KINETICS OF THE REACTION OF IODATE ION WITH HYPOPHOSPHOROUS ACID

Thesis by

Philip Hayward

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Table of Contents

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Abstract

The hypothesis that a normal and an active form of hypophosphorous acid coexist in aqueous solution, and that the conversion of the normal to the active form can be a rate-determining step in its reactions, is supported by a study of the kinetics of its reaction with iodate ion.

The rate law

$$-\frac{d(IO_3^-)}{dt} = \frac{k_1(H^+)(H_3PO_2)}{1+\frac{k_2(H^+)}{k_3(IO_3^-)}}$$

is found to be in agreement with observation, the best values of the constants at 30° being 9.7 moles^{-1} l hr^{-1} for k_1 and 0.44 for k_2/k_3. The respective activation energies are 17 kcal. and 4.5 kcal.

It is probable that the iodate ion reacts with the active form of hypophosphorous acid at a much lower rate than do other substances conforming to this rate law. No evidence could be detected for a reaction involving the hypophosphite ion.

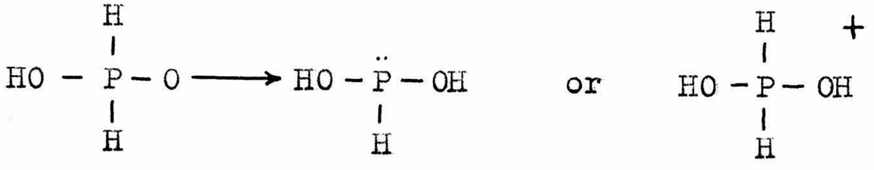
The addition of small amounts of n-propanol to the reaction mixtures is found to be helpful, in that some side reactions are thereby suppressed.

INTRODUCTION

Hypophosphorous acid, H_3PO_2, is a fairly strong reducing agent, although its action is usually slow. Studies of its oxidation have disclosed an unusual phenomenon, namely, that the rate of oxidation by many oxidizing agents becomes independent of the concentration of oxidant, when this reaches a sufficiently high level. Orlov (1) was apparently the first to advance the hypothesis that two forms of hypophosphorous acid exist in aqueous solution, and that the rate of conversion of the normal into the so-called active form determines the observed rate of reaction under certain conditions. A reaction scheme expressing this hypothesis may be written thus:

$$(H_3PO_2)_I \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (H_3PO_2)_{II} \xrightarrow{k_3} \text{products}$$

Here $(H_3PO_2)_I$ indicates the normal, $(H_3PO_2)_{II}$ the active form. The hypothesis has been refined by the assumption of a structure for the active form, as follows:



$$HO-\overset{H}{\underset{H}{P}}-O \longrightarrow HO-\overset{..}{\underset{H}{P}}-OH \quad \text{or} \quad HO-\overset{H}{\underset{H}{P}}-OH^{+}$$

although so far this seems to be only a more or less plausible guess, unsupported by direct experimental evidence. It is of interest in this connection, however, that tracer studies with deuterium (2) have shown that the free acid rapidly exchanges all three of its hydrogen atoms with water. The breaking of the phosphorus-hydrogen bond, postulated above, must therefore occur quite readily. On the other hand, the hypophosphite ion in neutral solution at room temperature does not exchange hydrogen with water to any marked extent (3), a fact which, in the light of the above hypothesis, is also in agreement with some observations on the reactivity of hypophosphites.

The interconversion of the two forms of hypophosphorous acid was shown by Mitchell (4) to be acid-catalyzed, and Griffith, McKeown and Taylor (5), in a later, more detailed investigation, showed this reaction to be subject to general acid catalysis.

On the basis of these facts and the above reaction scheme, Mitchell has derived a rate law in the following manner. Let

P_{II} = concentration of active hypophosphorous acid

P = total concentration of hypophosphorous acid
X = concentration of oxidizing agent
H = concentration of hydrogen ion
Z = concentration of some reaction product -- e.g., phosphorous acid

Then
$$dZ/dt = k_3 P_{II} X \qquad (1)$$

We now assume (a) that equilibrium between normal and active hypophosphorous acid is maintained, (b) that P_{II} is always a very small fraction of P. Then we have

$$k_1 HP = k_2 HP_{II} \qquad (2)$$

$$dP_{II}/dt = k_1 HP - k_2 HP_{II} - dZ/dt \qquad (3)$$

Eliminating P_{II} and dP_{II}/dt between (1) and (3), we get

$$Xd^2Z/dt^2 + (dZ/dt)^2 = k_3 X^2 (k_1 HP - dZ/dt(1 + k_2 H/k_3 X)) \qquad (4)$$

Neglecting the terms on the left-hand side of (4) as being of a lower order of magnitude (also of opposite sign), we obtain the final rate law

$$dZ/dt = k_1 HP/(1 + k_2 H/k_3 X) \qquad (5)$$

(5) obviously expresses the experimental fact that the rate becomes independent of X, the concentration of oxidizing agent, for X sufficiently large.

It should be observed that since the reaction is subject to general acid catalysis, (5) is really a special case of a more inclusive expression, which, following Griffith, McKeown and Taylor, may be written

$$dZ/dt = (\sum k_1^a\,[HA])P/(1+\sum k_2^a\,[HA]/k_3X) \qquad (6)$$

Here HA is any substance capable of yielding a proton, such as water, bisulfate ion, undissociated hypophosphorous or phosphorous acid, etc., and k^a is the corresponding catalytic coefficient.

The reactions of a number of oxidizing agents, including iodine (4), (5), bromine, chlorine (6), cupric ion (7), mercuric ion (8), and silver ion (9), have all been shown to conform to this rate law. Dichromate ion, however, has been found not to behave in this way (10), showing that reductions with hypophosphorous acid do not always go primarily by means of the above mechanism.

The central point of the problem is, of course, to get further evidence about the nature of the supposed active form of hypophosphorous acid. For lack of any more direct approach to the question, I proposed to study the action of certain other oxidizing agents, to see whether they also fitted into the general reaction scheme outlined above.

SPECTROPHOTOMETRIC INVESTIGATION OF HYPOPHOSPHOROUS ACID AND HYPOPHOSPHITE ION

One direct attack on the problem of the nature of the "active" form of hypophosphorous acid that at first sight showed some promise was the determination of the absorption spectrum of aqueous solutions of the acid. With the aid of a Beckman quartz spectrophotometer, this project was carried out. In addition to aqueous solutions of the acid, solutions of the acid in several ethanol-water mixtures were examined, on the theory that the tautomeric equilibrium $(H_3PO_2)_I \rightleftarrows (H_3PO_2)_{II}$ might be shifted in the presence of ethanol; an aqueous solution of barium hypophosphite was also studied. The results are shown in Fig. 1. The flattening of the absorption curve of hypophosphorous acid in water at about 250 mu may well be due to the effect of the hypophosphite ion, since this flattening is most pronounced with a solution of barium hypophosphite, and is wiped out to a considerable extent by the addition of ethanol. Any maxima in the curves come at wavelengths too short to be reached with the instrument used. The data obtained give no evidence for the existence of two forms of hypophosphorous acid.

THE IODATE-HYPOPHOSPHOROUS ACID REACTION

Previous work.-- No detailed kinetic study of this reaction seems to have been made. Hovorka (11) has published some observations on the nature of the reaction in both acid and basic solution, mainly at 100°. Neogi and Sen (12) have reported the existence of an induction period, which may be varied by addition of one of a number of substances.

Experimental.-- C. P. chemicals were used in general, and solutions were made up using ordinary distilled water. For about half of the experiments, stock solutions of hypophosphorous acid were prepared, either by treating phosphorus with barium hydroxide and obtaining the acid from barium hypophosphite, or by converting sodium hypophosphite to the acid by means of an Amberlite ion-exchange column. These solutions contained various amounts of phosphorous acid, the mole percentage being in no case higher than 4. For the rest of the experiments, stock solutions of sodium hypophosphite were used; these always contained negligible amounts of phosphite. Sulfuric acid was used when additional acid was needed. On occasion, the ionic strengths of the reaction mixtures were varied by adding potassium nitrate.

The reactions were usually carried out in glass-stoppered flasks placed in a water bath, the temperature of which was kept constant within 0.02°. Samples of the reaction mixture were analyzed for iodate by running them into acidified potassium iodide solution and immediately titrating the iodine liberated with thiosulfate. Experiment showed that the error caused by the iodine-hypophosphorous acid reaction in this procedure is negligible.

The reaction rates in this discussion are all given with respect to iodate ion, the units being moles per liter and hours. For purposes of calculation, the iodate concentrations were plotted against time on a large scale and a smooth curve was drawn through the points. From these graphically smoothed data the rates of reaction at various times were found by numerical differentiation. These rates were also smoothed graphically, and the smoothed values used in the calculation of rate constants. Eq. (5) was used as the rate expression for this purpose, rather than the more complicated (6), for the pragmatic reasons that the results thus obtained were sufficiently accurate to display the main features of the reaction, and that the calculations were much simpler. It must therefore be remembered that the values of the rate constants presented in this investigation are actually sums of several terms; however, the experimental conditions were almost always such that the dominant term was that corresponding to the hydrogen ion concentration.

The concentrations of undissociated hypophosphorous acid were calculated from the formula

$$[H_3PO_2] = \frac{[H^+]}{(K_c + [H^+])} \left([\Sigma H_3PO_2]_o - 3 \; [IO_3^-]_o \right) + \frac{3 \; [H^+]}{K_c + [H^+]} [IO_3^-]$$

which is based on reaction (7) below. Here K_c is the concentration ionization constant of hypophosphorous acid, and $[\Sigma H_3PO_2]_o$ and $[IO_3^-]_o$ are the initial concentrations of "total" hypophosphorous acid and iodate. The values of

K_c at various ionic strengths were taken from curves based on the following data of Griffith, McKeown and Taylor (5):

Table 1

Variation of K_c for Hypophosphorous Acid
With Ionic Strength

Temp.	μ	0.16	0.57	1.13	2.13
30°	K_c	.075	.079	.074	.056
16°	K_c	.096	.106	.094	.071

The data reported in the present study were taken at 30° and 20°. In order to get values of K_c at 20°, it was therefore assumed that K_c varies linearly with temperature at each value of the ionic strength, the following values being derived.

