I. The Kinetics of the Exchange of Radioactive Hydrogen between Hypophosphorous Acid and Water.

II. An Investigation of Some Aspects of the Chemistry of Hypophosphorous Acid and Thallous Hypophosphite.

III. A New Assay Method for Tritiated Water.

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Abstract

The kinetics of the exchange of radioactive hydrogen between hypophosphorous acid and water have been studied in acid, neutral, and basic solution. In acid solution the kinetics of the exchange were found to be the same as the kinetics of the oxidation of hypophosphorous acid by certain oxidizing agents. The mechanism common to both of these reactions is formulated and discussed. The isotope effect found in acid solution is explained, and a general theory of isotope effects in exchange reactions is presented. Exchange was found to be extremely slow in neutral solution and a little faster in basic solution; the results in basic solution, however, were complicated by the decomposition of the hypophosphite ion.

A new method for the purification of hypophosphorous acid is described.

Experiments on the preparation and thermal stability of thallous hypophosphite were conducted. These experiments are presented and discussed, along with some data on the reaction of hypophosphorous acid with persulfate and dichromate.

A new, rapid assay method for tritiated water, involving the use of solid samples and a windowless flow counter, is described.

Table of Contents

Part I. The Kinetics of the Exchange of Radioactive Hydrogen between Hypophosphorous Acid and Water.

Part II. An Investigation of Some Aspects of the Chemistry of Hypophosphorous Acid and Thallous Hypophosphite.

I. The Kinetics of the Exchange of Radioactive Hydrogen Between Hypophosphorous Acid and Water.

A. Introduction

The oxyacids of phosphorus have been a source of interest to chemists for many years. In particular, the kinetics of the oxidation of the lower-valent acids, H_3PO_2 and H_3PO_3, present some novel features and have received considerable attention. Part I of this thesis will be concerned with one aspect of this problem, namely, a study of the mechanism of the oxidation of hypophosphorous acid, H_3PO_2, to phosphorous acid, H_3PO_3.

Several investigators have studied the kinetics of this oxidation reaction in aqueous solution, using a variety of oxidizing agents. The oxidizing agents which have received most intensive study are iodine (1a,c), bromine (1b), chlorine (1b), iodate ion (1d,g), mercuric chloride (1a), cupric chloride (1a), and silver ion (1a). It has been found that in acid solution, all of the oxidation reactions,

$$H_3PO_2 + Ox \longrightarrow H_3PO_3 + Red, \qquad (1)$$

with $Ox = Cl_2, Br_2, I_2, IO_3^-, CuCl_2, HgCl_2,$ or Ag^+,
and $Red = Cl^-, Br^-, I^-, CuCl, Hg_2Cl_2,$ or Ag, (2)

obey the same rate law; furthermore, under certain conditions, the rate becomes independent of the concentration of the oxidizing agent, and all of the reactions 1 take place at the same rate. The work of Nylen (1e) and Griffith, McKeown, and Taylor (1c) showed that reactions 1 are subject to general acid catalysis, in the Brønsted sense.

The rate law common to all of these reactions in acid solution (pH <1 or 2) is:[*]

$$-\frac{d}{dt}(H_3PO_2) = \frac{(H_3PO_2)\sum_a k_a^o (HA)_a}{1 + \frac{\sum_a k_a^{o\prime} (HA)_a}{k_{ox}^o (Ox)}} . \qquad (3)$$

The notation $\sum_a k_a^o (HA)_a$ represents a sum of terms, each term being the product of the concentration of a catalyzing acid, HA, and its catalytic coefficient,[**] k_a^o. The sum contains terms corresponding to each of the Brønsted (proton donor) acids present in the system. These catalytic coefficients, k_a^o and $k_a^{o\prime}$, are the same for all of the oxidizing agents listed in equation 2.

When the concentration of the oxidizing agent is made fairly high (~ 0.01 f.), the rate law becomes

$$-\frac{d}{dt}(H_3PO_2) = (H_3PO_2)\sum_a k_a^o (HA)_a , \qquad (4)$$

and all of the reactions 1 take place at the same rate.

