CXVI.—*The Reaction between Phosphorous Acid and Mercuric Chloride.*

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THE reaction between phosphorous acid and mercuric chloride has been the subject of several researches, and the various conclusions have been very different. Montemartini and Egidi

(*Gazzetta*, 1902, **32**, ii, 182) concluded that the reaction was of the third order in very dilute solution, but their velocity coefficients were by no means constant. They did not attempt to trace the cause of the deviations from constancy, and their experimental results were so erratic that they probably attributed to experimental error the fact that the curve plotted therefrom is nearly linear over a considerable range. A " lag " in the precipitation of mercurous chloride, which they observed, has not been noticed by any other author. Garner, Foglesong, and Wilson (*Amer. Chem. J.*, 1911, **46**, 361) found that the reaction was quadrimolecular, but it was pointed out by the abstractor (Bray, *Chem. Abs.*, 1912, **6**, 17) that they had applied a formula which requires that both reactants should be present in equivalent proportions, whereas this requirement was not fulfilled in their experiments. Garner (*ibid.*, 648) acknowledged the justice of this criticism and promised to publish re-calculations, but these have not yet appeared. Linhart (*Amer. J. Sci.*, 1913, [iv], **35**, 353) found the reaction to be unimolecular with regard to phosphorous acid, the mercuric chloride functioning as the square root of its concentration, a behaviour which was attributed to the complex $H_2Hg_2Cl_6$, other possible complexes being inactive, but this hypothesis does not account for reactions in which hydrochloric acid is not present initially. He and Adams (*J. Amer. Chem. Soc.*, 1917, **39**, 948) subsequently gave reasons for supposing that the mercuric chloride was reduced to the metal, which reacted instantly with more mercuric chloride to give mercurous chloride. Purkayostha and Dhar (*Z. anorg. Chem.*, 1922, **121**, 156) studied the same reaction and concluded that it was bimolecular for phosphorous acid and semi-molecular (compare Linhart) for mercuric chloride, but they carried out only a few experiments, as their main object was the investigation of the induction of the reaction.

In studying the parallel reaction between phosphorous acid and iodine (J., 1923, **123**, 2241), the author drew attention to the fact that the course of many reactions is obscured by the application of the process of integration to results which do not justify it, and that marked drifts in the course of a reaction may be almost entirely without effect on an integrated velocity coefficient. A review of the work cited above showed that in no case was the indiscriminate use of integration warranted, and it seemed probable that the use of velocity differentials might aid the elucidation of the reaction, especially in view of certain new facts with regard to phosphorous acid which were discovered in its reaction with iodine. These facts were, briefly, that the acid is capable of a reversible change into a second form, and that it may react in virtue of both forms simultaneously.

A few preliminary experiments in which nitric acid or sodium chloride was used in conjunction with hydrochloric acid to vary either the concentration of hydrogen-ions or that of chloride-ions independently of each other, showed that chloride-ions depressed the velocity and that, within limits (see p. 1018), hydrogen-ions accelerated it. Linhart had used only hydrochloric acid and therefore was unable to discriminate between the effects of the two ions. His conclusions as to the function of hydrochloric acid are thus irrelevant and founded upon a superficial examination of the facts.

In order to test the hypothesis developed in the case of the iodine reaction, it was necessary to devise several series of experiments under selected conditions. The clue to the behaviour of the phosphorous acid is to be found by tracing the variations of reaction velocity in relation to the concentration, not of the acid itself, but of the mercuric chloride. For various reasons, none of the data published with regard to this reaction were suitable for such a critical examination, those of Linhart, for instance, being concerned chiefly with changes in the concentration of the hydrochloric acid and involving only comparatively small changes in the concentrations of the other reactants. An important series (III) was that with $M/11$-phosphorous acid and $N/2{\cdot}2$-hydrochloric acid, the initial concentrations of mercuric chloride varying from $M/200$ to $M/6$, and it afforded an extremely good verification of the hypothesis. It was shown, when studying the reaction between hypophosphorous acid and iodine (Mitchell, J., 1920, **117**, 1324), that if only the second form of the acid reacts with the iodine, and if the attainment of equilibrium between the two forms is accelerated in both directions by hydrogen-ions, the assumption requires an expression of the type

$$(ds/dt)(1 + k_5h/a) = k_2hl \quad . \quad . \quad . \quad . \quad . \quad (1)$$

s being the amount of phosphorous acid oxidised in the time t, h, l, and a being the concentrations of hydrogen-ions, phosphorous acid, and mercuric chloride respectively, and k_2 and k_5 being constants (see p. 1024). All concentrations are in moles per litre, and time is expressed in hours. For initial velocities, h is constant throughout this series, and the expression can be written

$$ds/dt(1 + r_1/a) = r_2l\,;$$

for six experiments in which a varied from 0·159 to 0·0045, the results could be closely represented by constant values of 0·0208 and 0·0222 for r_1 and r_2 respectively.

The reason for the partial success of the assumptions of Linhart and of Purkayostha and Dhar is now apparent. These authors assumed the velocity to vary as the square root of the mercuric chloride concentration; this assumption requires an expression of the type $ds/dt = rl\sqrt{a}$, and, as may be seen from the initial velocities, v_0, in experiments of this series, this holds fairly well within the range 0·0091 — 0·0364 for a if r = 0·0730, but breaks down outside this range (Table I). The experimental error on the initial velocity is of the order of 2 or 3 per cent.

TABLE I.