Table 2

Variation of K_c for Hypophosphorous Acid
at 20° With Ionic Strength

μ	0.16	0.57	1.13	2.13
K_c	.090	.098	.088	.067

The calculations of hydrogen ion concentrations were based on the extensive data of Harned and Hamer (13) on the activity coefficients of sulfuric acid. It is easily shown that, for the bisulfate ion

$$K_c = K_a/\gamma_{H_2SO_4}$$

where K_a is the thermodynamic ionization constant of bisulfate ion, $\gamma_{H_2SO_4}$ the activity coefficient of sulfuric acid, and K_c the "concentration" ionization constant of bisulfate ion. The values of $\gamma_{H_2SO_4}$ at 20° and 30° were got by interpolation from Harned and Hamer's data at 15°, 25°, and 40°, and using the values $K_a = 0.0113$ at 30° and $K_a = 0.0127$ at 20° (Hamer (14)), the following sets of values of K_c were obtained.

Table 3

Variation of K_c for Bisulfate Ion With Ionic Strength

μ	K_c	
	20°	30°
0.0	0.0127	0.0113
0.2	.027	.026
0.4	.046	.045
0.6	.066	.065
0.8	.079	.081
1.0	.089	.090
1.2	.093	.094
1.4	.095	.098
1.6	.096	.101

No correction was made in the calculation of hydrogen ion concentrations for the disappearance of hypophosphorous acid, both because the phosphorous acid produced is of approximately the same strength (5) and because actual measurements with a pH meter showed (with the exception of one class of experiments) no important changes in acidity. The exceptions to this occurred when n-propanol was present in the reaction mixtures; in these cases the calculated acidities were made proportional to their measured values.

Likewise, it was decided not to make any correction for incomplete dissociation of iodic acid. The data of Naidich and Ricci (15) and Li and Lo (16) are not in very good agreement on this matter, and in particular the latter authors' results vary most erratically with ionic strength and temperature. However, a few trial calculations showed that any such correction would change the results by only a few percent.

Results and discussion.-- The number of reactions that can take place in a mixture of hypophosphorous acid and iodate is formidable.

The possibilities are:

$$\mathrm{IO_3^- + 3H_3PO_2 = I^- + 3H_3PO_3} \qquad (7)$$

$$\mathrm{IO_3^- + 5I^- + 6H^- = 3I_2 + 3H_2O} \qquad (8)$$

$$\mathrm{I_2 + H_3PO_2 + H_2O = H_3PO_3 + 2I^- + 2H^+} \qquad (9)$$

$$\mathrm{IO_3^- + 3H_3PO_3 = I^- + 3H_3PO_4} \qquad (10)$$

$$\mathrm{I_2 + H_3PO_3 + H_2O = H_3PO_4 + 2I^- + 2H^+} \qquad (11)$$

The only hope of obtaining worthwhile information on the first reaction lies in finding conditions which reduce the interference of the rest to a negligible amount. Reaction (8) is very much faster than any of the others; (9) is found to take place at a rate comparable to that of (7). According to Griffith, McKeown and Taylor (5), reaction (11) is negligible compared to (9) in solutions of pH less than 3. This statement agrees with the analyses of several representative reaction mixtures after the reactions had run their course, which showed that the final concentrations of phosphorous acid were within 90% of the theoretical. Hence it appeared that the effects of (10) and (11) could be ignored, at least during the earlier stages of a run. The principal experimental difficulties were found in minimizing the contributions of (8) and (9), and three approaches to this problem were tried. The first consisted simply of measuring initial rates, abandoning the run as soon as a definite iodine color appeared in the solution. This method was tedious, and it precluded the possibility of getting data at relatively high iodate concentrations, since under these conditions iodine appeared in the solutions almost immediately. The second approach was based on keeping the concentration of iodide ion in the system as low as possible; it consisted of stirring the reaction mixture in the presence of silver chloride. This procedure permitted a greater variation in initial conditions, but the results obtained were not always consistent. Finally, an observation of Neogi and Sen (12) -- namely, that n-propanol appears to inhibit the reaction between iodate and hypophosphorous acid -- was utilized to give what appeared to be the most consistent and reliable data.

That the stoichiometry of the iodate-hypophosphorous acid reaction is actually that given by (7) (rather than being, for example

$$2H^+ + 2IO_3^- + 5H_3PO_2 = I_2 + 5H_3PO_3 + H_2O \quad)$$

was shown a number of times under different conditions by analyzing the reaction mixtures for hypophosphorous acid after a run and comparing with the amount of iodate used up. The validity of (7) is also supported by observations of the length of time required for an iodine color to appear in the solutions, which period was in some cases as long as an hour. Based on the assumption that iodide is produced at the same rate that iodate disappears, and on the known rate of the iodate-iodide reaction, some rough calculations were made of the length of time required to bring the iodine concentration up to a visible level; they were found to be in general agreement with the periods actually observed. It is therefore improbable that iodine is a direct product of the reaction between iodate and hypophosphorous acid.

1. Determination of initial rates.-- In these experiments the attempt was made to determine the order of the reaction with respect to the various reactants. Table 1 below gives the results of a set of experiments designed to test simultaneously the dependence of the order on the hydrogen ion concentration and the concentration of (undissociated) hypophosphorous acid. In these experiments, the iodate concentration and the total concentration of hypophosphorous acid

(undissociated acid plus hypophosphite ion) were kept constant, and the acidity varied by adding sulfuric acid. If the rate were proportional to the first power of both hydrogen ion and hypophosphorous acid concentrations, a straight line should result from plotting initial rate against $(H^+)^2/(K+[H^+])$, where K is the ionization constant of hypophosphorous acid. It will be seen from Fig. 2 that there is a linear relationship at lower acidities, but evidence of a falling off from this linear increase in rate at higher acidities. This, of course, is to be expected if the rate law derived by Mitchell is adhered to in this case, for when the ratio $(H^+)/(IO_3^-)$ becomes sufficiently large, the rate becomes independent of (H^+).

Table 4

Dependence of Initial Rate on (H^+)

$(\sum H_3PO_2) = 0.0529$, $(IO_3^-) = 0.0116$. Temp: 30.06°

(H^+)	.0025	.0053	.00835	.0129	.0166
Initial rate, moles/l./hr.,$\cdot 10^4$	.44	1.40	3.41	8.26	12.1

Table 5 and Fig. 3 present the results of a set of experiments testing the dependence of rate on

(IO_3^-). (See note, pp. 16a-16b).

Table 5

Dependence of Initial Rate on (IO_3^-)

$(\sum H_3PO_2) = 0.0395$, $(H^+) = 0.0095$. Temp: 30.06°

(IO_3^-)	.00374	.00750	.0112	.0149
Initial rate, moles/l./hr., $\cdot 10^4$	1.7	2.8	4.2	5.7

A few experiments at relatively high iodate concentrations were made, but owing to the quick appearance of iodine in the solutions only a few analyses of each reaction mixture could be made, and the results are correspondingly more uncertain. However, it appeared that on the basis of data already obtained the rates were somewhat less than would be predicted if the reaction were uniformly first order with respect to iodate.

Table 6

Initial Rates at High Iodate Concentrations

$(\sum H_3PO_2)$	(H^+)	(IO_3^-)	Rate, moles/l./hr., $\cdot 10^3$
.0131	.020	.138	1.4
.0232	.019	.144	1.1

Note.--After the foregoing was written, it was pointed out to me by Dr. Norman Davidson that the linear plot of initial rate against iodate concentration in Fig. 3 is actually not to be expected, since the value 0.44 for k_2/k_3 makes the quantity $k_2(H^+)/k_3(IO_3^-)$ of the order of magnitude of 1, instead of much larger than 1. It therefore was desirable to cast the data of Table 5 into a more suitable form. With the conditions of this set of experiments, the assumed rate law can be written

$$\frac{1}{(\text{initial rate})} = \frac{1}{k_1(H^+)(H_3PO_2)} + \frac{k_2}{k_3k_1(H_3PO_2)} \cdot \frac{1}{(IO_3^-)} = \frac{D}{(IO_3^-)} + C,$$

where C and D are constants. Fig. 3a shows the data of Table 5 plotted in this way. While the expected linearity is still fairly apparent, the intercept C is zero instead of having a positive value of about 2.3×10^3, as the data and the above equation require. In other words, the initial rates are higher than the rate law would predict. I think that the major part of this discrepancy may be explained by the fact, previously overlooked, that the reaction mixtures were heavily buffered with phosphate, being 0.31 M in NaH_2PO_4 and 0.19 M in H_3PO_4. The catalytic effect of these substances at these concentrations is considerably greater than that of the hydrogen ion alone, in this case; using the catalytic coefficients given by Griffith, McKeown and Taylor (5), we find the value of C to be reduced to about 0.2×10^3, which, in view of the uncertainties in the initial rates, is now in reasonable agreement with the value found graphically.

These phosphate buffers were not used in later experiments, which are therefore not subject to this correction.

The rate law (5) can be written in the form

$$k_1 = \frac{\text{rate}}{[H^+]\,[H_3PO_2]} + \frac{\text{rate}}{[IO_3^-]\,[H_3PO_2]}\,\frac{k_2}{k_3} = A + B\frac{k_2}{k_3}$$

The experimentally determined quantities A and B determine the intercept and slope of a straight line, any point of which gives a pair of values of k_1 and k_2/k_3. If we assume that (5) applies here, altering the experimental conditions should, by altering A and B, give a family of straight lines which intersect in a point, the coordinates of which are the required values of k_1 and k_2/k_3. How nearly this is true is shown in Figs. 4 and 5, which are based on data from experiments in which stock solutions of hypophosphorous acid and the sodium salt, respectively, were used. The scatter of the intersections is seen to be considerable, especially in the first case. Negative values of k_1 and k_2/k_3 are of course to be excluded. Table 7 gives the eleven most consistent pairs of values of these constants.

Table 7

Values of k_1 and k_2/k_3 Obtained from Determination of Initial Rates at 30°

H_3PO_2	k_1, moles/l./hr.		8.1	8.5	8.7	10.4	9.0
	k_2/k_3		0.50	0.54	0.57	0.82	0.84
NaH_2PO_2	k_1	10.0	9.4	9.4	9.3	8.7	7.9
	k_2/k_3	0.42	0.40	0.37	0.35	0.31	0.20

Mitchell obtained values for k_1 and k_2/k_3 at 25° of 0.26 moles^{-1} 1 min^{-1} and 0.012 respectively, which, with his temperature coefficient of 3.14 per ten degrees for k_1 and approximately unity for k_2/k_3, come to about 9 and 0.012 at 30° in my units. His value for k_1 probably does not differ significantly from the one obtained in the present study. However, the values of k_2/k_3 given above, although apparently quite sensitive to experimental error, are still definitely larger than those found by Mitchell. Recalling the interpretation of k_2/k_3, and assuming that k_2 has the same value in both cases, we should conclude from this that the reaction of the active form of hypophosphorous acid with the halogens and mercuric ion, is at least twenty or thirty times faster than with iodate.