It is generally agreed that the mechanism proposed by Mitchell (1a) explains the observed rate laws, 3 and 4:

$$(H_3PO_2)_I \xrightarrow{k_a^o} (H_3PO_2)_{II} , \qquad \text{slow} \qquad (5)$$

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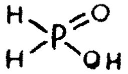
[*] In all equations, tables, and figures, brackets ( ) will be used to represent concentrations in units of moles per liter. Lower case k's will be used to represent rate constants. Those with "o" superscripts will refer to the oxidation reactions, and those with no superscript will refer to the exchange reaction. For the sake of convenience, (H_3O^+) will be written throughout as (H^+).

[**] The terms "rate constant" and "catalytic coefficient" are equivalent and will be used interchangeably.

$$(H_3PO_2)_{II} \xrightarrow{k_a^{o\prime}} (H_3PO_2)_I \,, \qquad \text{moderately rapid} \qquad (6)$$

$$(H_3PO_2)_{II} + Ox \xrightarrow{k_{ox}^{o}} H_3PO_3 + Red. \qquad \text{very rapid} \qquad (7)$$

In this scheme, $(H_3PO_2)_I$ represents the "normal" form of hypophosphorous acid, which presumably has the structure  (2). $(H_3PO_2)_{II}$ represents an "active" form, whose structure is as yet unknown but which is assumed to be so much more reactive towards oxidizing agents than the normal form that reaction 7 is the only appreciable oxidation reaction in the system. If one assumes that reactions 5 and 6 are subject to general acid catalysis, and that the active form exists at a small steady state concentration during the course of the reaction, equation 3 is easily derived. Experiment shows that for any acid, the magnitude of $k_a^{o\prime}/k_{Ox}^{o}$ is such that 3 reduces to 4 for (Ox) greater than ∼ 0.01 f.

Some of the oxidizing agents in equation 2 also react with the hypophosphite ion, but at widely varying rates. These reactions are simple bimolecular ones, and will not concern us here. However, they appear in the <u>overall</u> rate expression for $\frac{d}{dt}\sum(H_3PO_2)$ (1f) if the acid concentration is not kept high. In the bromine and chlorine reactions, the Ox - $H_2PO_2^-$ reactions are never negligible, and even at high (H^+), $\frac{d}{dt}\sum(H_3PO_2)$ is not equal to $\frac{d}{dt}(H_3PO_2)$.

The exchange studies to be described were undertaken in an attempt to verify, in an independent way, the existence of the equilibrium expressed by reactions 5 and 6, and thus to put the entire mechanism on a firmer experimental foundation. Exchange experiments should also lead to a deeper understanding of the nature of the active form. Previous investigators have speculated about its structure, and generally agreed that the difference between the two forms, $(H_3PO_2)_I$ and $(H_3PO_2)_{II}$, probably lay in the location of one of the undissociable* hydrogen atoms on the acid molecule. If the equilibrium

$$(H_3PO_2)_I \rightleftharpoons (H_3PO_2)_{II} \qquad (8)$$

exists in aqueous solutions of hypophosphorous acid, and if the two forms differ in the location of one of the undissociable hydrogen atoms on the molecule, then hypophosphorous acid in aqueous solution should exchange its undissociable hydrogen atoms with water.** It is, of course, evident that the one dissociable hydrogen of hypophosphorous acid will exchange immediately with water hydrogens. The reaction of interest, and the one whose kinetics was investigated in this work, is therefore best represented by the equation:

$$H_2POOH + TOH \rightleftharpoons HTPOOH + H_2O, \qquad (9)$$

where T represents an atom of tritium (radioactive hydrogen), which was the tracer used in this research to "tag" the

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* H_3PO_2 is a monobasic acid.

** Unless the hydrogen atom rearrangement is intramolecular.

hydrogen atoms so that the exchange might actually be observed. The atoms written in red are the undissociable ones whose exchangeability is under investigation.

