	.1555	.03053	5.09	4.2
			Average	4.02

differences in consecutive values) is 4.02 : 1 , in agreement with the average value obtained from the graph.

RELATION BETWEEN SILVER DEPOSITED AND PHOSPHOROUS ACID FORMED.

As has been stated, phosphorous acid is formed in considerable quantities when phosphorus acts on solutions of silver salts. The presence of this acid was neglected by former investigators who considered it to be a product of secondary reactions. Bird and Diggs supposed that the phosphorous acid produced in the action of phosphorus on copper sulphate solutions was formed by reduction of the phosphoric acid (which they took to be the main product) by the excess of phosphorus, but this seemed very improbable. Accordingly it was thought desirable to see whether any definite relationship existed between the amount of silver deposited and the amount of phosphorous acid formed, which might show that the latter was a direct product of the action between phosphorus and silver salt solution.

The further reaction between silver nitrate still in solution and the phosphorous acid formed would of course complicate matters, but any such action appeared to be negligible. Moser and Brukl (Z. anorg. Chem. 1922, <u>121</u>, 81) stated that the action of phosphorous acid on a $\frac{N}{10}$ solution of silver nitrate at the ordinary temperature was very slow;and indeed,in all the experiments with phosphorus and $\frac{N}{10}$ silver nitrate, the/

the silver was precipitated almost entirely at the surface of the phosphorus and only a very small amount throughout the solution. Solutions of silver nitrate and phosphorous acid were mixed so that the resulting solution was 0.1 molar with respect to $AgNO_3$ and 0.02 molar with respect to H_3PO_3. On standing, a small amount of silver was slowly precipitated, as shown by the following figures:

	Vol of $\frac{N}{10}$ KCNS for 10 cc of sol^n.
Immediately after mixing two solutions	9.60 cc.
After standing 18 hours	9.45 "
" " 42 "	9.40 "

No precipitation took place, however, at the surface of a silver wire placed in the solution.

Phosphorus sticks were placed in solutions of silver nitrate, and the amounts of phosphorous acid formed and of silver salt still in solution were determined at intervals. Phosphorous acid was estimated by the iodometric method of Boyer and Bauzil (J. Pharm. Chim. 1918, <u>18</u>, 321), after precipitating the excess of silver salt in the solution with potassium iodide. Deci-normal solutions were used at first, and it was found that the ratio of silver precipitated to phosphorous acid formed (Ag : H_3PO_3) was fairly constant, with the exception of determinations made near the/

TABLE 7.

Relation between silver precipitated and H_3PO_3 formed.

No. of Expt.	gram atoms of Ag used up per litre = a	% of total silver precipitated	gram mols of H_3PO_3 per litre = b	Ratio $Ag:H_3PO_3$ $= \frac{a}{b} : 1$	Ratio Ag:H obtd. by s tract^n of value in e expt.= a - / b -
	$\frac{N}{10}$ silver nitrate.				
1.	.0704(=a_o)	70	.01070(=b_o)	6.6 : 1	
	.0846	85	.01286	6.6 : 1	6.
	0975	98	.01496	6.5 : 1	6.
2.	.00988(=a_o)	9.9	.00124(=b_o)	8.0 : 1	
	.03232	32	.00488	6.6 : 1	6.
	.0420	42	.00654	6.4 : 1	6.
	.0492	49	.00770	6.4 : 1	6.
	.0988	99	.01638	6.0 : 1	5.
	$\frac{N}{2}$ silver nitrate				
3.	.0695(=a_o)	13.9	.00804(=b_o)	8.7 : 1	
	.0850	17	.01038	8.2 : 1	6.
	.1240	25	.01618	7.7 : 1	6.
	.4250	85	.06192	6.9 : 1	6.
4.	.0755(=a_o)	15.1	.00676(=b_o)	11.2 : 1	
	.0825	16.5	.00794	10.5 : 1	5.
	.0910	18.4	.00922	10.0 : 1	6.
				Average =	6.

the beginning of the reaction. The results are shown in experiments 1 and 2 of Table 7. In experiments 3 and 4 semi-normal solutions of silver nitrate were used and determinations of Ag : H_3PO_3 made before 25% of the total silver used was precipitated.

In experiment 3 the solution was made acid from the start by addition of phosphoric acid. The values of Ag : H_3PO_3 are much higher and not constant, as was found in the case of the ratio Ag : P. From the graph of Fig. 2, however, in which the values of silver precipitated are plotted against the amount of H_3PO_3 produced, it will be seen that practically all the points lie on straight lines with a slope corresponding to an average value of Ag : H_3PO_3 of 6.3 : 1.

(The zero ordinate is taken at a different point for each experiment and the graph of experiment 3 is drawn to a fifth of the scale shown, in order to keep all the points in the same figure. The values of experiment 4 are not plotted, as they lie fairly close together). As was found in the determination of the ratio Ag : P, the early stages of the reaction appear to be abnormal with respect to the subsequent main reaction, and consequently the values of Ag : H_3PO_3 calculated from determinations made in the early stages of the reaction are irregular. By subtracting in each experiment the first values of silver deposited and phosphorous acid formed from the subsequent ones, and by using the resulting values to calculate the ratio

Ag:/

[To face p.21.]