2. The reaction in the presence of silver chloride.-- While the data thus far presented are in general agreement with the postulated reaction scheme, there is still no direct evidence showing that the rate becomes independent of the iodate concentration when this is large enough. It is apparent that if the concentration of iodide ion in the system could be kept low, the iodate concentration could be made higher without getting into immediate difficulties with the production of iodine. Consequently a number of experiments were made in which the reaction mixture was stirred up with solid silver chloride, a procedure which, if successful, should keep the iodide ion concentration at something like 10^{-12}.

The experimental procedure was as follows. The reactants were placed in a wide-mouthed 500-ml Erlenmeyer flask and diluted to the requisite volume with a suspension of finely divided silver chloride. A representative reaction mixture would contain several grams of silver chloride in 200-300 ml of solution. The flask was fitted with a one-hole rubber stopper holding a lubricated glass sleeve, through which ran the shaft of the stirring motor. The solutions were stirred continuously except for periods of about thirty seconds just before taking samples, when the stirring was stopped to let the silver chloride settle; otherwise rather large amounts would be drawn into the pipet. If the iodate and acid concentrations were not too high, the reaction could be allowed to go to completion without the appearance of iodine. At the end of a run, the silver chloride particles were well coated with yellow silver iodide.

There are two possible objections to this procedure. First, silver ion is known to be an oxidant of hypophosphorous acid. The low concentration of silver ion, however, apparently kept this reaction from assuming importance, although once a darkening of the silver chloride particles was observed when a solution was allowed to stand overnight. Second, if the solutions were saturated with respect to silver chloride, they must have been supersaturated with respect to silver iodate, and the latter should have precipitated during the course of a run. Blank experiments showed that this did not occur to a measurable extent.

Since the reaction could now be followed through a considerably greater portion of its course, it was possible to make an estimate of k_1 and k_2/k_3 from each experiment. The concentration of hydrogen ion was observed not to change significantly in a run; consequently, from the rate equation written in the form

$$\left[H_3PO_2\right] /\text{rate} = \frac{1}{k_1\left[H^+\right]} + \frac{k_2}{k_3k_1} \cdot \frac{1}{\left[IO_3^-\right]}$$

it can be seen that by plotting (H_3PO_2)/rate against $1/(IO_3^-)$, a straight line should be obtained whose intercept and slope give the required values.

This was always found to be the case, during the first part of a run. Later on, the slope of the curve usually fell off, and sometimes even became negative. This behavior I attribute to the iodate-phosphorous acid reaction; this reaction would tend to make the rate larger, and the concentration of hypophosphorous acid (calculated from the observed iodate concentration) smaller, than would be expected. Both these effects would reduce the ordinate, (H_3PO_2)/rate. In confirmation of this guess, the reaction mixtures usually began to give positive tests for phosphate at about the point where the curves began to drop off. Figs. 6, 7, and 8 give a representative sample of the results obtained.

The rate constants thus determined are unfortunately quite sensitive to error in the hypophosphorous acid concentration, which on account of uncertainties in (H^+) and in the ionization constant of the acid, is just the quantity least accurately known. Also, owing to the impossibility of using high iodate concentrations, the errors are magnified in the relatively long extrapolation to $1/(IO_3^-) = 0$. Such difficulties are apparently unavoidable in a study of this reaction. Apart from this, however, there seemed to remain an uncontrolled factor which had a direct effect on the rate; even in supposedly duplicate experiments there were differences in dc/dt and d^2c/dt^2 ($c =$ concentration of iodate) too large to be explicable simply as random error. It was thought that the time of standing of the reaction mixture over silver chloride before the final component, either sodium iodate or sodium hypophosphite, was added, might influence the rate, or that it made a difference whether iodate or hypophosphite was used to start the reaction, but control of both of these factors did not improve the consistency of the results.

A possible explanation of the variability of the results obtained in the presence of silver chloride is that the reaction somehow becomes heterogeneous, and hence would depend on such things as amount of solid present, degree of subdivision of the particles, and the rate of stirring. The "supposedly duplicate" experiments just mentioned were carried out in different flasks equipped with different stirring motors, and undoubtedly the amounts of silver chloride present were not exactly the same in both cases. But it is difficult to imagine how silver chloride could take any significant part in the reaction.

Table 8 gives the values of k_1 and k_2/k_3 obtained by this procedure. In addition to these, five pairs of negative values were found.

Table 8

Values of k_1 and k_2/k_3 Obtained from Experiments with Silver Chloride

k_1	11.4	8.2	9.8	6.6	4.5	17.4	8.1	15.1	17.1
k_2/k_3	0.63	0.47	0.28	0.05	0.09	0.70	0.37	0.98	1.16

The "method of intersections" of plots of k_1 vs. k_2/k_3 previously referred to was also employed, and because of the greater variation in initial conditions and greater accuracy of the rate determinations, thirty pairs of values were obtained, ranging from 8.6 to 17.2 for k_1 and from 0.12 to 0.84 for k_2/k_3. The averages of these values and their comparison with others are given at the end of the section.

The values for k_1 given above and the linear relationships shown in Figs. 6 - 8 are clear indications that the iodate-hypophosphorous acid reaction conforms to the rate law (5). It may be noted that iodate ion, unlike all the other substances which have been found to react with hypophosphorous acid in this way, is not a simple neutral molecule or cation. As mentioned previously, the reaction with the more complex dichromate ion does not follow this rate expression.

3. <u>The reaction in the presence of n-propanol</u>.-- The observation of Neogi and Sen (12) that n-propanol delays the appearance of iodine in an acid iodate-hypophosphite mixture led me to test the value

of this substance in rate determinations.

Commercial C.P. n-propanol was used without further purification. The most used in any experiment was 7 volume percent. Tests showed that varying the concentration of alcohol in this range did not appear to have a significant influence on the rate, that there was no reaction between iodate and n-propanol, and that its presence did not interfere with the thiosulfate titrations. The dielectric constants of the solutions were lowered by as much as four percent by the addition of the alcohol (17), but the error thus introduced into the calculations of hydrogen ion and hypophosphorous acid concentrations is hard to estimate quantitatively. At any rate, it was considered to be negligible, in view of the already considerable uncertainty in these quantities.

It was found that, while there was no apparent retardation of the reaction rate between iodate and hypophosphorous acid, the time of appearance of iodine was indeed delayed to an extent which, other things being equal, was quite accurately proportional to the amount of n-propanol added. Another phenomenon noted was that, while in previous experiments the acidity remained sensibly constant, in these experiments it dropped continuously, as shown by a pH meter. On this account, sodium sulfate-sodium bisulfate buffer solutions were used in some of the experiments designed to evaluate k_2/k_3. The action of n-propanol here is not known, but a plausible guess based on these observations would be that it enters the iodate-iodide reaction to destroy or in some way stabilize an intermediate, the intermediate being a weak acid -- perhaps hypoiodous acid.

The variation in the hydrogen ion concentration during a run made it inconvenient to determine the rate constants by plotting (H_3PO_2)/rate against $1/(IO_3^-)$; however, it was now possible to work with such high iodate concentrations that a first approximation to k_1 could be determined directly from the limiting form of the rate law

$$k_1 = \frac{\text{rate}}{[H^+][H_3PO_2]} .$$

Using an average value of k_1 determined thus, values of k_2/k_3 could be found from experiments at lower iodate concentrations. These were used to correct the values of k_1, which in turn gave a final small correction in k_2/k_3. The final values of k_1 and k_2/k_3 obtained in some representative runs are given in Table 9.

Table 9

Rate Constants in Experiments With n-Propanol

	k_1			k_2/k_3	
Expt. No.	119	117	120	122	123
	9.4	10.0	9.6	0.51	0.46
	9.8	9.9	9.7	0.50	0.45
	10.0	9.9	9.9	0.48	0.44
	10.1	10.1	10.1	0.48	0.44
	10.2	10.0	10.1	0.47	0.44
	10.3	9.8	10.0	0.47	0.44
	10.1	9.6	10.2	0.47	0.45
	10.0	9.5	10.2	0.47	0.45
	9.8	9.2	10.3	0.47	0.44
	9.4	8.9	10.3	0.44	0.43

It can be seen that the variations in k_1 during a run do not quite seem to be random, but on the other hand they do not vary in the same direction in different experiments. The values of k_2/k_3 are much more stable, in contrast to the larger scattering of values obtained by other techniques.

Some experiments were made to test the influence of ionic strength on the magnitudes of k_1

and k_2/k_3, with the results given in Table 10.

Table 10

Effect of Ionic Strength on Rate Constants

μ	0.27	0.46	0.65	0.66	0.99	1.29
k_1	11.0	9.3	9.9			
k_2/k_3				0.47	0.44	0.42

These values of k_1 differ significantly among themselves, but do not seem to bear a regular relation to the ionic strength. It is possible that the variations are largely due to errors in the estimation of hydrogen ion concentration and the ionization constant for hypophosphorous acid in these solutions. For the same reason, it is doubtful if the small decrease in k_2/k_3 is real. The ionic strength is too high to make worthwhile a quantitative discussion of this effect from the standpoint of the Bronsted theory. The significant point here is that the indifference of $\frac{k_2}{k_3}$ to changes in ionic strength is in accord with the postulated reaction mechanism, in which both the k_2 and k_3 reactions involve a neutral molecule--i.e., the active form of hypophosphorous acid.

The rate constants were also determined by means of similar experiments at 20.27°, the values being 3.66 for k_1 and 0.35 for k_2/k_3; this is a temperature coefficient of 2.7 and 1.3 per 10.4°, respectively. The corresponding activation energies are 17 kcal. and 4.5 kcal. The value for the temperature coefficient of the k_1 reaction is considerably below that of 3.14 per 10° found by Mitchell for the iodine reaction. Also, he states that the temperature coefficient of k_2/k_3 is "approximately unity"; lacking the data on which he based this statement, it may be that his value is compatible with the one found here.

