CLXXVII.—*The Action of Phosphorus on Salts of Silver and Other Metals.*

By Oswald James Walker.

It has long been known that yellow phosphorus is able to precipitate many heavy metals from solutions of their salts, and attempts have been made to obtain quantitative information about the phenomenon by determining the ratio of metal deposited to phosphorus which had reacted. Using solutions of copper sulphate, Straub (*Z. anorg. Chem.*, 1903, **35**, 460) investigated the ratio of the amount of copper deposited to the total amount of phosphorus which had reacted (*i.e.*, phosphorus as phosphide and phosphoric acid), but he did not obtain any definite value. He concluded that the action proceeded in stages, and that when it was incomplete or when atmospheric oxygen was rigorously excluded 1 atom of phosphorus precipitated 2 atoms of copper. Tauchert (*Z. anorg. Chem.*, 1913, **79**, 350) obtained similar results, but stated that hypophosphoric acid was one of the products. Bird and Diggs (*J. Amer. Chem. Soc.*, 1914, **36**, 1382) also investigated the action of phosphorus on copper sulphate and concluded that the main action consisted in the transfer of positive charges from the copper ions to the phosphorus, as follows :

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

the positive phosphorus ions reacting immediately with water to form phosphoric acid. In support of their theory, Bird and Diggs found that the ratio of atoms 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 and as phosphide. They ascribed these products to secondary reactions.

EXPERIMENTAL.

In order to determine to what extent phosphorus reacts with solutions of salts of the heavy metals and to decide which metal would be most suitable for a more detailed investigation, sticks of phosphorus were kept in contact with solutions of salts of a large number of different metals. Deposits of metallic appearance were found on the surface of the phosphorus after varying intervals with neutral or slightly acid solutions of salts of the following metals—gold, platinum, palladium, silver, mercury, and copper. No action was observed, even after several weeks, with salts of metals below copper in the electrochemical series, provided that the solution was not alkaline. In ammoniacal solution, however, salts of the following metals also gave deposits on the surface of the phosphorus—lead, nickel, thallium, and, not quite so readily, tin, cobalt, cadmium, and zinc. An interesting point of considerable importance is revealed by comparing these results with the data which are available for the action of phosphine on metallic salt solutions in papers by Kulisch (*Annalen*, 1885, **231**, 327), Moser and Brukl (*Z. anorg. Chem.*, 1922, **121**, 73), and Brukl (*ibid.*, 1922, **125**, 252). An examination of their results shows that those solutions which react with phosphine are exactly those which give deposits on phosphorus, and the metals may be divided into the same two groups mentioned above with respect to the action of phosphine on their salt solutions. Reference to this point will be made at a later stage.

From the above experiments, the most suitable salts for a more detailed investigation seemed to be those of silver and copper. 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 especially on the nitrate. There is no possibility in this case of the metal being reduced to a lower stage of valency, and, as will be shown below, the complications due to the formation of phosphide are not so great as with copper salts. In order to minimise any oxidising effect due to the free nitric acid formed, concentrations not greater than $N/10$ were used as a rule.

Action of Yellow Phosphorus on Silver Salts.

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

When a stick of phosphorus was placed in a $N/10$-solution of silver nitrate, a black, shiny deposit was formed almost immediately on the surface of the phosphorus; bright crystalline silver was then slowly deposited which finally became grey and spongy when it was all out of solution. After complete deposition of the silver, the solution contained phosphoric, phosphorous, and nitric acids, and traces of nitrous acid. No hypophosphorous acid, hypophosphoric acid, or ammonia was detected. The deposit consisted almost entirely of metallic silver, but contained a small amount of phosphorus, due to a thin, darker layer next to the surface of the phosphorus stick. This thin layer appeared to be a phosphide of silver and was probably the same as the black deposit first formed when the phosphorus was placed in the silver nitrate solution. The amount of phosphorus present in the deposit was small compared with that in the solution as oxy-acids. The question of phosphide formation will be considered later.