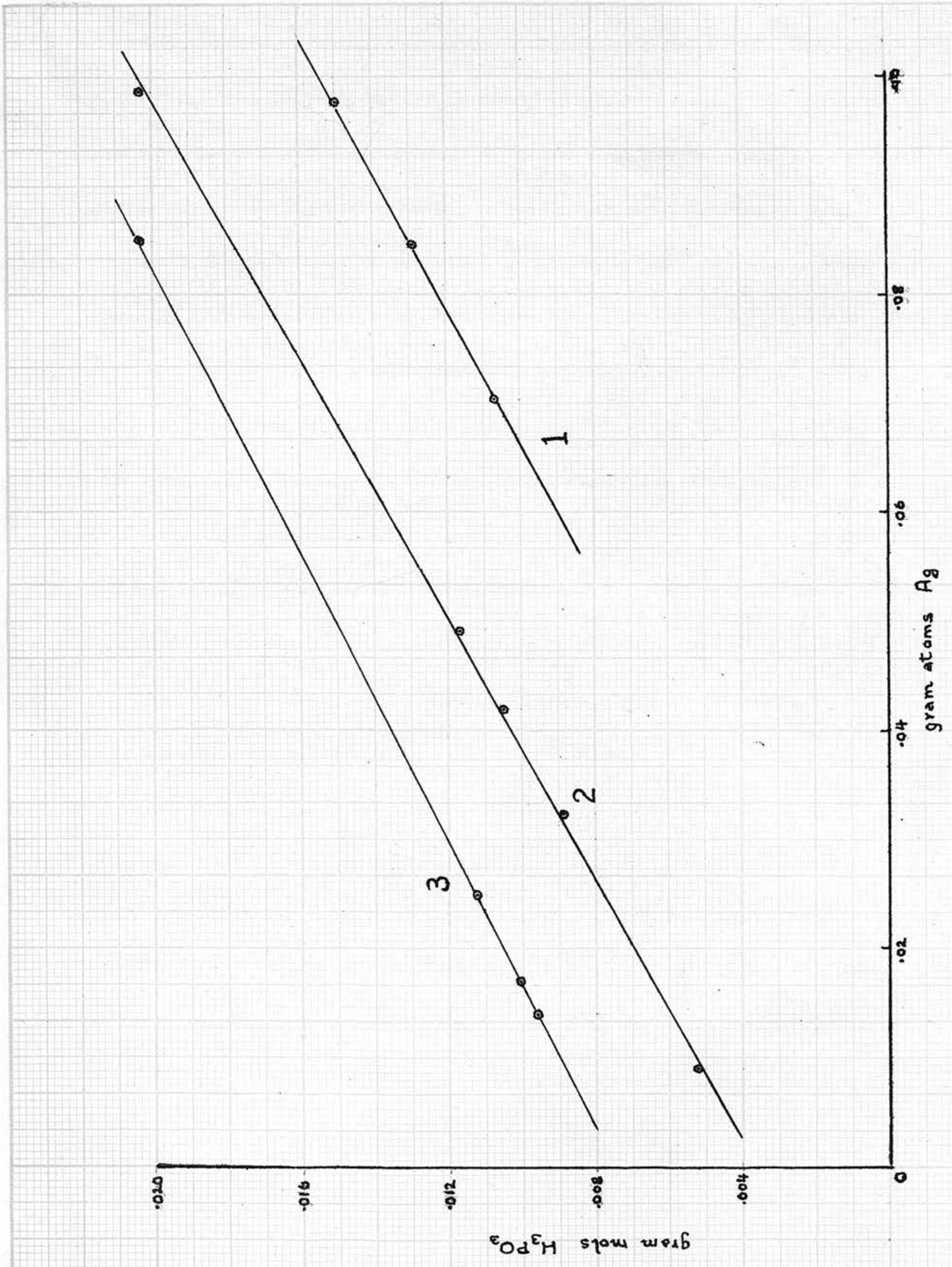

FIG. 2

Ag : H_3PO_3 more comparable results are obtained. These are shown in the last column of Table 7 and are seen to be fairly constant, the average value being 6.3 : 1. It appears from these results that, during the main course of the reaction, 1 atom of phosphorus is oxidised to phosphorous acid for every 6 atoms of silver precipitated.

From the quantitative experiments so far mentioned it would appear that both phosphorous acid and phosphoric acid are produced simultaneously in constant proportion during the action of phosphorus on silver nitrate, neglecting the first stage in the reaction. This is shown to be the case, with the same order of constancy already obtained, by the results of the following experiment in which both phosphorous acid and total oxidised phosphorus were determined, in a solution of silver nitrate in contact with yellow phosphorus, at varying intervals before complete precipitation of the silver.

TABLE 8./

TABLE 8.

H_3PO_3 gm mols/litre = a	$H_3PO_3 + H_3PO_4$ gm mols/litre = b	$\frac{H_3PO_3}{H_3PO_3 + H_3PO_4}$ = a/b	Ratio calculated by subtraction of first values. $= \frac{a - a_0}{b - b_0}$
.00318 (=a_0)	.00367 (=b_0)	.87	-
.01070	.0156	.69	.63
.01286	.0197	.65	.60
.01496	.0236	.63	.59

The figures in the third column show, however, that near the beginning of the reaction phosphorous acid is the chief product formed.

[To face p. 23.]