It is of course impossible to say what the separate temperature coefficients of k_2 and k_3 are. Griffith and McKeown (6), noting the low temperature coefficient of k_2/k_3 in the halogen reactions and its essential independence of the oxidant, have speculated that active hypophosphorous acid may react with oxidant at every collision, and that the lower efficiency of the k_2 reaction may be due to its requiring a small activation energy, which they estimate at about 2.7 kcal. On the basis of the temperature coefficient found here, and assuming iodate ions and active hypophosphorous acid molecules react at every collision, the k_2 activation energy would be about 4.5 kcal., and correspondingly more if the k_3 activation energy is not zero. Indeed, it is reasonable to suppose that it is not zero, and an approximate lower limit to its magnitude may be had from the following considerations. If we assume that the simple formula $k\ \ Z\exp(-E/RT)$ applies, and also that Z and k_2 are the same for both the iodate and (say) iodine reactions, it then follows that

$$RT\ln(k_2/k_3)_{IO_3^-}/(k_2/k_3)_{I_2} =$$

$$= RT\ln(k_3)_{I_2}/(k_3)_{IO_3^-} = RT\ln(0.44)/(0.012) =$$

$$= (E_{k_3})_{IO_3^-} - (E_{k_3})_{I_2} \approx 2\text{ kcal.}$$

On this basis, the k_2 activation energy would be at least 6 kcal. Griffith and McKeown estimated, on the basis of the data known to them, that the ratio $(H_3PO_2)_{II}/(H_3PO_2)_I$ at equilibrium would be about 10^{-12}, whereas the results of this study would put its value at something like 10^{-9} or even larger.

Table 11

Summary of Values of Rate Constants at 30.06° (1)

Conditions	k_1	k_2/k_3
No stabilizer, H_3PO_2	8.9 ± 0.8	0.65 ± 0.15
No stabilizer, NaH_2PO_2	9.1 ± 0.6	0.34 ± 0.07
AgCl, (H_3PO_2)/rate vs. $1/(IO_3^-)$	10.9 ± 4.4	0.53 ± 0.37
AgCl, intersections	12.6 ± 2.3	0.46 ± 0.20
n-Propanol, all intersections	11.6 ± 0.7(2)	0.69 ± 0.16
n-Propanol, expts. 115-130 only (3)	9.7 ± 0.8(2)	0.44 ± 0.03

(1) Each value is the mean of from 5 to 30 values. The ± figure is the standard deviation.

(2) These are values determined at 30.66° and corrected to 30.06° by use of the temperature coefficient given previously.

(3) These experiments were especially designed to give k_1 and k_2/k_3 separately, and probably give the best values.

EXPERIMENTS UNDER OTHER CONDITIONS

Iodate-hypophosphite reaction in neutral and basic solution.-- Neutral solutions containing 0.006 M sodium hypophosphite and 0.006 M sodium iodate, and similar solutions 0.0001 N in sodium hydroxide, were tested for reaction at 30°. There was no change in titer of the neutral solution after 22 days, and none in the basic solution after 3 days. Any direct or base-catalyzed reaction between hypophosphite ion and iodate seems to be absent.

The bromate-hypophosphorous acid reaction.-- Two solutions were prepared, each containing 0.005 M hypophosphorous acid and 0.005 M potassium bromate; one was made 0.02 N in acid, the other 0.1 N. The first solution showed no reduction in titer after 79 hours at 30°. The second showed no reaction after 6 hours, but when analyzed again after 77 hours, the reaction was found to have gone almost to completion. A bromate-hypophosphorous acid reaction probably similar to, but certainly slower than, the iodate reaction is therefore indicated.

Miscellaneous oxidizing agents.-- The action of several other oxidizing agents on hypophosphorous acid was examined in a more or less qualitative manner.

1. Effect of hydrogen peroxide.-- A solution 0.1 M in hydrogen peroxide and 0.02 M in hypophosphorous acid was heated at 60° for half an hour. The peroxide was then estimated colorimetrically by the molybdate method and compared with a blank which had undergone the same treatment. No evidence of reduction of hydrogen peroxide was found.

2. Reaction with permanganate.-- Permanganate is reduced almost instantly by hypophosphorous acid in moderate concentrations, the permanganate color changing to a pale brown which in turn fades out at a much slower rate. The resulting solution is found to contain phosphate. Freshly precipitated manganese dioxide reacts at a moderate rate with hypophosphorous acid; no phosphate is found in the resulting solution.

3. Reaction with vanadate.-- Hypophosphorous acid was added to a solution of ammonium metavanadate in sulfuric acid, the initial conditions being $(\sum H_3PO_2) =$ 0.0438, $(VO_3^-) = 0.0408$, and $(H^+) = 0.65$. The rate of

reaction was actually followed in this case, the initial rate of reduction of vanadate being $4.8 \cdot 10^{-3}$ moles l^{-1} hr^{-1}. Fig. 9 shows the relationship that would follow from these data if it is assumed that Mitchell's rate law applies, that all the vanadium is present as VO_3^- ion, and that this ion is the sole reacting species. The second assumption is certainly, and the third very possibly, not correct, of course. It may be said that if the above rate law does apply, the slope of the line in Fig. 9 is a lower limit; any other possible assignment of concentration to the reacting vanadium would mean an equal or larger slope.