With solutions of silver sulphate and of silver acetate the reaction proceeded in a similar way. When phosphorus was placed in an ammoniacal solution of silver nitrate, a black deposit was formed which was converted, after some time, into white, crystalline silver. With a solution of silver cyanide in potassium cyanide a black deposit was very slowly formed on the surface of the phosphorus.

Quantitative Experiments with Silver Salts.—Experiments were made in the first place to determine whether any definite relationship existed between the amount of silver deposited and the total amount of phosphorus oxidised. Preliminary determinations showed that the ratio of the number of atoms of silver precipitated to the number of atoms of phosphorus oxidised, denoted hereafter as Ag : P, varied with the length of time during which the phosphorus had remained in contact with the solution. Accordingly, the ratio Ag : P was determined before complete precipitation of the silver had taken place.

Sticks of phosphorus were placed in solutions of silver nitrate, and portions withdrawn at intervals for the determination of the amounts of silver salt and of phosphorus acids in the solution. The silver was determined in one portion by Volhard's method. A second portion was evaporated to dryness with aqua regia in order to ensure complete oxidation of the phosphorous acid, and the phosphoric acid was determined gravimetrically as magnesium pyrophosphate. In later experiments, this method was replaced by the more convenient volumetric method of Wilkie (*J. Soc. Chem. Ind.*, 1910, **29**, 794), in which the phosphoric acid was precipitated under given conditions as silver phosphate by means of standard silver nitrate solution, the excess of silver nitrate being titrated with thiocyanate solution after filtering.

Table I.

Expt	$AgNO_3$.	Time (hrs.).	Ag pptd. (= a).	P oxid. (= b).	Ag : P (= a/b).	$\frac{a-a_0}{b-b_0}$.
1	0·1008	19	0·0279	0·00588	4·74	—
		48	0·0764	0·01810	4·22	4·0
		55	0·0904	0·02207	4·10	3·9
		61	0·1008	0·02836	3·55	—
2	0·1000	24	0·0190	0·00367	5·18	—
		48	0·0704	0·0156	4·51	4·3
		54	0·0846	0·0197	4·29	4·1
		59	0·0975	0·0236	4·13	3·9
		72	0·1000	0·0303	3·29	—
3	0·1000	16·5	0·0112	0·00204	5·49	—
		24	0·0210	0·00428	4·91	(4·4)
		41	0·0608	0·01419	4·29	4·1
		65	0·0996	0·02686	3·70	3·6
4	0·1000	16·5	0·0120	0·00243	4·94	—
		24	0·0228	0·00470	4·85	(4·8)
		41	0·0624	0·01472	4·24	4·1
		65	0·1000	0·02826	3·54	—
5	0·502	—	0·1060	0·0187	5·66	—
		—	0·1555	0·0305	5·09	4·2

The results of several experiments with solutions of silver nitrate are in Table I, all concentrations being given in g.-atoms or g.-mols. per litre. The general conclusions may be summarised as follows :

1. The ratio Ag : P varied during the deposition of the silver from a value of more than 5 : 1 near the beginning of the reaction to about 3·6 : 1 at the point corresponding to complete deposition of the silver.

2. No appreciable oxidation of the phosphorus by the oxy-acid set free from the metallic salt took place. Experiments in which solutions of the sulphate were used, in order to avoid the formation of nitric acid, gave results similar to those obtained with the nitrate solutions.

3. The phosphorus was not appreciably oxidised by atmospheric oxygen. Similar results were obtained whether air was bubbled through the solution (Expt. 3) or completely excluded (Expt. 4) during the deposition of the silver.

4. The oxygen necessary for the oxidation of the phosphorus must therefore come from the decomposition of the water.

A further slow oxidation of the phosphorus took place even after complete precipitation of the silver. This is shown by the results in Table II. In these experiments equal quantities of a standard silver nitrate solution were sealed up with phosphorus sticks in small bulbs. After sufficient time had elapsed to allow all the silver to be deposited, the bulbs were opened at varying intervals and the total phosphorus acids were determined in the solution. It will be seen that the quantity of phosphorus oxidised increases with the time, and that the values of the ratio Ag : P are much lower than those obtained before complete precipitation of the silver.