It is further evident that if exchange takes place via reactions 5 and 6, with $k_a^{o'} \gg k_a^o$, one should find that the rate law for the exchange reaction is the same as the rate law for reaction 5, i.e.,

$$\text{rate of exchange} = (H_3PO_2) \sum_a k_a(HA)_a. \qquad (10)$$

Erlenmeyer and co-workers (3) first investigated the possibility of exchange of the undissociable hydrogens of hypophosphorous acid with the hydrogen atoms of water. They found that in acid solution, these atoms would exchange, but they made no rate measurements, and therefore did not establish any rate law or mechanism. Thus their results are consistent with, but do not verify, the existence of reactions 5 and 6. Brodskii, Strazhenko, and Chervyatsova (4)* investigated the exchange of radiophosphorus between H_3PO_2 and H_3PO_3 in the presence and absence of iodine. They claim that their results lend support to the existence of reactions 5 and 6, but in truth, all that their results show is that the reaction

$$H_3PO_2 + I_2 + H_2O \longrightarrow H_3PO_3 + 2I^- + 2H^+$$

is irreversible, a fact that was known about fifty years before they did their research.

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* I am indebted to Mr. W.J.Ramsey for a translation of this paper.

B. Experimental

Preparation of Materials

The tritium used in this research was obtained from the Argonne National Laboratories in the form of hydrogen gas which contained 2.6 curies of tritium. This gas mixture was converted to water in a vacuum system by diluting it with tank hydrogen and passing it slowly over copper oxide at 350°.* The resulting tritiated water vapor was collected in traps cooled with liquid air.

To assay for radioactivity the tritiated water so prepared, an aliquot portion was completely converted to hydrogen by passing it over magnesium turnings at 450° in a vacuum system (5). The absolute activity of the resulting hydrogen-tritium mixture was measured in an ionization chamber.** The activity found in this aliquot portion corresponded to a total activity of 2.4 curies of tritium in the tritiated water. This assay method is accurate to about 10%. Since one does not need to know the activity of the tritiated water in order to perform the required calculations in the exchange experiments, this accuracy was quite satisfactory.

To prepare stock solutions of tritiated water for the

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* Unless otherwise specified, all temperatures will be in degrees Centigrade.

** The ionization chamber assay was performed by Dr. D.L. Douglas.

exchange experiments, portions of the concentrated solution were removed, diluted, and distilled several times in a Pyrex still. The activity of the stock solutions used for the acid and basic solution exchange experiments varied from 0.1 to 0.2 millicuries per gram of water. For the neutral solution experiments, a stock solution with an activity of about 0.4 millicuries per gram was used.

Hypophosphorous acid was prepared by converting Baker's Analyzed, c.p. sodium hypophosphite to the acid in an ion exchange column, using Amberlite IR-120-AG as the ion exchange resin. Various other preparative methods were tried, including the method described in Part II, but the ion exchange method was found to be the most satisfactory, from the standpoint of purity of product and economy of effort.

The acid so prepared was analyzed for phosphorous acid by the method of Jones and Swift (6). It was found to contain, on the average, about 0.5 mole percent phosphorous acid. Stock solutions of hypophosphorous acid for the exchange runs were made up from this ion exchange product, standardized by titration with standard NaOH, and stored in the cold room at 5° when not in use. Experiments have shown that hypophosphorous acid stored in this way undergoes no detectable decomposition* in six to eight months (7).

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* Hypophosphorous acid is thermodynamically unstable with respect to air oxidation to phosphorous acid and to disproportionation into phosphine and phosphoric acid.

Carbonate-free solutions of sodium hydroxide were prepared and standardized with potassium acid phthalate in the usual way.

Thallous hypophosphite was prepared as described in Part II.

Thallous hydroxide solutions were prepared by shaking thin slices of thallium metal with water, while bubbling oxygen through the mixture. The resulting solution was filtered and then concentrated by aspirating off the solvent until the solution became saturated.

C.p. hydrobromic acid was used as purchased from the stockroom, after boiling out the bromine. It was standardized with standard NaOH. C.p. sulfuric acid was used as purchased from the stockroom and was standardized with NaOH in the usual way.