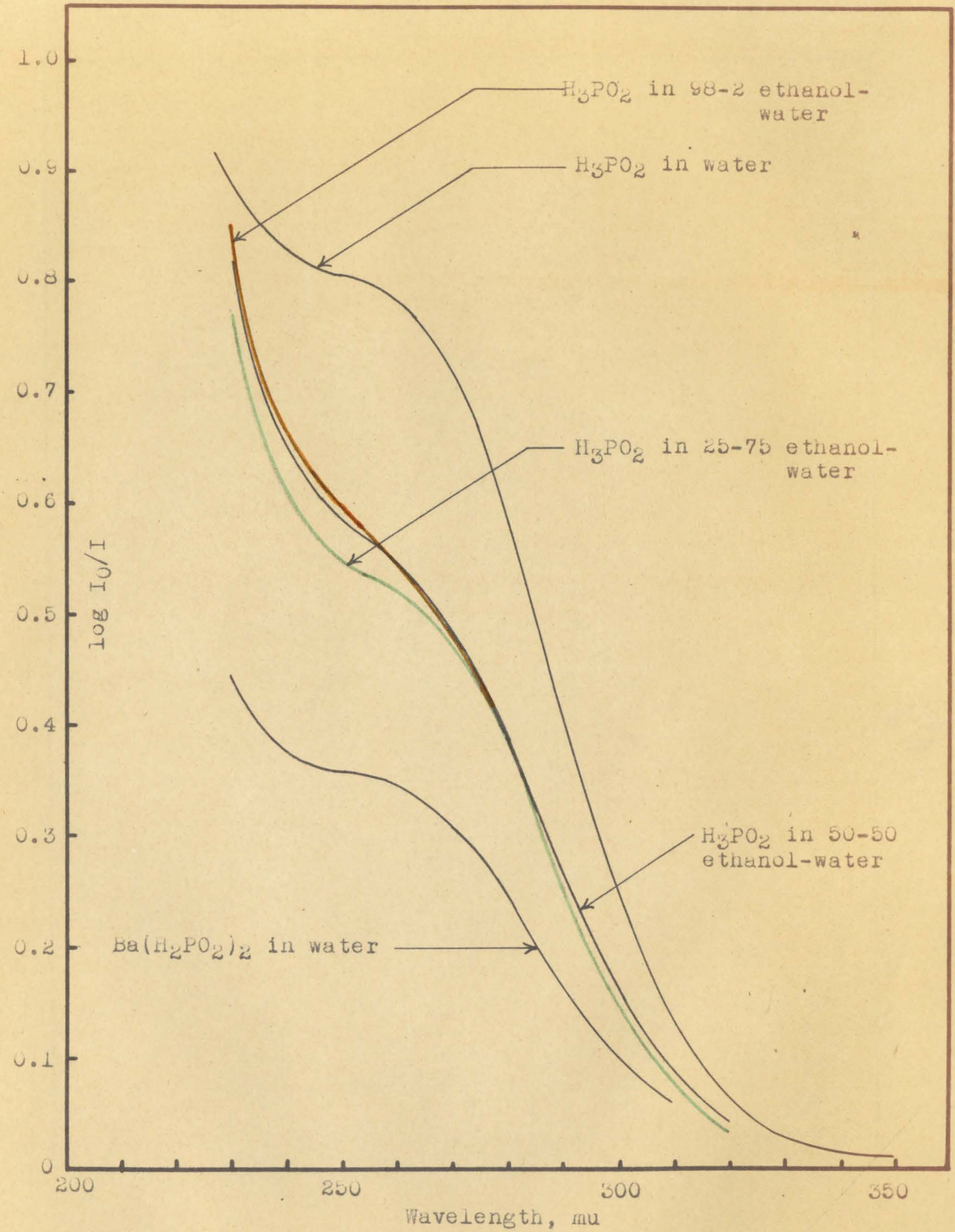


Fig. 34-1. Absorption spectra of H_3PO_2 solutions

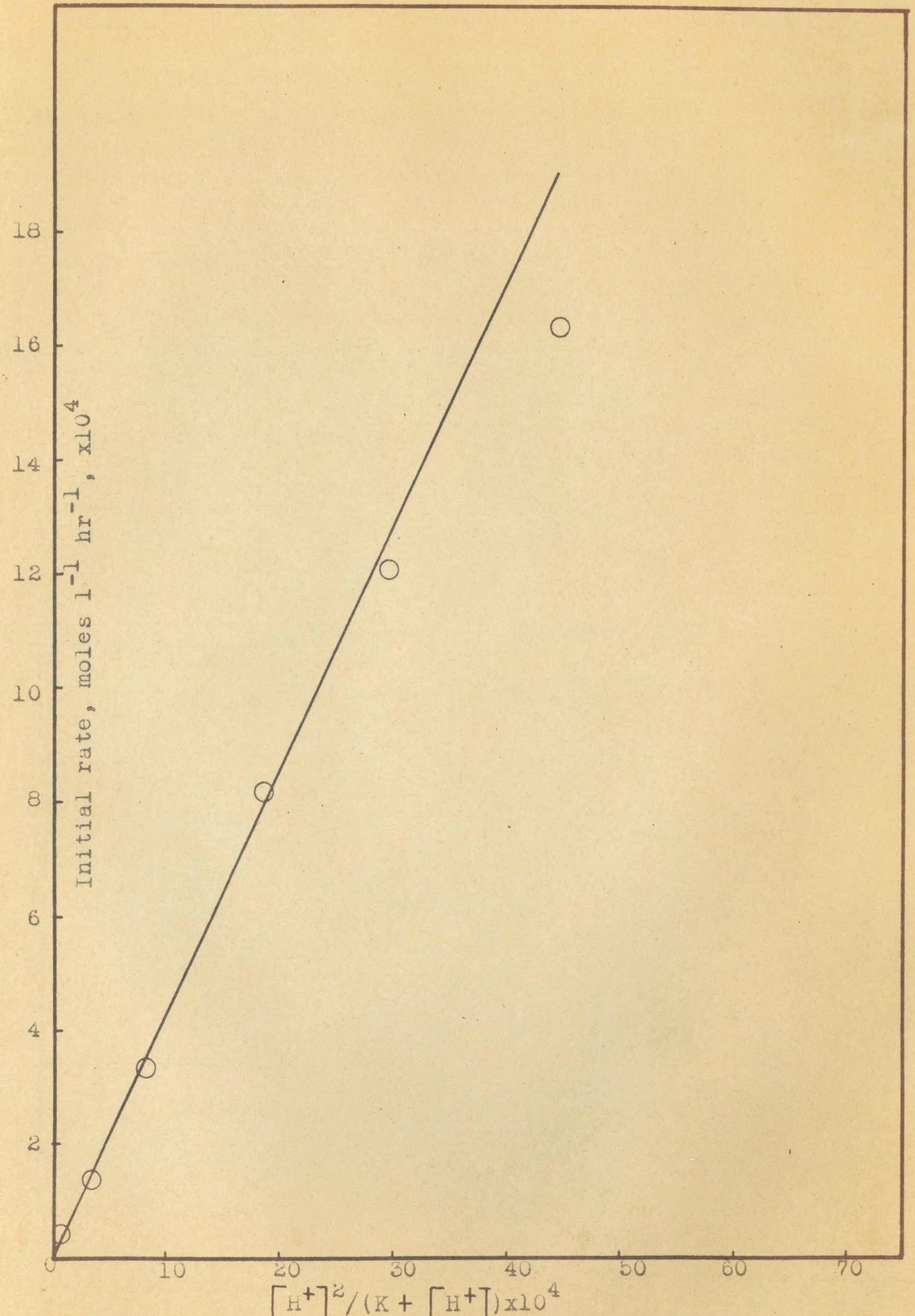


Fig. 34-2. Dependence of rate on $[H^+][H_3PO_2]$

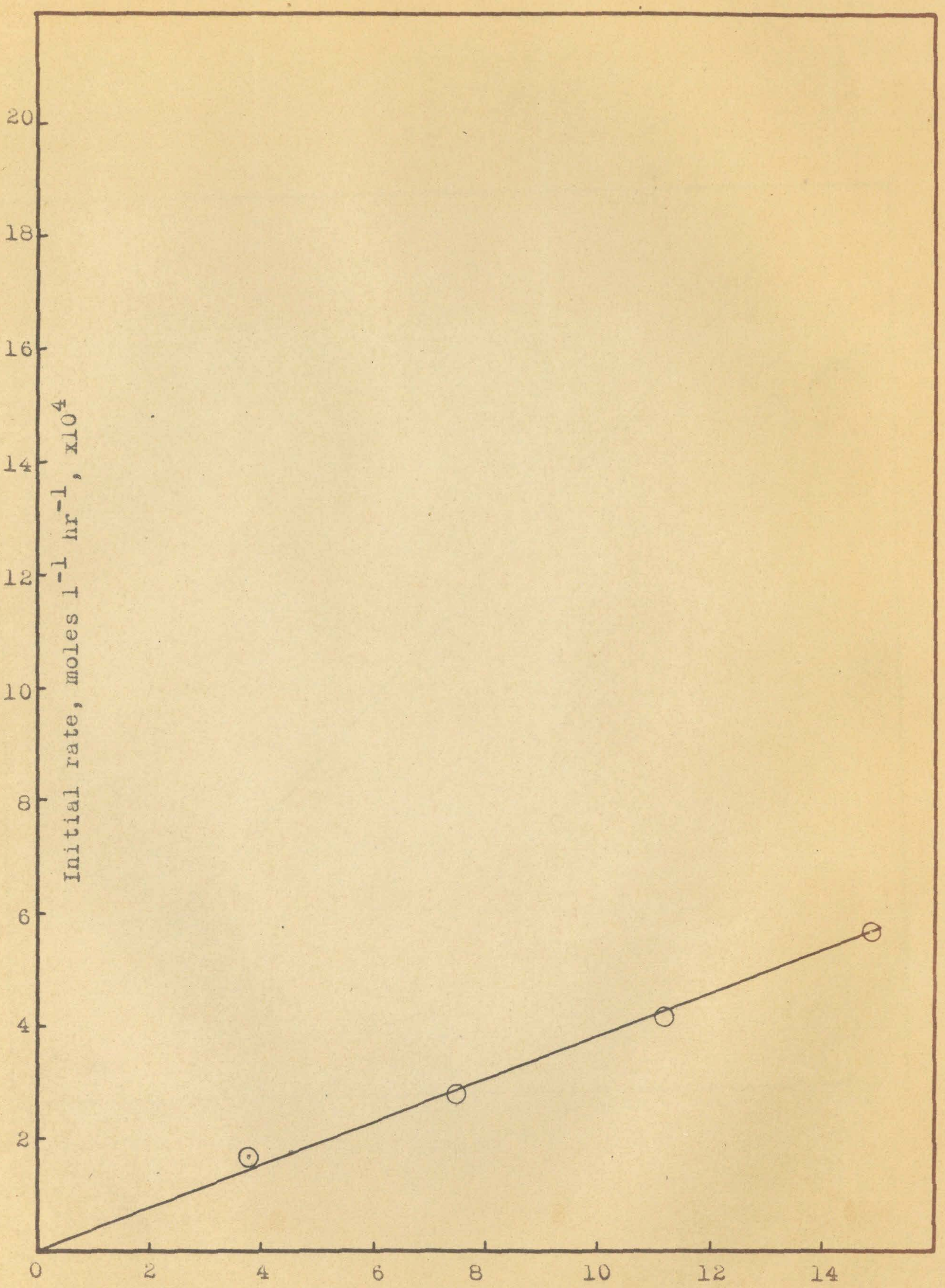


Fig. 34-3. Dependence of rate on $[IO_3^-]$

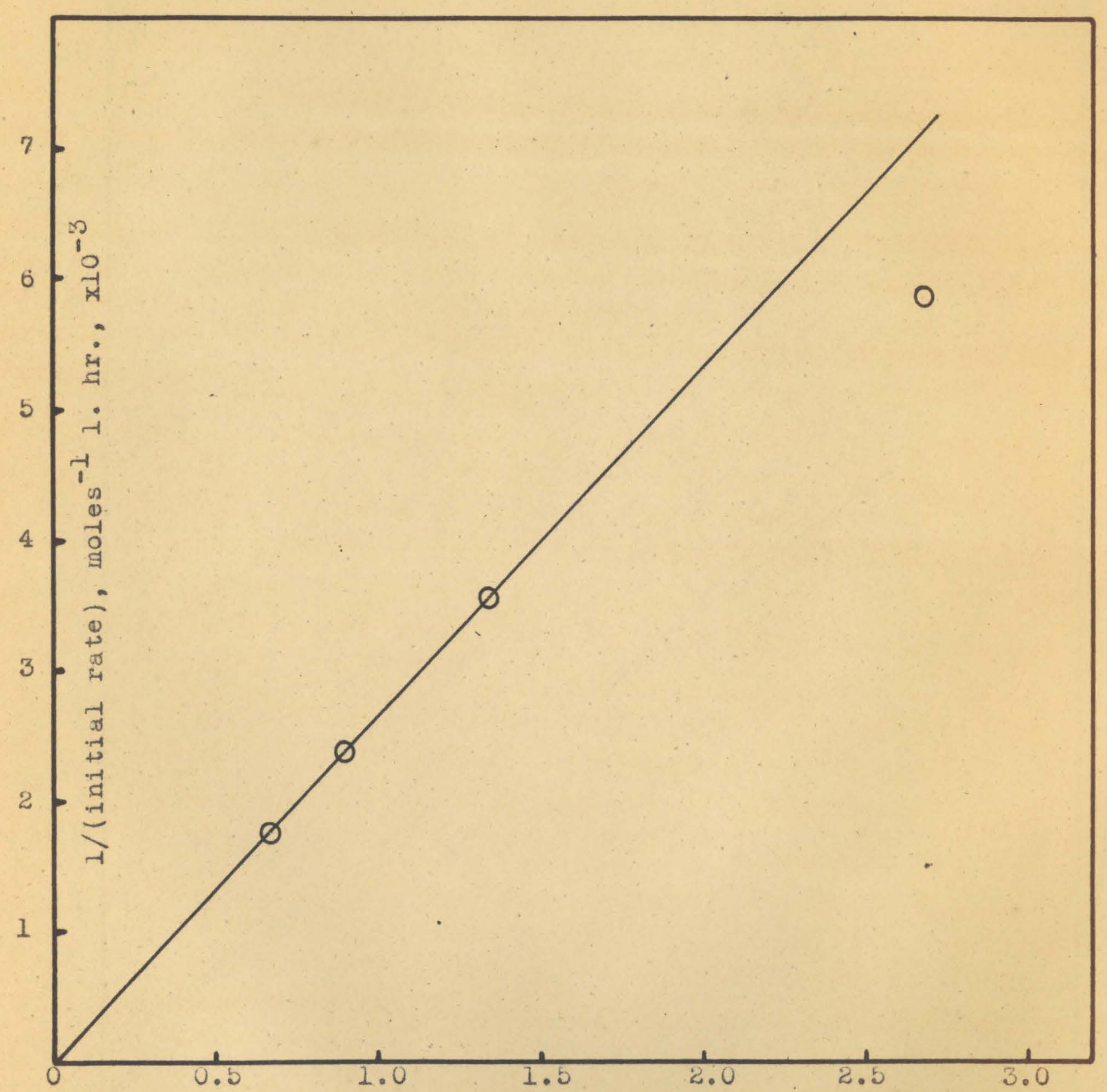


Fig. 34-4. Dependence of initial rate on (IO$_3^-$)