TABLE II.

Expt.	Time (days).	Ag pptd.	P oxid.	Ag : P.
1	6	0·00250	0·000717	3·49
	9		0·000807	3·10
	14		0·000865	2·89
2	7	0·00277	0·000857	3·23
	17		0·00120	2·31

The points obtained by plotting against one another the values of silver precipitated and phosphorus oxidised before complete precipitation of the silver lie approximately on a straight line which corresponds to a constant ratio of Ag : P of 4 : 1 but which does not pass through the origin. The ratio Ag : P calculated from the actual values of silver precipitated and phosphorus oxidised has, on the other hand, been shown to decrease with time. If, however, the ratio Ag : P is calculated by taking, not the values of total silver precipitated and total phosphorus oxidised from the beginning of the reaction, but the differences between subsequent values and the first value (a_0 or b_0) in each experiment, a much more constant ratio Ag : P is obtained, as shown in the last column of Table I. The average value is 4·0 : 1, if the two values shown in brackets, which are obtained from small differences, are neglected.

It would appear, therefore, that whilst at the beginning of the reaction the ratio Ag : P is higher than 4 : 1, after a certain time the main reaction taking place corresponds approximately to the precipitation of 4 atoms of silver for every atom of phosphorus oxidised.

Formation of Phosphorous Acid.—It was thought desirable to examine whether any definite relationship existed between the amounts of silver deposited and of phosphorous acid formed. Bird and Diggs supposed that the formation of phosphorous acid was due to the reduction of the phosphoric acid by the excess of phosphorus, but this is most improbable. The further reaction between the phosphorous acid formed and the silver nitrate still in solution would, of course, introduce a complication, but experiments made to test this reaction showed that it was negligible in the concentrations used.

Phosphorus sticks were placed in solutions of silver nitrate and the amounts of phosphorous acid and of silver salt in the solution were determined at intervals. Phosphorous acid was estimated by the iodimetric method of Boyer and Bauzil (*J. Pharm. Chim.*, 1918, **18**, 321), after the excess of silver salt had been precipitated with potassium iodide. The results of several experiments are in Table III.

TABLE III.

Expt.	$AgNO_3$.	Ag pptd. (= a).	% of total Ag pptd.	H_3PO_3 (= b).	Ag : H_3PO_3 (= a/b).	$\frac{a-a_0}{b-b_0}$.
1	0·10	0·0704	70	0·01070	6·6	—
		0·0846	85	0·01286	6·6	6·6
		0·0975	98	0·01496	6·5	6·4
2	0·10	0·0099	9·9	0·00124	8·0	—
		0·0323	32	0·00488	6·6	6·2
		0·0420	42	0·00654	6·4	6·1
		0·0492	49	0·00770	6·4	6·1
		0·0988	99	0·01638	6·0	5·9
3	0·481	0·0695	14	0·00804	8·7	—
		0·0850	17	0·01038	8·2	6·6
		0·1240	25	0·01618	7·7	6·7
		0·425	85	0·0619	6·9	6·4
4	0·502	0·0755	15	0·00676	11·2	—
		0·0825	16·5	0·00794	10·5	5·9
		0·0910	18·4	0·00922	10·0	6·3

With $N/10$-solutions, the ratio of silver precipitated to phosphorous acid formed (Ag : H_3PO_3) is fairly constant, with the exception of one determination which was made near the beginning of the reaction. In Expts. 3 and 4, $N/2$-silver nitrate was used and determinations of the ratio Ag : H_3PO_3 were made before 25% of the total silver had been precipitated. The results are higher and not constant. If, however, the values of silver precipitated and phosphorous acid formed are plotted against one another, the points lie on straight lines having a slope corresponding to a constant ratio of Ag : H_3PO_3 of 6·3 : 1. By subtracting in each experiment the first values of silver deposited (a_0) and of phosphorous acid formed (b_0) from the subsequent values, and by using these differences to calculate the ratio Ag : H_3PO_3, fairly constant figures are obtained, as is shown in the last column of Table III.