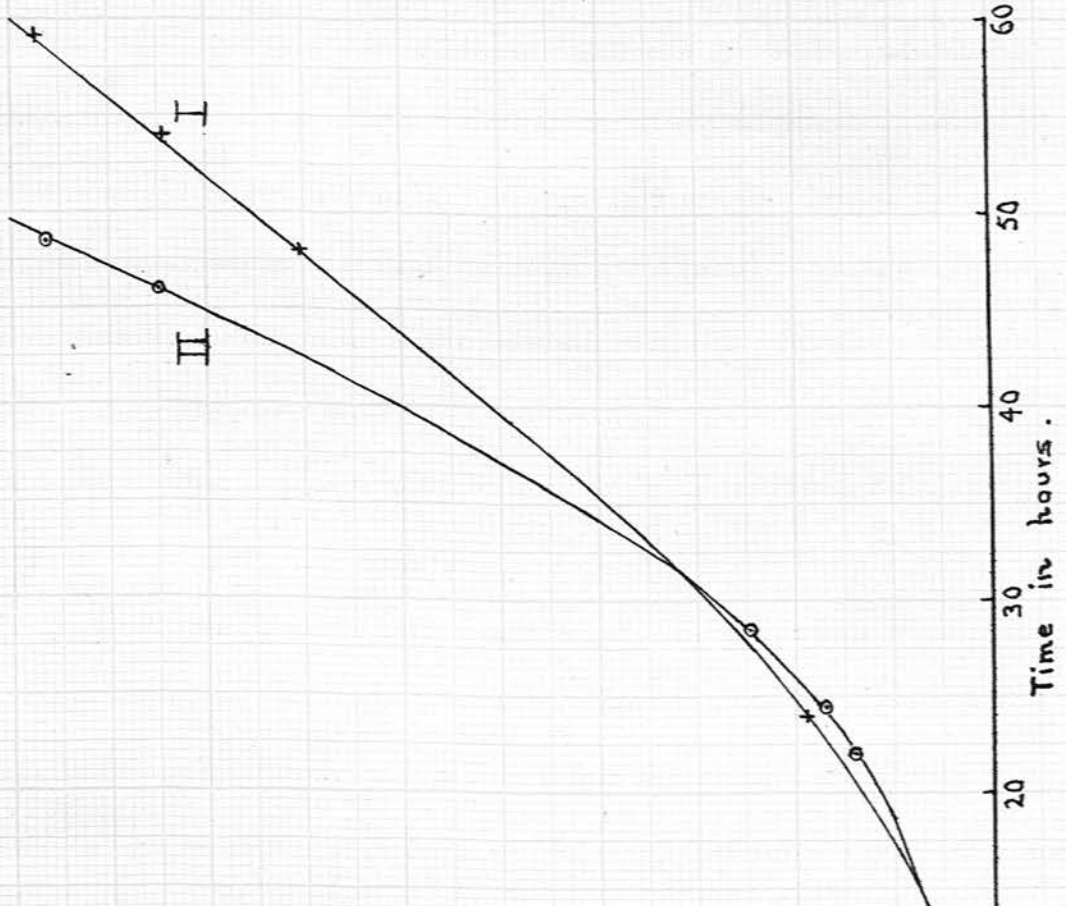

FIG. 3.

The rate of precipitation of silver from solutions of its salts by phosphorus was investigated to see whether any information could be obtained in this way regarding the mechanism of the reaction. Sticks of phosphorus were placed in solutions of silver nitrate which were kept stirred, and the concentration of silver salt in the solution was determined at intervals. In all cases curves similar to those shown in Fig. 3 were obtained, where the number of gram atoms of silver precipitated per litre are plotted against the time. Curve I was obtained using a $\frac{N}{10}$ solution, and curve II (the ordinate of which is drawn to a fifth of the scale of curve I) from a $\frac{N}{2}$ solution. The actual values which have been plotted are shown in Table 9. It will be seen that the rate of deposition of the silver is slow at first, gradually increases, and then during the greater part of the reaction remains practically constant. The reaction velocity is slowest at the beginning, although the concentration of the silver salt is greatest. In fact, in any experiment only about 20 - 30% of the silver is precipitated during the first half of the total time required for the silver to be completely precipitated. These experiments indicate that the main reaction, corresponding to the straight portion of the curve, does not commence/

TABLE 9.

Rate of precipitation of silver.

Curve I.		Curve II.	
$\frac{N}{10}$ $AgNO_3$ (0.1 gram mols per litre)		$\frac{N}{2}$ $AgNO_3$ (0.482 gram mols per litre)	
Time in hours	gram atoms of Ag precip^{d}. per litre.	Time in hours	gram atoms of Ag precip^{d} per litre
0	-	0	-
6	0.0010	2.5	0.0030
11	.0040	4.75	.0070
24	.0190	9.5	.0210
48	.0704	22.0	.0700
54	.0846	24.5	.0850
59.2	.0975	28.5	.124
		46.0	.425
		48.5	.482

commence until the slow primary reaction has proceeded to a certain extent. Indeed, as already stated on page 9 , the formation of a black deposit of silver phosphide appears to precede the formation of crystalline silver.

EXPERIMENTS WHICH INDICATE AN ACTION OF AN ELECTRO-CHEMICAL NATURE BETWEEN PHOSPHORUS AND SOLUTIONS OF METALLIC SALTS.

Wöhler (Annalen, 1851, 79, 126) had found that when phosphorus was placed in a solution of copper sulphate, copper was also deposited on a copper wire in contact with the phosphorus. Wicke (ibid. 1852, 82, 145) also noticed that silver was deposited from a solution of silver nitrate on a silver wire in contact with phosphorus. Bird and Diggs (loc. cit.) described similar experiments, which they took as strong evidence in favour of their electrochemical theory.

These experiments were confirmed and experiments were made to see whether metal would be deposited on any conducting surface in contact with the phosphorus. Platinum, gold, carbon, silver and copper were allowed to remain in contact with phosphorus sticks immersed in solutions of silver nitrate and of copper sulphate, and in every case there was deposition of silver or copper on the conducting surface as well as on the phosphorus. No deposition took place on non-conducting surfaces in contact with the phosphorus, such as glass, or on a conducting surface which was not/

[To face p.26.]