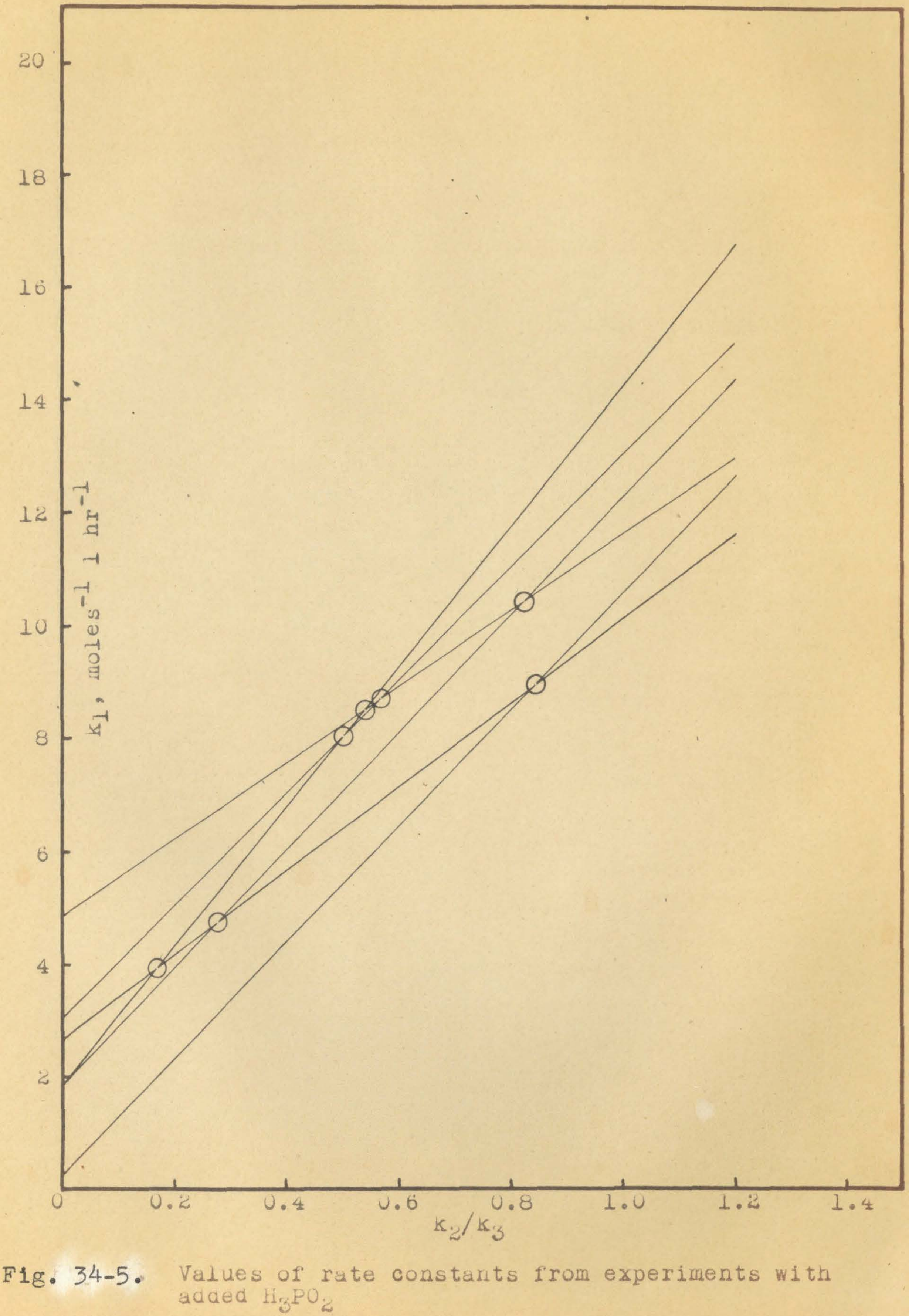


Fig. 34-5. Values of rate constants from experiments with added H_3PO_2

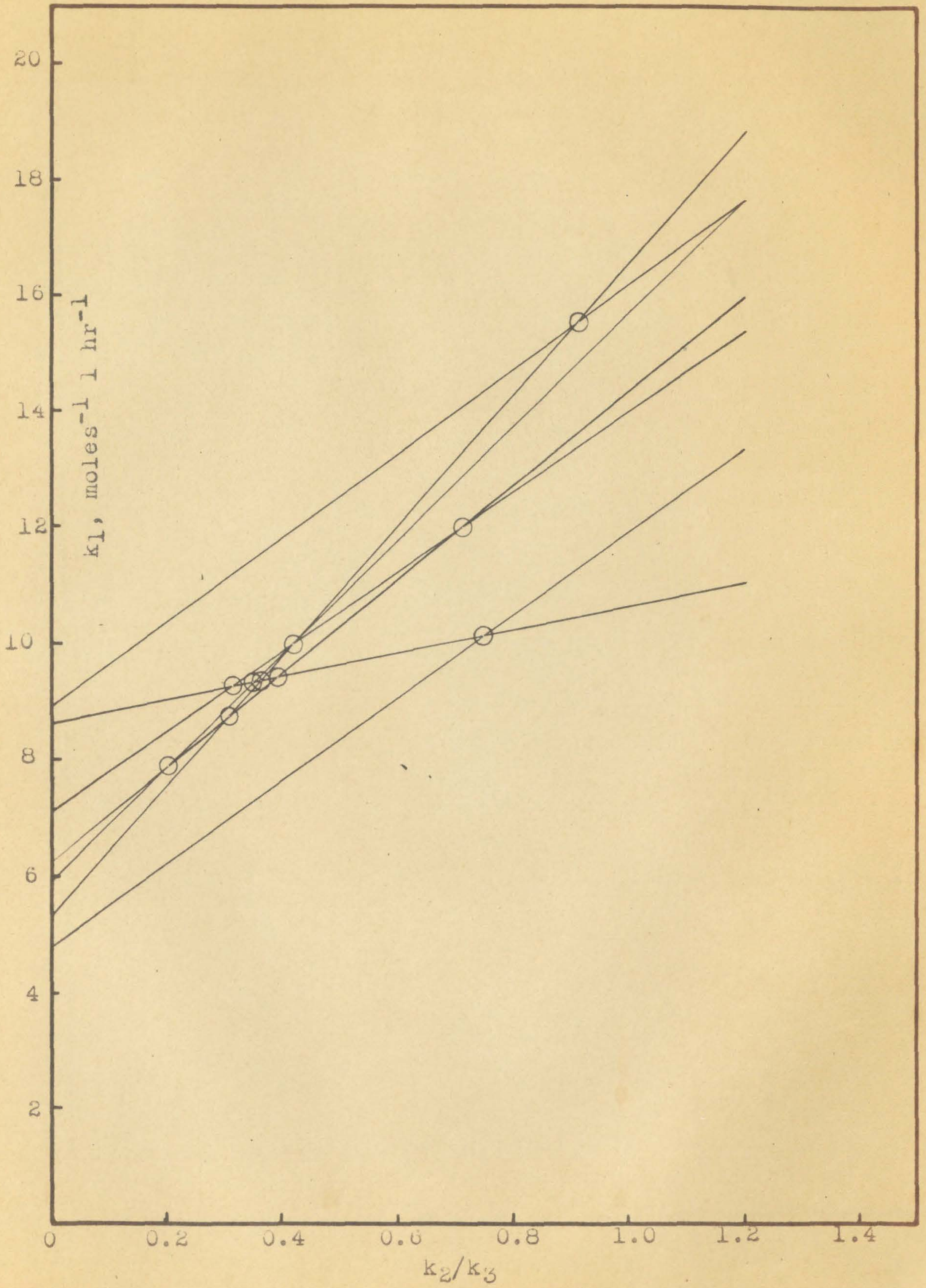


Fig. 34-6. Values of rate constants from experiments with added NaH_2PO_2

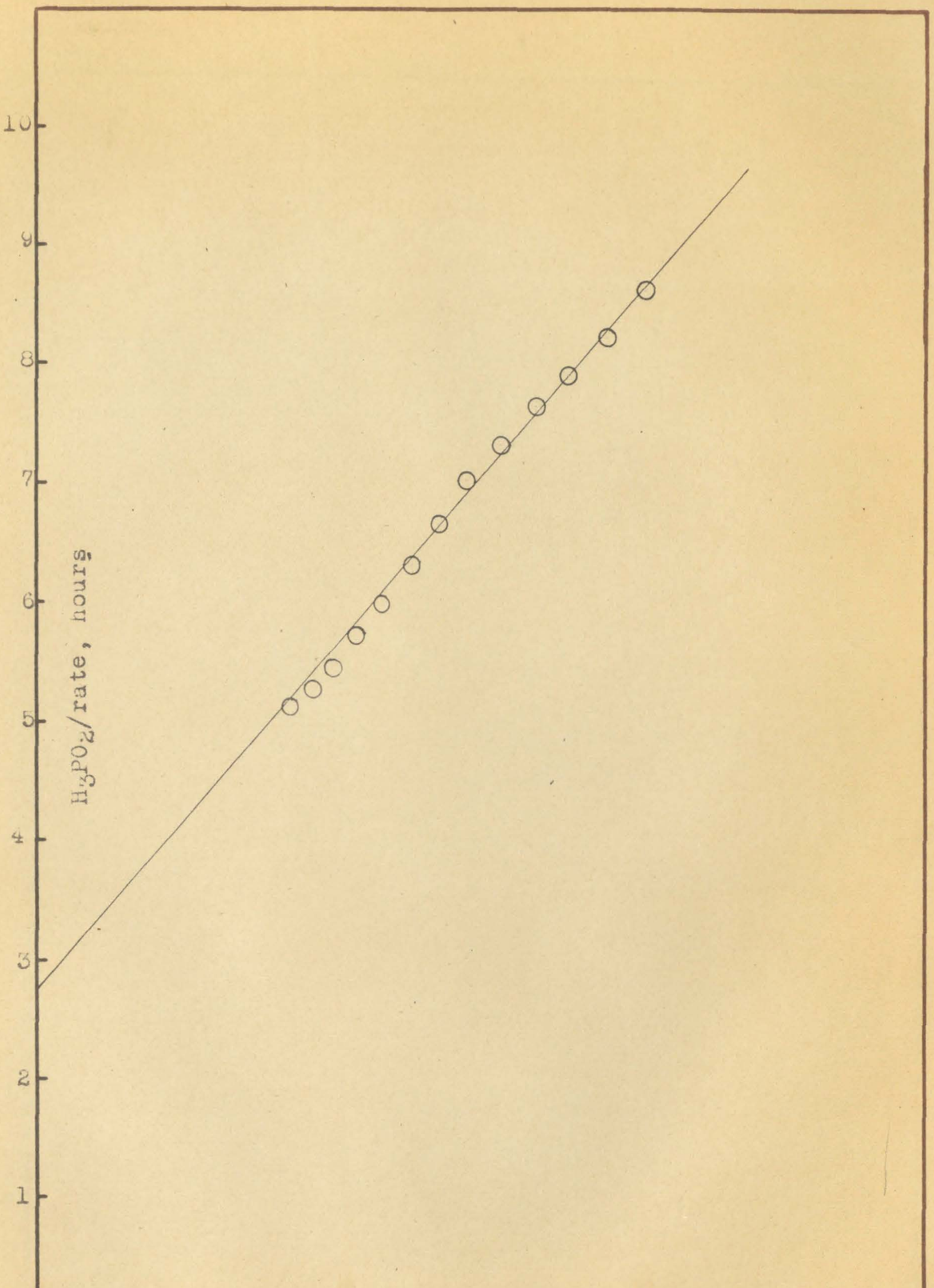


Fig. 34-7. Variation of $[H_3PO_2]$/rate with $1/[IO_3^-]$. Expt. 80

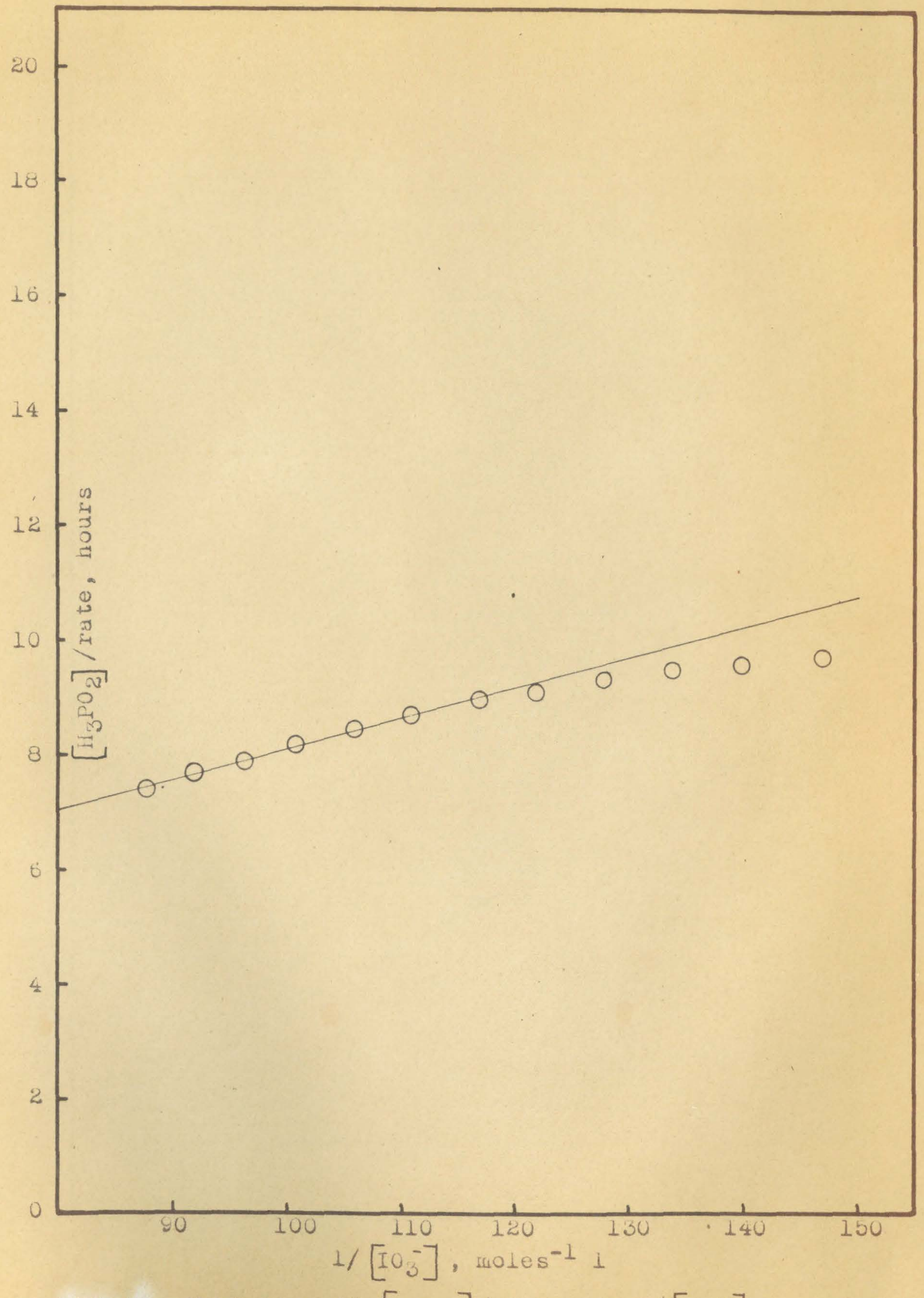


Fig. 34-8. Variation of $[H_3PO_2]$/rate with $1/[IO_3^-]$. Expt. 85

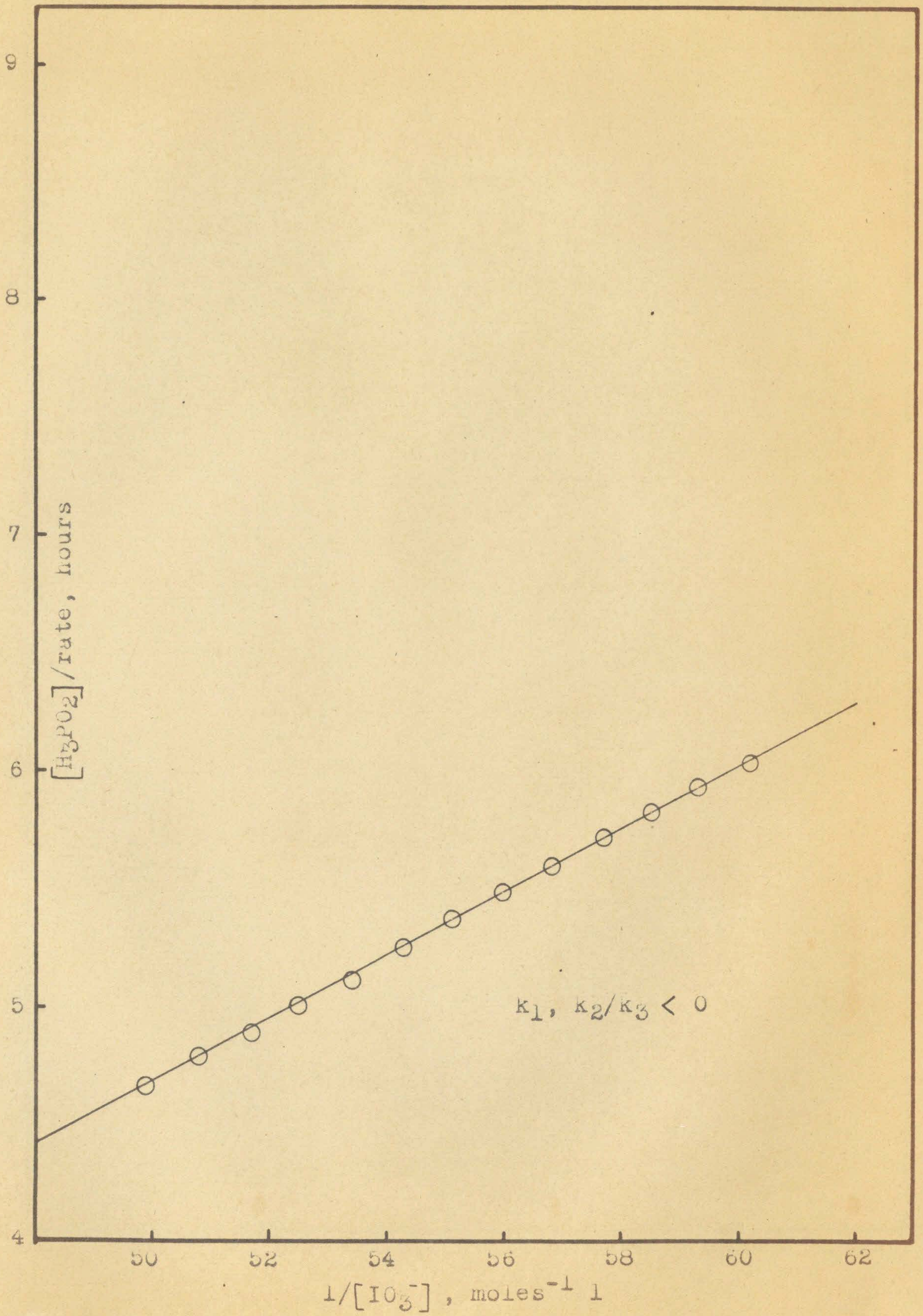


Fig. 34-9. Variation of $[H_3PO_2]$/rate with $1/[IO_3^-]$. Expt. 89

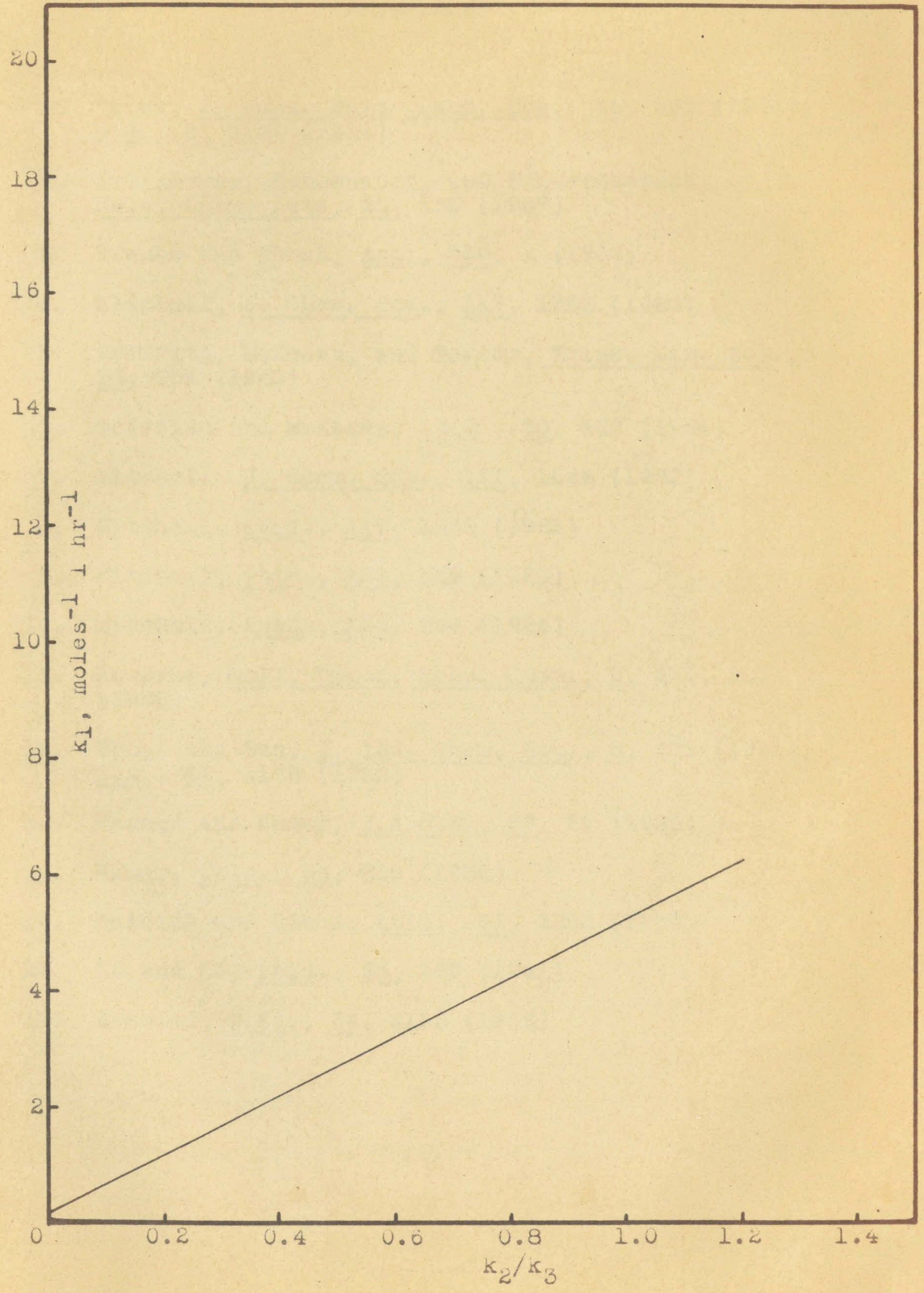


Fig. 34-10. Relation between k_1 and k_2/k_3 for H_3PO_2-NH_4VO_3 reaction

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17. Akerlof, ibid., 54, 4125 (1932)

PROPOSITIONS

1. The difference of 165° between the melting points of the rather similar compounds $(C_2H_5)_2O \cdot H_2SO_4$ and $(C_2H_4)_2O_2 \cdot H_2SO_4$ is probably ascribable to the ability of the latter to polymerize.

2. An accurate and fairly rapid method for determining iodate and iodine separately in the same solution is proposed; the method is based on the difference in behavior toward a neutral phosphite reagent.

3. The hypothesis of Harmon and Eyring (1), which attributes the peroxide effect on addition reactions to magnetic influences on the double bond, fails to explain why HBr alone of the halogen acids exhibits such an effect (2).

   1. Harmon and Eyring, J. Chem. Phys., 10, 557 (1942).
   2. Mayo and Walling, Chem. Rev., 27, 372, (1940).

4. The usual interpretation of the data on the heats of hydrogenation of cyclopentene and cyclopentadiene (1) may conflict, not with the Baeyer strain theory, as suggested, but with the requirement that the maxima of bond orbitals lie in the directions of the bonds (2).

1. Dolliver, Gresham, Kistiakowsky and Vaughan, J. Am. Chem. Soc., 59, 831 (1937).
2. Cf. Kilpatrick and Spitzer, J. Chem. Phys., 14, 463 (1946).

5. The clue to the anomalous melting point of methane, as compared with those of silane, germane, etc., may be found in its low moment of inertia. This, by increasing the spacing of the rotational levels of the molecule, would lead to a correspondingly greater population of the lower levels, and hence, conceivably, to a greater intermolecular attraction. Cf. London, Z. f. Physik, 63, 245 (1930), and Margenau, Rev. Mod. Phys., 11, 1 (1939).

6. The wide difference between the energy of activation (16 kcal.) of the reaction

$$\text{P(white)} \longrightarrow \text{P(red)} \qquad (1)$$

in PBr_3 solution, and the heat of dissociation (about 30 kcal.) for

$$P_4 \longrightarrow 2P_2 \qquad (2)$$

makes it doubtful whether the rate-determining step in (1) is (2). It seems more probable that the rate-determining step is a reaction with the solvent.