From the quantitative experiments already mentioned, it would appear that phosphorous and phosphoric acids are produced simultaneously in constant proportion during the action of phosphorus on silver nitrate, if we neglect the first stages of the reaction. In the following table are the results of an experiment in which the phosphorous acid and the total oxidised phosphorus (H_3PO_3 + H_3PO_4) were determined in a solution of silver nitrate in contact with phosphorus, at varying intervals before the silver was completely precipitated.

TABLE IV.

H_3PO_3 ($= a$).	$H_3PO_3 + H_3PO_4$ ($= b$).	a/b.	$\frac{a-a_0}{b-b_0}$.
0·00318 ($= a_0$)	0·00367 ($= b_0$)	0·87	—
0·0107	0·0156	0·69	0·63
0·0129	0·0197	0·65	0·60
0·0150	0·0236	0·63	0·59

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

Electrochemical Nature of the Reaction between Phosphorus and Metallic Salt Solutions.

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

Experiments were made to determine whether deposition of metal would take place on any conducting surface in contact with the phosphorus. Platinum, gold, silver, and carbon were kept in contact with phosphorus sticks immersed in solutions of silver nitrate or of copper sulphate. In every case silver or copper was deposited on the conducting surface at points far removed from the phosphorus. No metal was deposited on non-conducting surfaces in contact with the phosphorus, such as glass, or on a conducting surface which did not touch the phosphorus.

These experiments suggest that an action of an electrochemical nature is taking place and this is shown more clearly by the following experiment. A stick of phosphorus was fused on to a platinum wire and placed in a porous pot containing $N/10$-silver nitrate and standing in a beaker filled with silver nitrate of the same concentration. The free end of the platinum wire was bent over so as to make metallic connexion between the inner and outer solutions. Silver was deposited on the phosphorus and on the platinum wire in the inner solution, and after some time the platinum wire dipping into the outer solution was covered with a bright deposit of crystalline silver. Silver was also deposited on the outer wall of the porous diaphragm at points which had apparently no metallic connexion with the platinum wire or with one another. In experiments in which no platinum wire was used, a stick of phosphorus alone being placed in the inner solution, deposition of silver again took place on the outer wall of the porous cell. This was found to be due to silver being deposited in the pores of the diaphragm, thus establishing metallic connexion between the inner and outer solutions. Deposition of silver on the outer wall of the diaphragm took place only when the inner wall was in metallic connexion with the phosphorus. Similar results were obtained by using solutions of silver sulphate or silver acetate.

In all these experiments metal ions were discharged and metal deposited—in some cases at a considerable distance from the surface of the phosphorus—only at such points as were in metallic connexion with the phosphorus surface, the contact being established either by the metal already deposited or by another conductor. The physical state of the silver and copper deposited by means of phosphorus in these experiments strongly resembled the state in which these metals are deposited from their salt solutions by an electric current. These facts favour the view that an action of an electrochemical nature takes place, *i.e.*, a direct discharge of ions to the metallic state.

Formation of a Phosphide.

The quantitative results show that owing to the formation of a phosphide in the early stages of the reaction the precipitation of he silver is not accompanied by the oxidation of an exactly quivalent amount of phosphorus. It was not found possible to scertain the constitution of the phosphide formed, but indirect vidence indicates the probability that it is the compound Ag_3P. Moser and Brukl (*Z. anorg. Chem.*, 1922, **121**, 80) obtained this ompound by the action of phosphine on silver nitrate solution nd showed that it was an unstable substance capable of reacting ith an excess of silver salt to give metallic silver and acids of hosphorus. The phosphide obtained by the action of phosphorus n silver nitrate was likewise decomposed by excess of silver salt. he deposit obtained by keeping a stick of phosphorus in silver trate solution for a short time was separated from the phoshorus, washed, and placed in *N*/10-silver nitrate. Ten c.c. of this lution, immediately after introduction of the silver deposit, were uivalent to 9·85 c.c. of a thiocyanate solution. After a few days, 10 c.c. required only 9·05 c.c. of the thiocyanate, and the solution gave a precipitate with ammonium molybdate, thus showing that silver had been precipitated and phosphorus oxidised.