Expt.	a.	$10^6 \times v_0$.	$10^6 \times 0{\cdot}0730 \times l\sqrt{a}$ (old formula).	$\frac{10^6 \times 0{\cdot}0222\, l}{1 + 0{\cdot}0208/a}$ (new formula).	Deviation per cent.	
					Old.	New.
T	0·00455	360	449	363	24·7	0·8
G	0·00909	630	633	616	0·5	2·2
H	0·01818	925	898	943	3·0	1·9
I	0·03636	1260	1268	1286	0·6	2·0
J	0·0909	1660	2004	1646	20·7	0·8
W	0·1591	1810	2652	1789	46·5	1·2

Similarly, any other value which might be chosen for r would hold only over a limited range: thus, if r be chosen to give an average deviation of zero, the positive deviations range from 5 to 29 per cent. and the negative from 12 to 15 per cent.

The two expressions under discussion are identical when $rl\sqrt{a} = r_2l/(1 + r_1/a)$, or, substituting values for r, r_1, and r_2, when a = 0·011 or 0·040, these being the roots (other than zero) of the equation. This corresponds with the range indicated and differences between the two expressions are small within this range, but increase rapidly outside it. If Purkayostha and Dhar or Linhart had worked over wider ranges of concentration, they would have noticed the failure of their expression, and, as has been previously mentioned, the process of integration gave a false appearance of validity to the erroneous expression owing to the fact that considerable deviations in the later stages of an experiment do not carry much weight in an integrated constant. This may be shown graphically by a consideration of, for example, a unimolecular reaction. If, as is usual, time is plotted against amount changed (s), considerable deviations in the later stages of the curve have only a small effect on the total area which represents s/k, this area being bounded by the s-axis, the s-asymptote, the moving t-ordinate, and the curve itself, k being the velocity coefficient.

In further support of this hypothesis, it may be mentioned that experiment W gives a unimolecular velocity coefficient for phosphorous acid alone while the concentration of mercuric chloride is decreasing from 0·1591 to 0·0727 * (Table II), thus indicating

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* The differential velocity curve falls after this stage, but the integrated velocity coefficient shows no fall till after the next determination. In this particular table, variation of hydrogen-ions is ignored: if this is taken into account, the fall in the value of the velocity coefficient is noticeable at an earlier stage.

that the measurable reaction concerns only the phosphorous acid, since the mercuric chloride is not in excess but is actually in a stoicheiometric deficiency. Obviously, therefore, a necessary antecedent of reaction is a re-arrangement or activation of the phosphorous acid molecule, and the rate of reaction is limited by the maximum rate at which this can take place. As the concentration of mercuric chloride falls, the reaction in which it takes part becomes slower and affects the measurable rate of reaction. All the evidence supports the conclusion that the function of the mercuric chloride is unimolecular in the reaction concerning it. One can therefore postulate the reactions (I) and (II), in which (I) is always of measurable dimensions, whereas (II) is comparatively fast if mercuric chloride is in considerable concentration :

$$H_3PO_3 \text{ (normal form)} \rightleftharpoons H_3PO_3 \text{ (second form)} \quad . \quad . \quad \text{(I)}$$

$$H_3PO_3 \text{ (second form)} + HgCl_2 + H_2O = Hg + H_3PO_4 + 2HCl \text{ (II)}$$

assuming, with Linhart, that these are followed instantly by

$$Hg + HgCl_2 = Hg_2Cl_2 \quad . \quad . \quad . \quad . \quad \text{(III)}$$

Table II.

t.	*s.*	*a*−2*s*.	*l*−*s*.	Unimolecular co-efficient for *l*−*s*.
0	—	0·1591	0·09110	—
1·05	0·00187	0·1554	0·08923	0·0197
2·2	0·00382	0·1515	0·08728	0·0194
3·5	0·00610	0·1469	0·08500	0·0198
4·85	0·00825	0·1426	0·08285	0·0196
6·65	0·01134	0·1364	0·07976	0·0200
8·85	0·01485	0·1294	0·07625	0·0201
14·4	0·02282	0·1135	0·06828	0·0200
19·3	0·02940	0·1003	0·06170	0·0201
24·2	0·03487	0·0894	0·05623	0·0199
32·0	0·04321	0·0727	0·04789	0·0201
44·2	0·05350	0·0521	0·03760	0·0200
64·2	0·06424	0·0306	0·02686	(0·0190)

This series is, however, a special case, inasmuch as the high concentration of hydrogen-ions not only emphasises the reactions (I) and (II), but also represses another reaction, and moreover, the high concentration of chloride-ions also represses a further reaction. These obscured reactions can be detected under other definite conditions.