Yost and Russell, Systematic Inorganic Chemistry, p. 161.

7. The denaturation of egg albumin by ultrasonic waves, observed to occur in cavitated solutions containing dissolved CO_2 and O_2, but not with H_2 or N_2, may be due to disruption of a hydrogen-bonded structure by oxygen-containing molecules under high pressure.

1. Chambers and Flosdorf, J. Biol. Chem., 114, 75 (1936).
2. Rayleigh, Phil. Mag., 34, 94 (1917).

8. The frequent appearance in scientific papers, in more or less implicit form, of the logical fallacy of affirming the consequent is deplorable, since it tends to blind the reader to the possible existence of alternative hypotheses.

For pertinent examples, see Senior, J. Chem. Ed., 15, 464 (1938) (conceptual basis of stereochemistry); Mulliken, J. Chem. Phys., 7, 339 (1939) (application of the theory of hyperconjugation); Johnson, Amer. Sci., 32, 1 (1944) (explanation of Carolina coast craters).

9. The current theory of the toxic action of mustard gas (1), while leading to a reasonable explanation of the

relative non-toxicity of β,β'-dichlorodiethyl ether, runs into difficulties when the properties of the corresponding sulfoxide and sulfone are considered (2).

1. Gilman and Philips, Science, 103, 409 (1946).
2. Jackson, Chem. Rev., 15, 425 (1934).

10. The directions of progress in biology and physics make it seem likely that some of the "simple" and old-fashioned domains of mathematics will be the next to be brought into touch with the natural sciences--e.g., the properties of polyhedra, in biology, and Diophantine analysis, in the study of the nucleus.

11. A straightforward quantum-semantical analysis of the problem of ghost lines, sometimes observed in spectroscopic work, leads to the conclusion that they must be attributed to phantom orbitals in the substance being examined.

NOTE: TWO INORGANIC PREPARATIONS

1. Preparation of B_2O_3 from $CaF_2 \cdot BF_3$.-- In connection with some work being done by Professors Fowler and Lauritsen on nuclear reactions, it became of interest to obtain B^{10} in a form suitable for use as targets, starting from the compound $CaF_2 \cdot B^{10}F_3$, supplied by the Manhattan project. The method of conversion used was that of Chapin (1), in which methyl borate is formed and distilled off. The distillate, which contains some hydrochloric acid, is diluted somewhat, made neutral with ammonium hydroxide, and allowed to stand several hours to insure complete hydrolysis of the ester. The solution is then evaporated to dryness in a platinum crucible and heated to drive off ammonium chloride, only boric oxide remaining. It was found that redissolving the residue in water and again evaporating to dryness sometimes gave a cleaner looking product.