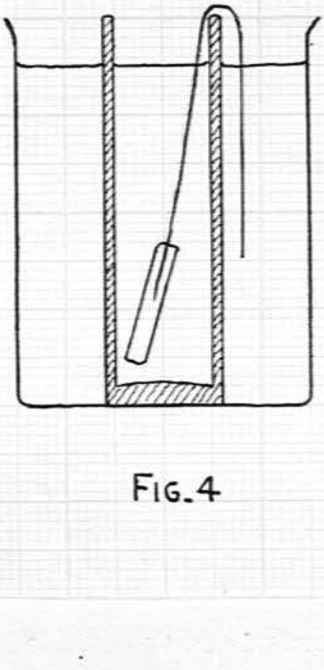

FIG. 4

not making contact with the surface of the phosphorus.

When a stick of phosphorus was placed in a solution containing both silver and copper ions the silver was first completely deposited on the phosphorus, after which the copper began to be deposited on the surface of the silver. In another experiment a piece of phosphorus was fused on to the end of a copper wire and both were placed in a solution of silver nitrate. Silver was deposited as usual on the surface of the phosphorus and also on the copper, copper going into solution. When, however, all the silver had been precipitated, the copper which had gone into solution was deposited on the precipitated silver.

These experiments point to an action of an electro-chemical nature taking place, and this is shown more clearly by the following experiment. A piece of phosphorus which had been fused on to a platinum wire was placed in a porous pot containing $\frac{N}{10}$ silver nitrate solution and standing in a beaker containing silver nitrate of the same concentration. The free end of the platinum wire was bent over into the solution outside the porous pot, as shown in Fig. 4, so as to make metallic connection between the two solutions. Silver was deposited on the phosphorus and platinum wire in the inner solution and, after some time, also on the platinum wire dipping into the outer solution, as a bright crystalline deposit. It was found, however,/

[To face p.27.]

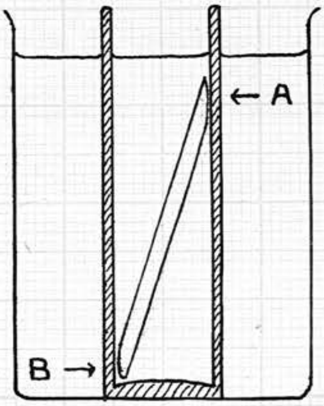

Fig. 5

however, that silver was also deposited on the outer wall of the porous cell at points which had apparently no metallic connection with one another or with the platinum wire. In experiments in which no platinum wire was used and a piece of phosphorus alone placed in the inner solution, silver was again found to deposit gradually on the outer wall of the porous cell. In all cases the silver was deposited on the outer wall only where the corresponding point on the inner wall was in metallic connection with the surface of the phosphorus. This was shown more clearly by the experiment illustrated in Fig. 5, in which a stick of phosphorus was placed in a slanting position inside a porous cell with silver nitrate solution inside and outside. Deposition of silver on the outer wall of the cell was found to take place only at the points A and B , where the silver deposit on the phosphorus was touching the corresponding points on the inner wall of the cell.

Similar results were obtained using solutions of silver sulphate and of silver acetate.

Experiments were made to see whether the same phenomenon occurred in the case of the precipitation of silver by another metal. Silver nitrate was placed, as before, inside and outside a porous diaphragm, and copper or zinc placed inside. In both cases the result was the same as when phosphorus had been used: crystalline/

crystalline silver was slowly deposited on the outside surface of the porous cell as well as on the copper or zinc inside.

The simplest explanation of the deposition of silver on the outer surface of the porous cell would be that silver is deposited in the pores of the diaphragm owing to the silver deposit inside the porous pot touching the inner surface of the porous cell. In this way metallic connection would be established through the pores of the cell. Some of the porous cells used were broken up and on examination under the microscope small particles of silver could be seen embedded in the interior of the porous substance. Giurgea (Chem. Zentr. 1913, I, 677) noticed this type of phenomenon in the precipitation of metallic salt solutions by other metals using porous cells and ascribed the action to electro-capillary potential differences. This view is discussed by Freundlich (Kapillarchemie, 1922, p. 371).

The important point to be noted is that in all these experiments metal ions are discharged and metal is deposited at points removed from the surface of the phosphorus. Metal is deposited, however, only at such points as are in metallic connection with the surface of the phosphorus, and this metallic connection is established either by the metal already deposited or by another conductor.

This/

This is strong evidence in favour of the view that an action of an electrochemical nature is taking place, that is to say, a direct discharge of ions to the metallic state, as represented e.g. by

$$\mathrm{Ag} \longrightarrow \mathrm{Ag}$$

The physical state of the silver and copper deposited by means of phosphorus strongly resembles the state in which these metals are deposited from their salt solutions by an electric current. This electrochemical view of the action of phosphorus on metallic salts will be referred to in the discussion at the end.

EXPERIMENTS WITH SILVER PHOSPHIDE.