Solutions of oxalic acid were made up by dissolving the c.p. crystals in a slight excess of distilled water. The solutions were standardized by titration with standard NaOH to the phenol red end point, using a solution of sodium oxalate and phenol red to match the end point.

Solutions of calcium bromide were prepared by drying the commercial "c.p." product at 140° and dissolving a weighed amount in a known volume of distilled water. The resulting murky solutions were centrifuged to remove wood, grease and other suspended matter.

Solutions of barium bromide were made up in the same way. Barium bromide was prepared by dissolving solid barium hydroxide in HBr, evaporating to recover crystals, recrystallizing, and drying at 140°.

Radioassay of Thallous Hypophosphite Samples

In all of the exchange runs, total hypophosphite[*] in solution was analyzed for tritium activity by isolating total hypophosphite from the reactant solution in the form of thallous hypophosphite. This was done by neutralizing, with thallous hydroxide, the sample which had been withdrawn from the reaction mixture; the resulting solution was evaporated in vacuo to obtain solid thallous hypophosphite. This procedure left the dissociable hydrogen in solution, in the form of water, and isolated the two undissociable hydrogens as thallous hypophosphite. Preliminary experiments were performed, prior to the exchange experiments, to make sure that the hypophosphite ion did not undergo any decomposition in the evaporation process. Analysis of the evaporated product showed that no decomposition had taken place.

The solid product obtained by evaporation was mixed up well and packed into circular, flat planchets. These planchets were then placed in the planchet holder of a windowless, Q-gas[**] flow, Geiger-Muller counter (manufactured by the Nuclear Instrument and Chemical Co., Model D-46A), and after thirty seconds or so of "preflushing", counted in the usual

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[*] Total hypophosphite $\equiv$ hypophosphorous acid + hypophosphite ion. Both species are present in significant amounts in acid solutions of H_3PO_2.

[**] 99% helium, 1% butane.

way. Pulses from the counter were detected with a Berkeley Decimal Scaler, Model 1000.

The counter was operated at 1200 volts, in the center of a plateau which was about 250 volts long and which had a slope of about 0.04% per volt at 1200 volts. Counter and scaler were checked from time to time with a cobalt 60 source of known activity.

The reproducibility of the activity observed in successive planchet fillings was found to be about 1%.* It was also found that a thallous hypophosphite sample of a given activity could be redissolved in water, re-evaporated, and recounted with a reproducibility of about 1%. In all cases, the planchets, which had an area of about 7 cm.^{2}, contained from 140 to 280 mg/cm.^{2} of material. "Infinite thickness" for tritium beta rays, which have a mean energy of about 5 kilovolts (8), is about 0.7 mg./cm.^{2}. This means that when a planchet is filled to a depth which corresponds to 0.7 mg./cm.^{2} or greater, the only activity that will be "seen" by the counter is the activity in a thin layer of the material at and just below the surface. Under these conditions, the observed counting rate will obviously be independent of the amount of material in the planchet, so long as there is enough to maintain the thickness above infinite thickness, and will depend only on the specific activity of the material

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* Except in runs in which H_2SO_4 and oxalic acid were added to the reaction mixture.

counted. This accounts for the good reproducibility observed when successive planchets were filled with thallous hypophosphite of a given activity and counted.

To my knowledge, this is the first time that such an assay technique has been used in an exchange reaction in which tritium was used as a tracer. The method was first applied to tritium by Eidinoff and Knoll (9), who discovered that active samples of a steroid could be assayed for tritium in this way. This assay method has several tremendous advantages over the older method of gas-phase assay. Its major disadvantages are threefold: 1) One cannot obtain the absolute activity of a radioactive sample by this procedure. However, this is no disadvantage in an exchange reaction, since, as will be apparent later, all one needs to know to carry out the calculations is a quantity which is proportional to the absolute or specific activity. As explained above, a quantity proportional to the specific activity is obtained in this assay method. 2) One must use samples of a relatively high specific activity, of the order of 1000 counts/minute/mg. of material in the planchet, to give convenient counting rates (100 c/m or greater). 3) A relatively large amount of material is required to fill the planchet evenly to the required depth.