While no data on the yield of boric oxide were taken, it seemed to be rather low, perhaps because of incomplete conversion of BF_3 to H_3BO_3, or because of loss of H_3BO_3 (which is known to be somewhat volatile in steam) during the evaporation. It may be that loss due to the first-mentioned effect could be diminished by refluxing the

$CaF_2 \cdot BF_3$ with calcium hydroxide before beginning the Chapin procedure; this preliminary treatment would be expected to give more complete conversion to borate (2).

1. Scott, Standard Methods of Chemical Analysis. 4th Revised Edition, v. 1, p. 88. New York: 1927.
2. Cf. Gasselin, Ann. Chim. Phys., (7), 3, 5 (1894).

2. Preparation of C from KCN.-- Also for the purposes of nuclear investigations, it was necessary to prepare C^{13} from $KC^{13}N$. This was accomplished by heating the cyanide with magnesium powder (1). In numerous trials with ordinary potassium cyanide, the yields of carbon obtained by Eidmann's original procedure were never greater than fifty to sixty percent, a fact which was attributed to side reactions with atmospheric nitrogen and oxygen. It was therefore decided to carry out the reaction in a helium atmosphere, the nickel crucible containing the reaction mixture being heated by a high frequency induction coil (2). This modification of the procedure led to markedly better results, yields of eighty to one hundred percent being obtained consistently.

While it is not claimed that the optimum conditions were found, the following procedure is satisfactory. Mix intimately in a nickel crucible several grams of potassium cyanide with twice the theoretical weight of magnesium powder (i.e., approximately equal weights of cyanide and magnesium). Place in a vacuum system, and evacuate and flush with dry helium twice; then introduce helium to a pressure of about one atmosphere. Bring the crucible to incipient red heat and hold it there for five minutes; then gradually increase the temperature over a period of five minutes to bright red heat and hold it there for fifteen minutes. Cool, add water cautiously to the residue until the ensuing vigorous reaction stops, wash it into a beaker and acidify with HCl to dissolve excess magnesium. Let stand an hour or two, boil the mixture for five minutes, and wash with water by centrifuging at least six times. Finish up with two alcohol washes, and dry for four or five hours at 110°. This leaves in the centrifuge tube a cake of carbon which is easily broken up to a fine, silky, jet-black powder.

1. Eidmann, J. Prakt. Chem., 59, 1 (1899).
2. I acknowledge the courtesy of Mr. Robert Grinstead in instructing me in the operation of the Westinghouse induction heater.