The work of Christomanos (*Z. anorg. Chem.*, 1904, **41**, 309) on the action of phosphorus dissolved in ether or in benzene on solutions of copper salts pointed to the formation of a phosphide having the formula Cu_5P_2. In the case of silver salts, a black phosphide was formed, but no definite compound was isolated. Experiments were made to determine the constitution of the phosphide obtained by shaking a solution of silver nitrate with solutions of phosphorus in ether, benzene, and carbon disulphide. The black precipitate so obtained became greyer in colour after standing in contact with excess of silver salt, and it gradually assumed the appearance of metallic silver. The proportion of silver to phosphorus in the black precipitate first formed varied considerably owing to the difficulty in washing it free from excess of phosphorus without causing decomposition. The values obtained for the ratio Ag :P in the washed, but damp, precipitate varied between 2·5 : 1 and 3·9 : 1. It seems probable that, in this case also, Ag_3P is formed.

After a solution of silver nitrate had been shaken with a solution of phosphorus, the aqueous layer always contained phosphorous and phosphoric acids. The ratio of silver precipitated to phosphorus oxidised was determined. In the early stages, when the precipitate was quite black and consisted almost entirely of phosphide, high values of the order of 10 : 1 were obtained for the ratio Ag : P. When the mixture had stood for several days until the precipitate appeared to consist wholly of metallic silver, the ratio Ag : P lay between 5 : 1 and 3 : 1, *i.e.*, the values were of the same order as those obtained in the experiments with phosphorus sticks. The presence of phosphorous acid in the above experiments was due to the first reaction, *viz.*, the formation of phosphide. Silver phosphide, prepared by the action of phosphine or of solutions of phosphorus in various solvents, was washed and placed in a fresh quantity of silver nitrate solution. The phosphide was slowly oxidised to silver and phosphoric acid, no phosphorous acid being produced.

Action of Phosphorus on Solutions of Copper Salts.

The amount of phosphide formed in the case of copper salts was quite appreciable. Experiments with *N*/10-copper sulphate showed that, at the point corresponding to complete precipitation of the copper, about 13% of the total phosphorus which had reacted was present as phosphide, the remainder being in the solution as phosphorous and phosphoric acids. In the case of silver salts, practically all the phosphorus which had reacted was present in the solution as oxy-acids.

If, however, the stick of phosphorus covered with the deposit of phosphide and copper was kept in contact with the solution for a long period, more phosphorus was oxidised, even if atmospheric oxygen was excluded, and eventually no phosphide was left in the deposit. This disposes of the suggestion of Bird and Diggs, who stated that the bright deposit of copper on remaining in contact with the phosphorus was gradually converted, as a secondary reaction, 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, but it then contained no phosphorus. The deposit obtained from copper nitrate solutions retained its bright coppery colour for months. The experimental evidence shows that the phosphide formation takes place between phosphorus and metal ions, and not between phosphorus and the metal.

A determination was made of the ratio between the amounts of copper precipitated and of phosphorus oxidised before complete precipitation of the metal, the procedure being the same as in the case of silver nitrate. *N*/10- and *N*/2-Solutions of copper sulphate and copper nitrate were used. Copper was estimated in the solution volumetrically by means of thiosulphate solution. The values of copper precipitated and of phosphorus oxidised, expressed in g.-atoms per litre, are in Table V, the concentrations of copper salts being expressed in g.-mols. per litre.

TABLE V.

Expt.	Cu salt.	Time (hrs.).	Cu pptd. (= a).	P oxid. (= b).	Cu : P (= $2a/b$).	$\frac{a-a_0}{b-b_0}\times 2$.
1	0·05	39	0·0351	0·0145	4·8	—
	$CuSO_4$	47	0·0394	0·0170	4·6	3·8
		69	0·0470	0·0209	4·5	3·8
2	0·05	39	0·0319	0·0135	4·7	—
	$Cu(NO_3)_2$.	47	0·0361	0·0156	4·6	4·1
		69	0·0445	0·0199	4·5	3·9
3	0·25	48	0·1523	0·0622	4·9	—
	$CuSO_4$	88	0·2407	0·1051	4·6	4·1
4	0·25	40	0·1437	0·0549	5·2	—
	$Cu(NO_3)_2$	88	0·2483	0·1115	4·5	3·7