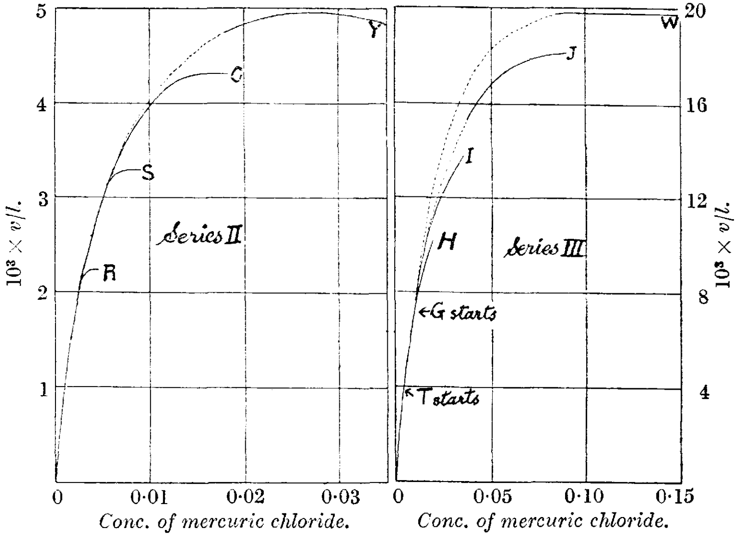
When no extraneous chloride-ion is present initially, the reaction is extremely rapid, but falls off very quickly as chloride-ions accumulate in the course of the reaction; thus, in experiment N, where only $HgCl_2 = 0{\cdot}1818$ and $H_3PO_3 = 0{\cdot}0911$ are present initially, the amounts of mercuric chloride reduced in successive periods of $\frac{1}{2}$-hour are 0·00390, 0·00188, 0·00144, and 0·00114 moles per litre, although the decrease in concentration of these two reactants during the whole 2 hours is less than 5 per cent., the increase in hydrogen-ion concentration being about 10 per cent. The only ionic or molecular species which alter greatly during this time are the chloride- and $HgCl^{\bullet}$-ions, and the rapid reaction is attributed to the latter, since it is the only possible constituent which could be so sensitive to the increase of chloride-ions, the precise extent of which is shown in Table VI. Also, since reaction is faster than the possible rate of formation of the second form of phosphorous acid, it must be due to the normal form. Thus one has

$$H_3PO_3 \text{ (normal form)} + HgCl^{\bullet} + H_2O \longrightarrow Hg + H_3PO_4 + 2H^{\bullet} + Cl' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (IV)$$

If the reaction is conducted in the presence of sufficient sodium acetate to neutralise mineral acid, it becomes of quite a different order of velocity. For instance, $M/55$-mercuric chloride and $M/11$-phosphorous acid with approximately $N/2$-sodium acetate and $N/12$-acetic acid give 96 per cent. of the total reaction within 9 minutes, whereas in the presence of hydrogen-ion concentrations of the order of $N/10$ this extent is not attained in less than 24 hours. This is definite evidence of a reaction which is obscured under other conditions. It will be referred to as reaction (V) and is analogous to one of the reactions between phosphorous acid and iodine which has been shown to be due to the normal form of phosphorous acid and predominates in weakly acidic solutions.

A further reaction can be detected by an examination of curves derived from experimental results (Figs. 1 and 2). If v/l is plotted as ordinate, v being the velocity ds/dt, against a as abscissa, the slight branches from the main curve for any one series show that an experiment which has just been started has a lower value for v/l than a similar one having all other conditions comparable but which is already in progress. In the curves each experiment is represented by a full line only over a range such that the concentration of hydrogen-ions has not changed beyond a limit of 10 per cent.; a broken line indicates that this limit has been exceeded. The beginning of each experiment is indicated, with this restriction when necessary, and the end of each is also shown because, when a becomes small, the velocity tends to become independent of hydrogen-ion concentration, since the expression (1) approaches the form $k_5v/a = k_2l$ and all curves merge in the same "stem." When a is large, the increase in hydrogen-ion concentration, as reaction proceeds, may cause a rise in the curve as indicated by that for experiment Y. It should be emphasised that the branching is far outside the limits of experimental error, since in many cases the first portion of the curve is very closely linear over a considerable range. The deduction to be drawn from these curves is that a part of the reaction velocity is contributed by an intermediate additive compound which is only formed slowly, taking some time to attain its maximum, and which is lacking at the beginning of an experiment. This also tends to account for another pronounced feature of several reactions, namely, as mentioned above, that reduction is very nearly a linear function of time throughout a large proportion of the total reaction; for instance, in experiment F no change can be detected in reaction velocity while the mercuric chloride decreases from 0·036 to 0·022, the other constituents being in relatively high concentration. This linearity is doubtless the result of two opposing tendencies: the gradual accumulation of the intermediate compound tends to increase the velocity, while the reactions (I) and (II) tend to decrease only slowly—considerably more slowly than *a* decreases—owing to the form of expression (1).

FIG. 1. FIG. 2.



The linear portion described above has to be neglected in calculating constants for these experiments according to the expression (4) (p. 1024) and the initial velocities are used separately to calculate other values in this expression. The difference between the two pairs of values thus calculated for a series is very slight in Series III (with *N*/2·2-hydrochloric acid) where the linear portion and the branching are both slight, but is more distinct in Series II (with *N*/11-hydrochloric acid) where both the linear portions and the branching are more pronounced. The difference between the experimental velocity at any stage of an experiment and the velocity calculated from the expression for the initial velocities of the corresponding series gives a measure of the formation of the intermediate compound. This is illustrated by experiment S in Table III; v_i is the velocity calculated from the initial velocities of the series as being equal to $10^{-6} \times 0{\cdot}0477hl/(1 + 0{\cdot}0577/a)$, and v_s, the "stem" velocity calculated from the expression $v_s \times 10^6 = 0{\cdot}046hl/(1 + 0{\cdot}038/a)$ as given by experiments V and Y (see Table IV), is also shown. It will be noticed that the experimentally-found velocity agrees with the stem velocity, within the limits of experimental error, after the stage at which the intermediate compound, as represented by the difference column, attains its maximum.