The experiments just described show that an action of an electro-chemical nature is taking place. The quantitative results, however, make it clear that the action taking place is not simply the precipitation of silver with an equivalent amount of phosphorus going into the solution. In the early stages the formation of a phosphide appears to play an important part, and throughout the reaction a small amount of phosphide is present in the deposit. The direct determination of what particular compound of silver and phosphorus is present cannot be decided, as the relatively small amount of it formed and the difficulty of separating it completely from silver and from phosphorus make a quantitative investigation impossible. Indirect evidence indicates the probability of it being the phosphide Ag_3P. Moser and Brukl (Z. anorg. Chem. 1922, <u>121</u>, 80) obtained this compound by the action of phosphine on silver nitrate solution and they showed that it was an unstable substance and in presence of excess of silver salt reacted further to give metallic silver and phosphorus acids. The deposit formed on phosphorus in silver nitrate solutions can react with excess of silver nitrate. Some phosphorus sticks were placed in $\frac{N}{10}$ silver nitrate solution/

solution and when about half the silver had been precipitated the deposit was removed from the phosphorus, washed, and dried between filter paper. It was then placed in 50 cc. of $\frac{N}{10}$ silver nitrate solution. 10 cc. of this solution immediately after putting the silver deposit into it, were equivalent to 9.85 cc. KCNS solution. After a few days 10 cc. were found equivalent to 9.05 cc. of KCNS, and the solution gave a noticeable precipitate with ammonium molybdate, showing that silver had been deposited and phosphorus had gone into the solution.

The work of Christomanos (Z. anorg. Chem. 1904, <u>41</u>, 309) on the action of phosphorus dissolved in ether and benzene on solutions of copper salts pointed to the formation of a phosphide having the formula Cu_3P_2. In the case of silver salts he stated that a black phosphide was formed, but did not isolate any definite compound. Some experiments were made, therefore, with solutions of phosphorus in ether, benzene and carbon disulphide and silver nitrate. On shaking up the phosphorus solution with a dilute solution of silver nitrate a brownish black precipitate was obtained, which on standing in contact with the excess of silver nitrate solution became greyer in colour and gradually assumed the appearance of metallic silver. The aqueous solution was found to contain phosphorous and phosphoric acids. The proportion of silver/

silver to phosphorus in the black precipitate first formed varied considerably owing to the difficulty in washing it free of phosphorus without allowing it to decompose. Some of the figures obtained for the ratio Ag : P in the washed but not dried precipitate are shown below:-

TABLE 10.

	Ratio Ag : P in black precipitate
Precipitate obtained using Solutions of phosphorus in carbon disulphide	2.84 : 1
	3.90 : 1
	3.85 : 1
Precipitate obtained using solutions of phosphorus in benzene.	2.53 : 1
	2.62 : 1

The results, although somewhat inconsistent, make it likely that Ag_3P is formed.

Experiments were also made to see whether there was any connection between the amount of silver precipitated and the total phosphorus present as phosphorus acids in the aqueous solution. Solutions of phosphorus in ether, benzene and carbon disulphide were shaken with solutions of silver salts and the aqueous layer analysed at intervals. The values of the ratio of silver precipitated to phosphorus oxidised fluctuated greatly, but in all cases the ratio decreased the longer the precipitate remained in contact with the solution. In the early stages when the precipitate/

precipitate was quite black and consisted almost entirely of phosphide, high values of the order of 10 : 1 were obtained for Ag : P . If the mixture was allowed to stand several days till the precipitate appeared to consist wholly of metallic silver, the ratio Ag : P was found to lie between 5 : 1 and 3 : 1 . In the first stage, therefore, when a phosphide undoubtedly is formed, less phosphorus is oxidised than corresponds to a ratio of 5 : 1 for Ag : P .

Silver phosphide prepared by the action of phosphine and of solutions of phosphorus in various solvents, was washed and placed in a fresh quantity of silver nitrate solution. In both cases it was found that the phosphorus in the phosphide was slowly oxidised to phosphoric acid, practically no phosphorous acid being formed. The presence of this lower acid, therefore, in the aqueous solution after shaking up a solution of silver nitrate with a solution of phosphorus must be due to the first reaction, viz. the formation of the phosphide.

ACTION OF PHOSPHORUS ON SOLUTIONS OF COPPER SALTS.

It seemed desirable to make some further experiments on the action of phosphorus on copper salt solutions to see whether in this case there is an exact equivalence between the amount of metal precipitated and the amount of phosphorus oxidised. As has been stated in the introduction, the study of the action of phosphorus on metallic salt solutions has been directed mainly to the case of copper salts; but the quantitative work of Straub and of Bird and Diggs does not show good agreement.

The action of yellow phosphorus on copper salts appears to be more complicated, as the amount of phosphide formed in this case is quite considerable, about 13% of the total phosphorus which has reacted being present as phosphide; whereas in the case of silver salts, as has been stated, practically all the phosphorus which has reacted is found in the solution as oxy-acids. This was shown by the following experiments.

Solutions of copper sulphate of known concentration, mostly decinormal, were allowed to remain in contact with sticks of phosphorus. After complete precipitation of the copper, the phosphorus in solution as oxy-acids was determined and also the total phosphorus/

phosphorus which had reacted, i.e., phosphorus as phosphide + oxy-acids. This latter determination was made by dissolving the deposit by means of cold dilute nitric acid and adding this solution to the solution containing the oxy-acids of phosphorus. It was shown by control experiments that no appreciable quantity of the free phosphorus was oxidised by the dilute nitric acid during the time required to dissolve the deposit. The phosphorus was determined in the usual way after oxidising the solution. It was found that quite consistent results could be obtained if the analysis was carried out within a short time after complete deposition of the copper. The following table gives the values obtained for the ratios of the number of atoms of copper precipitated to (1) the number of atoms of phosphorus as oxyacids and, (2) the number of atoms of phosphorus as phosphide + oxyacids.

TABLE 11.