The values of the ratio Cu : P have all been multiplied by 2 in order to make them comparable with the values of Ag : P. It will be seen that the value of Cu : P depends on the extent to which the reaction has proceeded. If, however, this ratio is calculated as shown in the last column, the disturbing effect of phosphide formation near the beginning is avoided and more constant values are obtained. As in the case of silver nitrate, after the reaction between phosphorus and the metallic salt has proceeded for some time, 1 atom of phosphorus is oxidised for every 4 equivalents of the metal deposited.

Discussion and Summary.

From the experiments with silver and copper salts it appears that when a stick of phosphorus is placed in a solution of the metallic salt solution a reaction proceeds in two distinct stages. The first process is the formation of a black phosphide on the surface of the phosphorus; at the same time, the solution is found to contain phosphorous acid. After a layer of the phosphide has been formed, metal begins to be deposited in a bright crystalline state, and phosphorus is oxidised to phosphorous and phosphoric acids. During this stage, approximately 4 equivalents of the metal are deposited for every atom of phosphorus oxidised.

With regard to the formation of a phosphide, there can be little doubt that it is due to the prior production of phosphine by the action of phosphorus on water, another portion of the phosphorus being simultaneously oxidised to phosphorous acid. Strong evidence for this view is obtained from the exact parallelism which exists between the actions of phosphorus and phosphine on salt solutions of the heavy metals; only those metallic salt solutions which give phosphides by the action of phosphine are able to react with phosphorus. Cross and Higgins (J., 1879, **35**, 255) found that boiling water was decomposed by phosphorus, which was partly reduced to phosphine and partly oxidised to oxy-acids, and that, in the absence of oxygen, decomposition of the water took place only in the presence of certain metallic salts.

It is suggested, therefore, that the first stage in the action of phosphorus on the metallic salt takes place as follows (M and X representing an equivalent of the positive and negative radicals, respectively):

$$\left.\begin{array}{r}2P + 3H_2O = PH_3 + H_3PO_3\\ PH_3 + 3MX = PM_3 + 3HX\end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The appearance of a deposit of the metal evidently depends on the preliminary formation of the phosphide. It has already been shown that the phosphides of silver and of other metals are capable of reacting with excess of the metallic salt to give the metal and phosphoric acid. The second stage, therefore, appears to be

$$M_3P + 5MX + 4H_2O = 8M + 5HX + H_3PO_4 \quad . \quad . \quad (2)$$

According to these equations, 4 equivalents of the metal should be deposited for every atom of phosphorus oxidised, and this was the ratio actually obtained with silver and copper salts. The amount of phosphorous acid, however, was somewhat greater than that required by these equations. It is quite possible that this may be due to the following reaction proceeding to a small extent along with reaction (2):

$$M_3P + 3MX + 3H_2O = 6M + 3HX + H_3PO_3 \quad . \quad . \quad (3)$$

As regards the phenomena which have been described as electrochemical, it must be assumed that reaction (2) is responsible for their appearance. This reaction consists essentially in the discharge of positive metal ions while phosphorus becomes oxidised, *i.e.*, loses electrons. The ionic process may be represented as $M_3P + 5M^{\cdot} = 8M + P^{\cdot\cdot\cdot\cdot\cdot}$, the positive phosphorus ions reacting immediately with water to form phosphoric acid. According to this view, the $P^{\cdot\cdot\cdot\cdot\cdot}$ ions constitute an intermediate stage in the transition from phosphide to phosphoric acid. The discharge of $M^{\cdot}$ ions and the formation of $P^{\cdot\cdot\cdot\cdot\cdot}$ ions may occur at points widely separated from one another, provided that a metallic conducting path be available for the passage of the necessary electrons.

In conclusion, I wish to thank Professor Sir James Walker, F.R.S., for his interest and helpful advice during the course of this work.

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[*Received, March* 10*th*, 1926.]