Exchange Studies in Neutral Solution

The work of Erlenmeyer, et. al. (3) showed that in neutral solution, the hypophosphite ion would not exchange deuterium with deuterated water over periods of "a few hours".

This fact, if true, seemed to offer an excellent way of simultaneously quenching the tritium exchange reaction (the rate of which was being measured in <u>acid</u> solution), and preparing the total hypophosphite for removal from solution as thallous hypophosphite, since both of these operations could be carried out by simply neutralizing samples of the reaction mixture with thallous hydroxide. Accordingly, an investigation was made to confirm Erlenmeyer's results.

Two sets of experiments were carried out, one set in which inactive thallous hypophosphite was added to active water, and the other set in which thallous hypophosphite, rendered active by an acid solution exchange, was added to inactive water. Except for the initial location of the tritium activity, both sets of experiments were carried out in the same manner: inactive (active) thallous hypophosphite was dissolved in active (inactive) water, allowed to stand for a period of time, and the solution was then evaporated in the apparatus shown in Figure 1. Thallous hypophosphite was scraped out of the evaporating bottle, packed into a planchet, and counted as described above.

All neutral solution experiments were carried out at room temperature.

Table 1 contains the results of the first set of experiments. It is seen that in all cases, a small amount of "exchange" (1 to 3%) was found, the amount of "exchange" depending upon the washing process, the number of times the

HTO had been distilled, and being independent of the time of contact between TlH_2PO_2 and HTO. The reason for this small amount of "exchange" is not known. Many experiments were carried out to find out why it occurred, since it was evidently not true exchange. (Lack of time dependence, the results of the second set of experiments, and the results of Erlenmeyer all lead to this conclusion). It would be pointless to go into the details of the search for an answer to this problem, since it later became evident that if one reduced the specific activity of the HTO, the effect diminished to a point where it was no longer troublesome.

The results of the second set of neutral solution exchange studies ($TlHTPO_2$ plus H_2O), given in Table 2, confirm completely the conclusion that over short periods of time, the hypophosphite ion in neutral solution will not exchange its hydrogen atoms with water.

The longest period of contact time given in Table 2 is thirty-one days, and the last result in Table 2, although it seems to conflict with the last result in Table 1, indicates that a very slow exchange may be taking place. For this reason, attempts were made to extend the reaction to longer periods of time, in order to see if this very slow exchange was a real effect. However, all these attempts failed, due to the slow decomposition of the hypophosphite ion which always takes place in neutral aqueous hypophosphite solutions (7).

Exchange Studies in Acid Solution

The major aim of this research was to study the kinetics of the exchange in acid solution. The general experimental procedure which was used in all the runs will be discussed first.

Stock solutions of the reagents, prepared and standardized as previously described, were diluted with distilled water as desired, and appropriate volumes were pipetted into dry, glass-stoppered, Pyrex flasks, which were then placed in a thermostat where the temperature was held constant to ± 0.03°. After the solutions had reached the temperature of the thermostat bath, they were mixed by pipetting the correct volume of acid into the flask which already contained the correct volume of tritiated water. At appropriate time intervals, samples were pipetted out, discharged into a small flask, and immediately neutralized with thallous hydroxide. The end point of the neutralization was detected with pH paper. This entire sampling and neutralizing procedure usually took less than one minute, a time which was very short compared to the reaction times in the great majority of cases. Time of reaction was taken at the beginning of the neutralization procedure, which usually took about ten to fifteen seconds. In those rare cases in which the half times of the reaction were of the order of fifteen to twenty minutes, the withdrawn samples were discharged into an equivalent amount of thallous hydroxide. This discharge procedure took about three seconds.