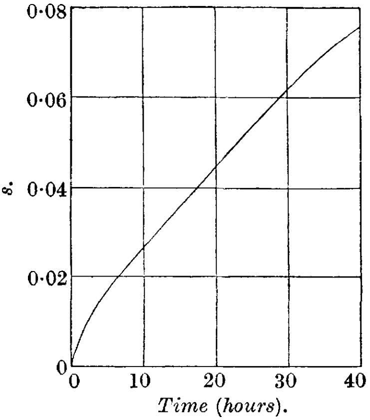
TABLE III.

(hl = 0·0108 = constant).

a = $HgCl_2$.	$v \times 10^6$ (found).	$v_i \times 10^6$.	Diff. $\times 10^6$.	$v_s \times 10^6$ (calc.).
0·009	301	297	(−4)	331
0·008	300	281	19	318
0·007	297	264	33	301
0·006	283	243	40	275
0·005	261	219	42	259
0·004	233	191	42	230
0·003	195	157	38	195
0·002	146	116	30	148
0·001	87	65	22	87

An examination of the results of previous workers shows that the linearity would not be expected in the work of Linhart or of Garner, Foglesong, and Wilson, since they almost invariably restricted themselves to experiments in which the phosphorous acid was not greatly in excess, so that the ordinary curve, in which reduction of mercuric chloride is plotted against time, would not be linear; also, all but one of Linhart's experiments are in the presence of hydrochloric acid ranging in concentration up to $2N$, in which the main reactions (I) and (II) preponderate to such an extent as to obscure the subsidiary reactions. Curves plotted from Purkayostha and Dhar's work, however, give a definitely linear portion, since they used phosphorous acid in moderate excess, and those from the work of Montemartini and Egidi, in spite of erratic results, also give definite indications both of similar linear portions and of the large initial fall in velocity mentioned on p. 1017 as characterising experiments in which there is no extraneous chloride-ion. In the latter type of experiment the large initial fall is succeeded by a period in which the velocity is nearly constant until the last part of the reaction, when it again falls rapidly. For experiment B, which is of the type under discussion, the initial concentrations of phosphorous acid and mercuric chloride were $M/11$ and $M/55$, respectively, and Fig. 3 represents the ordinary time–reduction curve, and Fig. 4 the v/l—a curve, that is, velocity per unit concentration of phosphorous acid plotted against mercuric chloride concentration.

FIG. 3.



Still another factor has to be considered and that is the effect of the chloride-ions on reactions in which they have reduced the reaction (IV) to negligible proportions. This consideration is deferred till the discussion of results.

A detailed examination of all the experimental results has shown that in most of the cases where one or more reactions are superimposed on the reactions (I) and (II), the contribution to be ascribed to the minor reactions is too greatly influenced by experimental error to be suitable for critical examination, since this contribution

FIG. 4.

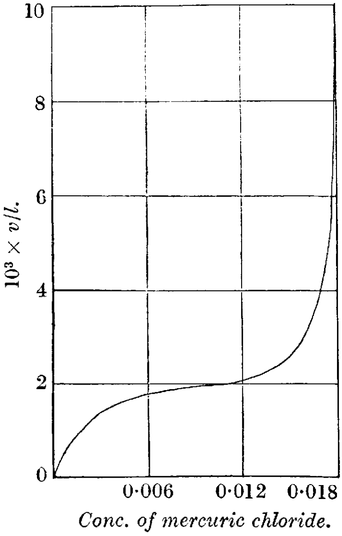
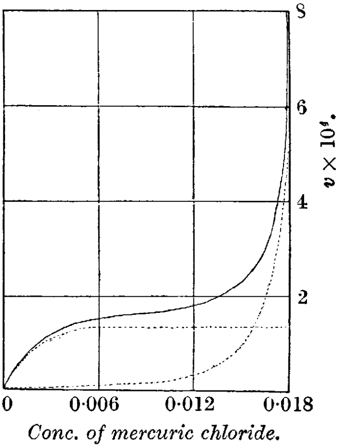


FIG. 5.



has to be ascertained by the difference between the actual experimental velocity and that calculated as being due to the reactions (I) and (II). In the circumstances, all that it is possible to do is to find the value of k_5 which gives the most consistent value for k_2 in each experiment (neglecting linear portions for reasons already advanced) and to judge the influence of the minor reactions by their effect on the values of k_2 and k_5 thus obtained. These values are recorded in Table IV. Series I is omitted from this table because the experiments were in absence of initial extraneous chloride and the initial velocity falls off so rapidly that it is impossible to represent it with any approach to accuracy.

Unfortunately, owing to the form of the v/l—a curve (for example, Fig. 1), especially in experiments which have an initial linear portion, it is necessary to resort to integration to obtain the above constants for the following reason. In early attempts by the differential method to obtain the values of v, it was assumed that the velocity corresponding to a fall from a_1 to a_2 in mercuric chloride concentration may be ascribed to a concentration of $(a_1 + a_2)/2$, but an examination of the ordinary unimolecular expression shows that this process involves an error of 1 per cent. when 0·7—0·8 of the substance has been transformed, and of 4 per cent. when 0·8—0·9 has been transformed. In a bimolecular reaction the error attains a value of 1 per cent. half-way through the reaction and increases rapidly, reaching 11 per cent. over the range 0·8—0·9 of total reaction. It is therefore evident that the method is very inaccurate when the velocity changes relatively rapidly, and in the present reaction it is only when this is the case that the desired information can be obtained, since the linear portion of the velocity curve is useless for this purpose, as already noted. Integration affords a method of avoiding this error, which would have a large incidence on the velocity differential method, and it is justified here because examination of the curves has shown them to be of the type on which the integration formula is based.