	Ratio $Cu : P_{\text{oxy-acids.}}$	Ratio $Cu : P_{\text{total}}$
	4 : 1.82	4 : 2.16
	4 : 1.86	4 : 2.12
	4 : 1.86	4 : 2.12
	4 : 1.84	
Aver.	4 : 1.85	4 : 2.13

These/

These figures show that, after complete deposition of the copper, about 13% of the total phosphorus which has reacted is present as phosphide.

It was found, however, that if the phosphorus and deposit were allowed to remain in contact with the solution for a long period, more phosphorus was oxidised, even if the solution was sealed up free from atmospheric oxygen.

In two experiments in which the solution was allowed to stand for 4 months before determining the phosphorus oxidised, the following values of Cu : $P_{oxy\text{-}acids}$ were obtained, 4 : 2.45 and 4 : 2.52, showing that more phosphorus than that present as phosphide had been oxidised. There was no phosphide left in the deposit. As in the case of silver salts, therefore, there is a slow oxidation of the phosphorus after complete deposition of the metal. The above experiments also dispose of the suggestion of Bird and Diggs that the phosphide is formed in a secondary reaction between metallic copper and phosphorus. They stated that the bright metallic copper, on remaining in contact with the phosphorus, was gradually all converted into the black phosphide. In the case of copper precipitated from a solution of the sulphate, the deposit was certainly found to turn black on standing in contact with the phosphorus in the solution from which it had been deposited; but it was found that/

TABLE 12.

Relation between copper precipitated and phosphorus oxidised.

Time in hours	gram-atoms Cu precipitated/litre = a	gram atoms P as oxy-acids/litre = b	Ratio Cu : P = $\frac{a}{b}$	Cu : P obtained by subtracting first values = $\frac{a - a_o}{b - b_o}$
	$\frac{N}{10}$ Copper Sulphate			
39	.03508 (=a_o)	.01468 (=b_o)	4.8 : 2	
47	.03937	.01697	4.6 : 2	3.8 : 2
69	.04696	.02090	4.5 : 2	3.8 : 2
	$\frac{N}{10}$ Copper Nitrate			
39	.03187 (=a_o)	.01352 (=b_o)	4.7 : 2	
47	.03608	.01557	4.6 : 2	4.1 : 2
69	.04452	.01994	4.5 : 2	3.9 : 1
	$\frac{N}{2}$ Copper Sulphate			
48	.1523 (=a_o)	.0622 (=b_o)	4.9 : 2	
88	.2407	.1051	4.6 : 2	4.1 : 2
	$\frac{N}{2}$ Copper Nitrate			
40	.1437 (=a_o)	.0549 (=b_o)	5.2 : 2	
88	.2483	.1115	4.5 : 2	3.7 : 2
			Average	3.9 : 2

that, as mentioned above, the deposit after several months contained no phosphorus. The deposit obtained from copper nitrate solution retained its bright coppery colour for months. The experimental evidence goes to show that the phosphide formation is a primary reaction between phosphorus and metal ions, and not between phosphorus and metal. With copper salts this phosphide formation proceeds to a much greater extent than with silver.

The following experiments were made to see whether there was any relationship between the amount of copper precipitated and the amount of phosphorus oxidised to form oxy-acids before complete precipitation of the copper. Equal quantities of phosphorus sticks were placed in 1 litre of $\frac{N}{10}$ copper sulphate and 1 litre of $\frac{N}{10}$ copper nitrate contained in rubber stoppered flasks, and the solutions were allowed to stand with occasional shaking. At intervals two portions were removed from each solution and evaporated to dryness with aqua regia. In one portion the copper was determined volumetrically by means of standard thiosulphate solution; in the other the phosphoric acid was determined gravimetrically as $Mg_2P_2O_7$. The values of copper precipitated and phosphorus oxidised, calculated from the experimental results and expressed in gram atoms per litre, are shown in Table 12.

Some/

[To face p.38.]