The formula used for integration in order to find k_2 and k_5 is derived in the same way as that used in studying the reaction between iodine and hypophosphorous acid (*loc. cit.*), but a modification is necessary to allow for the fact that 2 mols. of mercuric chloride are involved in the stoicheiometric equation in the place of 1 mol. of iodine. Also, the constants have been designated with different suffixes in order to bring the notation of the reaction now under discussion into line with that between phosphorous acid and iodine. The assumptions involved are that there is a reversible change between the two forms of the acid, which is accelerated in both directions by hydrogen-ions, and that the second form only reacts

TABLE IV.

Series.	Expt.	a.	HCl.	NaCl.	HNO_3.	Mean h.	Mean c.	$10^6 \times v_0$.	$10^3 \times k_2$.	$10^3 \times k_5$.	Mean α.	$\frac{k_2}{(1-\alpha)}$.	Mean f.
II	C	0·0182	0·0909	—	—	0·12	0·09	390	42—45	30—40	0·39	0·071	0·50
	R	0·0045	,,	—	—	,,	0·09	204	42	35	0·39	0·070	0·51
	S	0·0091	,,	—	—	,,	0·09	300	41	30	0·39	0·069	0·51
	V	0·0909	,,	—	—	,,	0·11	480	45–47	30—50	0·38	0·074	0·55
	Y	0·0364	,,	—	—	,,	0·12	425	47	38	0·37	0·074	0·50
III	G	0·0091	0·4545	—	—	0·41	0·40	630	52	47·5	0·25	0·069	0·18
	H	0·0182	,,	—	—	0·42	0·41	925	52	,,	,,	0·069	,,
	I	0·0364	,,	—	—	0·43	0·41	1260	53	,,	,,	0·071	,,
	J	0·0909	,,	—	—	0·44	0·42	1660	53·5	,,	,,	0·071	,,
	T	0·0045	,,	—	—	0·41	0·39	360	52	,,	,,	0·069	,,
	W	0·1591	,,	—	—	0·45	0·43	1810	53·5	,,	,,	0·071	,,
IV	E	0·0182	—	0·0909	—	0·05	0·09	150	36·5	40	0·52	0·075	0·53
	F	0·0364	—	,,	—	0·06	0·09	170	40	36—48	0·52	0·083	,,
	X	0·0909	—	,,	—	0·07	0·10	231	>50 *	—	0·48	>0·096	,,
V	U	0·0182	—	0·4545	—	0·05	0·34	127	33	40	0·51	0·067	0·20
	B′	0·0364	—	,,	—	0·06	0·35	139	(35)	40	0·51	(0·071)	0·21
	E′	0·0182	—	0·0091	—	0·05	0·02	175	48	46	0·51	0·098	0·86
	A′	0·0182	0·0455	—	—	0·09	0·05	269	42·5	36–44	0·445	0·075	0·65
	M	0·0182	0·1818	—	—	0·20	0·17	535	47	40	0·325	0·070	0·35
	O	0·0182	0·0909	—	0·0909	,,	0·09	600	43·5	(30)	0·325	0·065	0·51
	Q	0·0182	—	—	0·1818	,,	0·01	850	49	30	0·325	0·072	0·93
	L	0·0182	—	—	0·0909	0·12	0·01	545	(53)	(40)	0·39	(0·087)	0·95
	Z	0·0182	0·0455	—	0·0455	,,	0·05	390	44·5	31	0·39	0·071	0·66
	F′	0·0182	0·0909	0·3636	—	,,	0·36	335	41·5	42·5	0·39	0·068	0·20
	K	0·0182	—	—	0·4545	0·41	0·01	1175	53	28	0·25	0·070	0·93

* $k_2 = 50 \times 10^{-3}$ in $ds/dt = k_2hl$, the term involving k_5 being negligible over the range studied.

with mercuric chloride in such a way that the reaction is unimolecular with respect to the latter. Thus one has

$$(ds/dt)(1 + k_3h_t/k_4a_t) = k_2l_th_t \quad . \quad . \quad . \quad . \quad (2)$$

where the suffix t denotes concentration after time t, k_2 is the velocity coefficient of the direct change of the normal form of phosphorous acid to the second form, k_3 is that of the reverse change, and k_4 that of the reaction between the second form and mercuric chloride; the significance of a, l, h, and s has already been explained (p. 1015). Putting the ratio $k_3/k_4 = k_5$, and expressing (2) in terms of concentrations at zero-time, we have

$$(ds/dt)[1 + k_5(h + ms)/(a - 2s)] = k_2(l - s)(h + ms) \quad . \quad . \quad (3)$$

since the variation of h with s is nearly a linear function and m is a coefficient expressing this connexion. Integration gives

$$k_2t = [\log_e l/(l - s) + \log_e (h + ms)/h]/(h + ml) + \\ k_5/(2l - a)\,[\log_e l/(l - s) - \log_e a/(a - 2s)] \quad . \quad . \quad (4)$$

In the discussion it is shown that k_2 is proportional to $(1 - \alpha)$, α being the degree of ionisation of phosphorous acid, thus showing that the molecule is concerned in the preliminary change (I); and also that, when the necessary allowance is introduced for the different conditions, this velocity coefficient agrees closely with that found for the same change underlying the reaction between phosphorous acid and iodine, thus showing the essential uniformity of the change.

EXPERIMENTAL.

The method chosen for following the reaction was to weigh the mercurous chloride produced; its solubility in water at 25° is approximately 0·0002 gram in 50 c.c., which was the volume usually employed, but in the strongest chloride concentrations it is 0·0008 gram, for which allowance is made. The method necessitates the use of a separate reaction-mixture for each determination, which tends to increase the experimental error, but duplicates show that the weights of mercurous chloride rarely differed by as much as a milligram in an average weight of 0·2 gram. For each experiment a stock of 500 or 1000 c.c. was made containing all the constituents required except the phosphorous acid, and portions of 50 c.c. (or occasionally 20 or 10 c.c.) were placed in wide test-tubes, the requisite volume (usually 5 c.c.) of a molar phosphorous acid solution being added at zero-time, both solutions being at 25°.

An unexpected difficulty was encountered in drying the filtered mercurous chloride. Linhart had dried his material slowly at 85°, in order to avoid loss with the water vapour, and finally at 105°.

In the author's experiments, it was desirable to localise experimental error by restricting each experiment to as few Gooch crucibles as possible, and more rapid drying was therefore necessary. The precipitate was washed with water and subsequently with a few c.c. of alcohol and ether successively and dried for 70 minutes at 95°. At 120° there was rapid loss, 3 mg. per hour, and at 110° about 0·6 mg. per hour, in spite of the fact that the vapour pressures of mercurous chloride at these temperatures are as low as 0·02 and 0·01 mm. respectively; at 95°, no further loss was ever noticed in half-an-hour's additional heating.

The methods of calculating the hydrogen-ion concentration are the same as those used in the reaction with iodine (*loc. cit.*), since Leblanc and Noyes (*Z. physikal. Chem.*, 1890, **6**, 329) have shown that the presence of mercuric chloride does not affect it.

In the concentrations in which it was employed, nitric acid was found to have no appreciable effect on either phosphorous acid or mercurous chloride.

Discussion of Results.

Certain of the results have already been discussed in the theoretical treatment. A more general survey will now be made of the results tabulated in Table IV, which shows for each experiment, other than some of Series I, the values obtained for k_2 and k_5, or, where the values are not very definite, the range of possible values; it also indicates the initial velocity, v_0, and the mean values during each experiment of the concentrations of hydrogen- and chloride-ions, of α, the degree of dissociation of the phosphorous acid, and of f, the average proportion of mercuric chloride which exists as such and is not combined in the complex ion $HgCl_3'$. All experiments given here started with the same concentration, 0·0911, of phosphorous acid, and the initial concentrations of mercuric chloride (a), and hydrochloric acid, nitric acid, or sodium chloride are shown.

Dealing first with Series III, the validity of the same two constants for the wide range covered by the whole course of each of the six experiments is noteworthy. It is illustrated by the use of the value 0·0475 for k_5 in two experiments (J and T) which represent widely different concentrations (Table V); and in experiment W, when readings are carried beyond the stage shown in Table II, all fourteen values of k_2 are between 0·0528 and 0·0542. The same two constants also express very closely the course of the only two comparable experiments in Linhart's work, namely, those in the presence of $N/2$-hydrochloric acid. It is of interest that, just as equation (1) tends to give a unimolecular form for the phosphorous acid when the

TABLE V.

(Experiment J).

$HgCl_2$ = 0·0909, H_3PO_3 = 0·0911, HCl = 0·4545, h_0 = 0·41, m = 1·64, k_5 = 0·0475.

t.	s.	$a-2s$.	$l-s$.	$k_2\times 10^3$.
4·5	0·00722	0·0765	0·0839	54·1
6·1	0·00938	0·0721	0·0817	52·9
8·1	0·01243	0·0660	0·0787	54·0
8·65	0·01317	0·0646	0·0779	53·9
14·4	0·02015	0·0506	0·0708	53·0
18·9	0·02538	0·0391	0·0657	53·6
24·1	0·03032	0·0303	0·0608	53·6
30·0	0·03513	0·0206	0·0560	54·0
39·2	0·04011	0·0107	0·0510	53·8
				Mean 53·6

(Experiment T).

($HgCl_2$ = 0·004545; other data as for J).

t.	s.	$a-2s$.	$l-s$.	$k_2\times 10^3$.
1·0	0·000324	0·00390	0·0908	(49·2) *
2·1	0·000665	$0{\cdot}00321_5$	0·0904	52·3
3·45	0·000998	0·00255	0·0901	52·0
4·8	0·001255	0·00203	0·0898	51·3
6·6	0·001545	0·00145	0·0896	51·9
8·65	0·001782	0·00098	0·0893	52·6
14·35	0·002095	$0{\cdot}00035_5$	0·0890	(50·8)
				Mean 52·0

* Based on 0·0084 gram Hg_2Cl_2.

mercuric chloride is in high concentration, as illustrated by experiment W, so it tends towards a unimolecular form for mercuric chloride when this is in very low concentration, owing to the fact that the second form of the acid is produced as rapidly as the mercuric chloride can utilise it; in agreement with this, all the determinations in experiment T give a unimolecular velocity coefficient for mercuric chloride which only deviates by 4 per cent. from the mean value until the reaction has exceeded 90 per cent. of the whole, at which stage the remaining mercuric chloride, being obtained by difference, is too largely influenced by experimental error to be known with sufficient accuracy.

For the majority of experiments in the table, it is seen that the value of k_2 is closely proportional to $(1 - \alpha)$ and the ratio $k_2/(1 - \alpha)$ is nearly constant at 0·070: this constancy is evidence in support of the hypothesis frequently advanced by the author in dealing with the reactions of hypophosphorous acid, that the reversible change between the two forms of the acid is due, not to the ion, but to the undissociated molecule. If it were due to the ion, k_2/α should be constant, but this is far from being so. The cause of the deviations from the above generalisation is examined later.