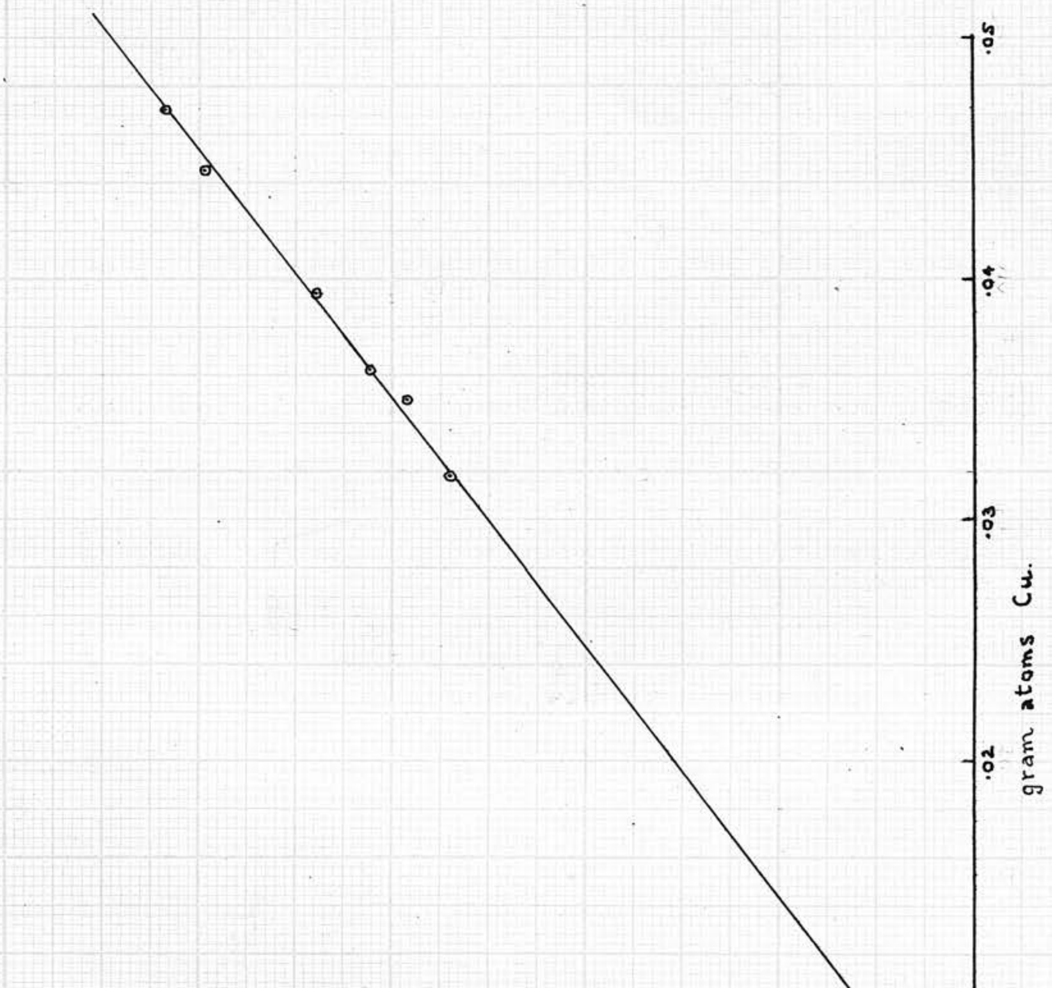

FIG. 6

Some results of similar experiments with seminormal solutions of copper sulphate and copper nitrate are also given. Column 4 contains the ratio Cu : P calculated for each pair of values, and it will be seen that this decreases with the time just as in the case of silver salts. If the ratio Cu : P , however, is calculated by subtracting the first values in each experiment, as was done with the ratio Ag : P , a much more constant ratio is obtained having an average value for Cu : P of 3.9 : 2. This is also shown in Fig. 6, where the results of the experiments with decinormal solutions are plotted. The points are seen to lie nearly all on a straight line not going through the origin and having a slope corresponding to a ratio of 4.1 : 2. During the main part of the action between phosphorus and copper salt solutions, 1 atom of phosphorus appears to be oxidised for every 2 atoms of copper deposited. The phosphorus is oxidised to both phosphorous and phosphoric acids, as in the case of silver salts, but the separate determination of the phosphorous acid was not made in this case. The first reaction which takes place, however, is the formation of a black phosphide. There is no exact equivalence, throughout the whole course of the reaction, between the amounts of copper and of phosphorus which have reacted.

DISCUSSION OF RESULTS.

The results of the experiments outlined in this work on the action of phosphorus on solutions of silver and of copper salts bring out the following three general conclusions:

(a) The reaction taking place is not solely a precipitation of the metal with an equivalent amount of phosphorus going into solution as phosphoric acid, as was suggested by Bird and Diggs. The formation of phosphide also takes place as a primary reaction.

(b) An action of an electrochemical nature does appear to take place.

(c) Slow oxidation of phosphorus also takes place after complete deposition of the metal.

It appears, then, that during the deposition of the metal two reactions at least take place.

1. Formation of a phosphide.

This is the first reaction and commences as soon as the stick of phosphorus is placed in the solution of the metallic salt. With regard to the production of a phosphide, the most probable mechanism seems to be the formation of phosphine by the action of phosphorus on the water, phosphorus being oxidised at/

at the same time to phosphorous acid. The phosphine would immediately react with the metal ions to give a phosphide. While not susceptible of direct proof, this view is supported by the fact, mentioned at an earlier stage, that phosphorus and phosphine both react with the same series of metallic salts. Cross and Higgins (J. Chem. Soc. 1879, 35, 255) showed that under ordinary conditions boiling water is decomposed by phosphorus, which is partly reduced to phosphine and partly oxidised to oxy-acids. In the absence of oxygen, decomposition of the water takes place only in presence of certain metallic salts. It seems reasonable to assume that, in the action of phosphorus on solutions of salts of the heavy metals at the ordinary temperature, the first stage consists in the decomposition of water by the phosphorus, as described above. At all events, the fact that a phosphide is produced would indicate the formation of negative phosphorus ions P^{---}.

2. Deposition of the metal on the surface of the phosphide and simultaneous oxidation of phosphorus to phosphorous and phosphoric acids.

With regard to the method of deposition of the metal, there are two possibilities:

(a)/

(a) The metal is formed as a product of a secondary reaction in which the phosphide obtained in the primary reaction acts, in turn, upon the excess of metallic salt in the solution. It has been shown that the phosphides of the heavy metals can react in this way to give metal and phosphoric acid.

(b) The metal is deposited in a primary reaction directly from the ionic state, as was suggested by Bird and Diggs, without any intermediate compound being formed. In other words, the action is an electrochemical one and may be represented as follows:

$$Ag^{\bullet} \longrightarrow Ag \qquad \text{or} \qquad Cu^{\bullet\bullet} \longrightarrow Cu$$

Strong evidence for this view is obtained from the fact that, whereas the phosphide is formed in a thin layer uniformly over the surface of the phosphorus, the metal is deposited in a bright crystalline state resembling that deposited electrically, the deposit growing outwards and in some cases extending to points far removed from the surface of the phosphide. While Method 2a is not excluded, the main reaction appears to take place according to Method 2b. Since this constitutes essentially an exchange of ionic charges, the formation of positive phosphorus ions must be assumed, at least as an intermediate stage. This conclusion/

conclusion was the one come to by Bird and Diggs, but the formation of both phosphorous and phosphoric acids would necessitate the assumption of both P^{+++} and P^{+++++} ions.