In dealing with the reaction between phosphorous acid and iodine, it was pointed out that k_2, which was obtained by methods ignoring the hydrogen-ion concentration, was roughly proportional to this concentration. It is now seen that, when divided by the concentration, it is equal to $0{\cdot}073(1 - \alpha)$, as a mean, in four of the six series, the other two series being untrustworthy because of the large preponderance of another reaction which therefore introduces a large experimental error into the evaluation of k_2. There is thus but little doubt that in both these reactions of phosphorous acid the undissociated molecule is concerned, and the agreement between the values found for k_2 in the two reactions is cumulative (but not conclusive) evidence in favour of the assumptions involved.

Where reactions other than (I) and (II) are largely suppressed, there is good evidence that the function of the hydrogen-ion has been correctly interpreted—that it accelerates both the forward and the reverse attainment of equilibrium between the two forms of phosphorous acid.

The function of the chloride-ion has now to be considered. In the table it is seen that the chief deviations from the normal value of $k_2/(1 - \alpha)$ occur in experiments A′, E, E′, F, and X, since experiment L, having no initial extraneous chloride, is more appropriately considered with Series I. In the last one the high value of $k_2/(1 - \alpha)$ occurs with a high value of a coincident with a relatively low value of h : this divergence is attributable to reaction (V) (see p. 1018) by analogy with the iodine–phosphorous acid reaction. The first four of these experiments are characterised by low concentrations of either hydrogen- or chloride-ions or of both, so that the reaction which is suppressed by chloride-ions is still appreciable owing either to the low chloride concentration (for example, E′) or to the relative slowness of the other reaction which is accelerated by hydrogen-ions (for example, F). The phenomenon discussed with regard to Series I thus accounts qualitatively for these deviations and is applied quantitatively to experiment E′ on p. 1029, but, in the cases of experiments L and Q it is slight compared with the other reactions, which predominate in virtue of the high hydrogen-ion concentration, and in experiment K it is inappreciable for the same reason.

On the other hand, the active mass of the mercuric chloride is affected by the formation of complexes, so that even when reaction (IV) is quite suppressed the chloride-ions still have this other effect—compare experiments E and U, or F and B′. The column in Table IV which shows the proportion of mercuric chloride (f) which is not thus combined is calculated from the data of Sand (*Z. physikal. Chem.*, 1907, **59**, 424), who corrected the interpretation of Sherrill's results (*ibid.*, 1903, **43**, 705) and gave: $[HgCl_3'] = 11{\cdot}5 \times [HgCl_2][Cl']$. The values of k_5 are somewhat ill-definep because considerable variations in the value often cause comparatively small changes in k_2; but, from experiments in which the value is well established, it may be concluded that low values for the proportion of free mercuric chloride correspond with high values for k_5, that is, if a in (4) is corrected to represent a diminished active mass for mercuric chloride, k_5 would have to be proportionally diminished. It is found that the correction of a to agree with *free* mercuric chloride introduces larger deviations in the opposite direction, from which it may be concluded that the complex is not inactive, but is nearly as active as the mercuric chloride to which it corresponds, and a similar conclusion is drawn from a consideration of Series I. This conclusion is, of course, subject to modification in the sense that the increase of chloride concentration may result in a negative "salt effect."

In order to investigate more closely the reaction which predominates in the early stages of experiments in Series I, the observed velocity has been reduced by that which may be calculated as due to reactions (I) and (II) from the expression $v_1 = 0{\cdot}070(1 - \alpha)hl/(1 + 0{\cdot}03h/a)$, since k_2 has been shown to approximate to $0{\cdot}070(1 - \alpha)$, and k_5 tends towards the value 0·030 when the chloride-ion concentration is low. The residual velocity thus found, v_2, is almost entirely due to reaction (IV), and the two component velocities are indicated by broken lines in Fig. 5 for experiment B as an example, one curve being nearly hyperbolic and the other of the form required by the combination of reactions (I) and (II), which is given by the expression for v_1. When v_2 is thus obtained as the difference between v and v_1 for the experiments of Series I, in which the initial concentration of phosphorous acid is uniformly 0·0911 and that of mercuric chloride ranges from 0·1818 to 0·0045, it is found that v_2 is approximately equal to $1{\cdot}8 \times 10^{-4}al/c_1$, where c_1 represents chloride-ions which are free and not involved in the complex ion $HgCl_3'$, as found from the data of Sand previously quoted. Using the data of Morse (*Z. physikal. Chem.*, 1902, **41**, 709), which were confirmed, as to order of magnitude, by Buttle and Hewitt (J., 1908, **93**, 1405), for the first stage dissociation of mercuric chloride $[HgCl^{\bullet}][Cl'] = 28 \times 10^{-8}[HgCl_2]$, we have $a/c = [HgCl^{\bullet}]/28 \times 10^{-8} = 35{\cdot}7 \times 10^5 \times [HgCl^{\bullet}]$, whence $v_2 = 640 \times l \times [HgCl^{\bullet}]$. The application of this idea is shown in Table VI, where experiment N is analysed in this way. It will be noted that the total mercuric chloride (a) is used and not that which is free; no constancy could be obtained by the use of the latter or by any assumption involving the concentration of hydrogen-ions. The deductions to be drawn from these facts are that the complex ion $HgCl_3'$ takes part in the reaction with the same order of rapidity as the free mercuric chloride, and, secondly, that hydrogen-

TABLE VI.

t.	$v \times 10^6$.	a.	c.	c_1.	$v_1 \times 10^6$.	$v_2 \times 10^6$.	l.	la/c_1.	$v_2c_1 \times 10^4/la$.
0	?	0·1818	0·0002	—	143	?	0·0911	—	—
0·5	?	0·1779	0·0037	0·0012	149	?	0·0892	—	—
1·0	1600	0·1760	0·0054	0·0018	152	1450	0·0882	8·60	1·68
1·5	1300	0·1746	0·0068	0·0023	155	1145	0·0875	6·65	1·72
2·0	1120	0·1734	0·0079	0·0027	156	965	0·0869	5·57	1·73
3·0	900	0·1714	0·0098	0·0034	160	740	0·0859	4·35	1·70
4·0	800	0·1698	0·0113	0·0040	162	640	0·0851	3·65	1·75
6·9	640	0·1659	0·0149	0·0054	167	475	0·0831	2·58	1·84
9·15	570	0·1631	0·0175	0·0064	171	400	0·0818	2·10	1·90
14·6	470	0·1574	0·0228	0·0086	178	290	0·0789	1·45	2·00
18·9	420	0·1536	0·0263	0·0102	182	240	0·0770	1·16	2·07
24·3	373	0·1493	0·0303	0·0122	186	190	0·0748	0·92	2·06
32·3	333	0·1429	0·0352	0·0146	192	140	0·0722	0·71	1·97
47·4	298	0·1340	0·0443	0·0198	200	98	0·0672	0·46	2·13
63·4	275	0·1247	0·0539	0·0257	205	70	0·0626	0·30	2·33

A difference of 2 units in the value 70×10^{-3} for $k_2/(1-a)$ causes a difference of 9 per cent. in the value of v_2 for the last determination, and, in the same determination, the experimental error of, say, 5 units in $v \times 10^6$ causes an error of 7 per cent. in v_2.

ions do not repress this reaction, so that it should be represented as (IV) rather than as

$$HgCl_2 + H_3PO_3 \text{ (normal form)} \rightleftharpoons X + H^{\cdot} + Cl' \quad . \quad . \quad \text{(IV}a\text{)}$$

(X being an intermediate complex formed by the equilibrium) which is an alternative interpretation of the facts described on p. 1018. A slight increase in the value of v_2c_1/al, as the reaction proceeds, could be explained by an equilibrium such as $HgCl_2 + H_3PO_3$ (normal form) $\rightleftharpoons (XH)^{\cdot} + Cl'$, but the additional arbitrary constant involved would make it more probable that the better agreement obtained is purely empirical. Similar alternative mechanisms were left undecided in the parallel reaction with iodine. The value of $1{\cdot}8 \times 10^{-4}$, which is mentioned above, is the mean of a great number which vary as much as from $1{\cdot}4 \times 10^{-4}$ to $2{\cdot}3 \times 10^{-4}$, but the method of deriving v_2 is extremely sensitive to experimental error, and, as a wide range of mercuric chloride concentrations is involved (0·004 to 0·182), the deviations are not regarded as unduly large. Moreover, experiment N, covering the widest variations in conditions, offers the most stringent test available, and the rapid change in velocity is liable to cause considerable errors in this differential method.

It is of interest to note that experiment E′, which was devised to test this hypothesis, has an initial velocity of 175×10^{-6}, whereas that due to reactions (I) and (II) is calculated as 129×10^{-6}, and v_2 is calculated as equal to 42×10^{-6}—a total of 171×10^{-6}.

Summary.

1. Former investigators have obtained widely divergent results owing to failure to detect the chief underlying reaction, namely, the reversible change of the normal form of phosphorous acid to another form which is responsible for a large proportion of the reaction, except in certain circumstances (see 5 and 6). Thus one has

$$H_3PO_3 \text{ (normal form)} \rightleftharpoons H_3PO_3 \text{ (second form)} \quad . \quad . \quad \text{(I)}$$

$$H_3PO_3 \text{ (second form)} + HgCl_2 + H_2O \longrightarrow H_3PO_4 + Hg + 2HCl \quad \text{(II)}$$

$$Hg + HgCl_2 \longrightarrow Hg_2Cl_2 \text{ (instantly)} \quad . \quad . \quad . \quad \text{(III)}$$

2. Their failure is due to the indiscriminate use of the process of integration.

3. The equilibrium (I) is accelerated in both directions by hydrogen-ions, and, as in the similar reaction of hypophosphorous acid, the undissociated molecule of the normal form is concerned.

4. The velocity coefficient for the forward change in this equilibrium is shown to be in substantial agreement with that deduced for the same change which has previously been found to underlie the reaction between phosphorous acid and iodine.

5. In the absence of extraneous chloride-ions initially, another reaction preponderates until the accumulation of chloride-ions reduces it to a lower order of magnitude :

$$HgCl^{\bullet} + H_3PO_3 \text{ (normal form)} + H_2O \longrightarrow H_3PO_4 + Hg + 2H^{\bullet} + Cl' \quad . \quad . \quad \text{(IV)}$$

6. In very low concentrations of hydrogen-ions (that is, in the presence of excess of sodium acetate) yet another reaction takes place which is almost instantaneous.

7. Evidence of still another reaction, involving the formation of an intermediate compound, is also advanced.

8. The effect of these reactions being superimposed, and also the effect of chloride-ions on the active mass of the mercuric chloride, are analysed qualitatively, but only reactions (I) and (II), and, to some extent (IV), are capable of quantitative demonstration.

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