The formation of phosphide is the first reaction which takes place and no metal appears until this reaction has proceeded to a certain extent, which is different in the case of silver and of copper salts. Exactly how far the second reaction depends on the first is not, however, at this stage apparent.

The complete representation of the experimental facts by any simple equation or set of equations has not been found possible. Of the equations so far proposed we have that of Bird and Diggs,

$$5\ CuSO_4 + P + 4H_2O = 5\ Cu + 5\ H_2SO_4 + H_3PO_4\ ,$$

but the quantitative experiments described in this work do not justify a single equation of this type. They necessitate two equations at least, which may be written in a general form as follows, where M stands for an equivalent of the metal radical, and X for an equivalent of the salt radical:

$$5\ MX + P + 4\ H_2O = 5\ M + 5\ HX + H_3PO_4$$

$$3\ MX + P + 3\ H_2O = 3\ M + 3\ HX + H_3PO_3$$

or, written from the point of view of ions:

$$5\ M^{+} + P = 5\ M + P^{+++++}$$

$$3\ M^{+} + P = 3\ M + P^{+++}\ .$$

According to the proportion in which these two reactions take place, the ratio of equivalents of metal deposited to atoms of phosphorus oxidised should lie between 5 : 1 and 3 : 1. As has been shown in the case of silver and copper salts, the ratio is approximately 4 equivalents of metal to 1 atom of phosphorus during the greater part of the reaction.

The formation of a phosphide must be represented by some method like the following:

$$2\,P + 3\,H_2O = P\,H_3 + H_3PO_3$$

$$PH_3 + 3\,MX = P\,M_3 + 3\,HX$$

The phosphide may react further with the excess of metallic salt, giving metal and phosphoric acid.

$$PM_3 + 5\,MX + 4\,H_2O = 8\,M + 5\,HX + H_3PO_4$$

The process is not, however, so simple as this, for these equations do not account for the high ratios of silver deposited: phosphorus oxidised near the beginning of the reaction. One <u>primâ facie</u> explanation of these high values of Ag : P might be that the phosphorus oxidised is not all present in the solution, but remains partly in the deposit, combined with silver, e.g. as silver phosphate; but this explanation is rendered improbable by the fact that the solution soon contains acid, which would dissolve such a compound. In experiment 3 of Table 7, the solution was made strongly acid with phosphoric acid from the start, and the results still gave a high ratio/

ratio of Ag : H_3PO_3.

Another tentative explanation is that the phosphide formed contains excess of the metallic salt combined with it to give a compound of the type $PM_3 . 3MX$. Poleck and Thümmel (Ber. 1883, <u>16</u>, 2442), from their experiments on the action of phosphine on silver nitrate solution, supposed that the product first formed was not the simple phosphide Ag_3P but a compound $Ag_3P.3AgNO_3$; and they concluded that the same compound was formed in the action of yellow phosphorus on silver nitrate, as follows:

$$2P + 6\,AgNO_3 + 3H_2O = Ag_3P.3AgNO_3 + 3HNO_3 + H_3PO_3 .$$

There is no means, however, of proving this directly.

As has been stated, a slow oxidation of the phosphorus takes place after the complete deposition of the metal. It has been shown that this action makes unreliable values of the ratio metal deposited: phosphorus oxidised obtained from determinations made after complete precipitation of the metal. The mechanism of this oxidation has not been investigated to any extent, and all that can be said is that it must be of a catalytic nature. As was shown in the case of copper salts, more phosphorus is oxidised than corresponds to that present as phosphide. The metal present on the surface of the phosphorus seems to assist its oxidation. An experiment showing this more clearly was performed as follows. A stick of phosphorus/

phosphorus was covered with a deposit of silver by allowing it to stand in a solution of silver nitrate. The stick of phosphorus + deposit was then removed from the solution, washed, and placed in air-free distilled water kept in an atmosphere of nitrogen. At the same time a stick of phosphorus alone was placed under the same conditions. After some time an appreciable quantity of oxidised phosphorus was found in the first flask, and only a small trace in the second.

The oxidation of the phosphorus appears to take place just as readily when atmospheric oxygen is excluded.

SUMMARY OF RESULTS.

(1) Metallic looking deposits are obtained when yellow phosphorus is placed in acid or neutral salt solutions of the following metals : Au, Pt, Pd, Ag, Hg and Cu. In ammoniacal solution salts of the following metals also give deposits : Pb, Ni, Tl, Sn, Co, Cd and Zn. The metals may be divided into practically the same two groups with respect to the action of phosphine on solutions of their salts.

(2) The action of yellow phosphorus on solutions of silver and of copper salts has been investigated in greater detail, especially with regard to the quantitative relationships between the amounts of metal deposited and phosphorus oxidised. Throughout the greater part of the reaction approximately 4 equivalents of metal are deposited for every 1 atom of phosphorus oxidised. In the early stages less phosphorus is oxidised than corresponds to this ratio.

(3) At least two reactions take place during the precipitation of the metal, viz.,

(a) Formation of a phosphide.

(b) Direct discharge of metallic ions and simultaneous oxidation of phosphorus to H_3PO_3 and H_3PO_4.

The/

The second reaction does not take place appreciably until the first has proceeded to a certain extent. Much more phosphide is formed in the case of copper salts than in that of silver salts.

(4) After the metal has been precipitated completely, there is a further slow oxidation of the phosphorus.