Each neutralized sample was immediately filtered into an evaporating bottle and vacuum evaporated as soon as possible. On the average, a sample usually stood about one hour before being evaporated; in rare cases, samples stood overnight. The solid $TlHTPO_2$ obtained by evaporation was then washed by redissolving it in 20 to 25 ml. of inactive distilled water and re-evaporating the resulting solution. Experiments showed that this washing technique serves to dilute the activity of the tritiated water which remains adsorbed on the solid after the first evaporation to the point where it is no longer detectable. The washed solid was then scraped out of the evaporating bottle, mixed up well, packed in a planchet, and counted.

To calculate the results of the exchange experiments, one must know, among other things, the concentration of active total hypophosphite in the reaction mixture at "infinite" time.* This value will be denoted by the symbol x'_∞. In this work, a quantity proportional to the <u>specific</u> activity of total hypophosphite at infinite time was measured. This measured quantity will be denoted by x_∞. Values of x_∞ were obtained for every run by letting a portion of the reaction mixture stand for at least ten half times, neutralizing and evaporating it, and counting the $TlHTPO_2$ thus obtained.

Most of the solid samples were re-packed and re-counted

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* See Section C.

several times, as a check on the reproducibility of the planchet filling procedure. With the exception of the runs made with oxalic and sulfuric acids, this reproducibility was always better than 4% and usually ran around 1-2%. In some cases, solid samples were redissolved in inactive water and re-evaporated with no significant change in activity.

The background rate of the counter was 34-38 c/m, and the sample activities ranged from 400 to 1600 c/m. No coincidence corrections were made, since at these low counting rates, such corrections were negligible in comparison to the other uncertainties in the assay procedure.* Samples were counted for times long enough so that the statistical error in counting was always less than the other errors inherent in the work. The long half life of tritium (12.5 yr. (8)) made decay corrections unnecessary.

One of the many disadvantages of the evaporation method for recovering total hypophosphite as thallous hypophosphite was that prior to evaporation, all ions other than Tl^+, $H_2PO_2^-$, H^+ and OH^- had to be removed from the samples by precipitation. This severely limited the number of different chemical compounds that could be added to the reaction mixture. From this standpoint, the runs can be divided into five groups:

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* The resolving time of this counter-scaler combination is about 100 μ sec.

1) In Group One, hypophosphorous acid and tritiated water were the only reactants. Here, the problem of removing ions other than H^+, OH^-, $H_2PO_2^-$, and Tl^+ from the neutralized samples did not exist.

2) In Group Two, hypophosphorous acid, thallous hypophosphite, and tritiated water were the only reactants. Here again there was no problem.

3) In Group Three, hypophosphorous acid, hydrobromic acid, and tritiated water were the only reactants. Here, the offending Br^- ion was automatically removed upon neutralization, due to the insolubility of TlBr.* Filtration then removed the TlBr.

4) In Group Four, hypophosphorous acid, sulfuric acid, and tritiated water were the reactants. In this Group, a measured amount of a standard solution of barium bromide was added to the neutralized samples. This removed SO_4^{--} as $BaSO_4$ and the excess Tl^+ (resulting from the neutralization of H_2SO_4 as well as H_3PO_2) as TlBr. The combined precipitates were removed by centrifugation. As will be seen later, this procedure was only moderately successful.

5) In Group Five, hypophosphorous acid, oxalic acid, and tritiated water were the reactants. In this Group, a measured amount of a standard solution of calcium bromide was added to the neutralized sample; in this way, oxalate was removed as calcium oxalate, and excess Tl^+ was removed

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* $K_{sp} = 3.6 \times 10^{-6}$.

as TlBr. These samples were centrifuged and then evaporated as were those in Group Four. As will be seen later, this procedure was also only moderately successful.

In those Groups in which a mixture of acids was added to the tritiated water to start the reaction (Groups Three, Four and Five), the acids were always premixed and brought to the required temperature before beginning the reaction. In Group Two, solutions of hypophosphorous acid and thallous hypophosphite were premixed by weighing out vacuum dried samples of TlH_2PO_2 and dissolving them in the acid. In all Groups except the first, the ionic strength was kept constant from series to series and Group to Group by varying the acid concentrations in an appropriate manner. Groups One, Two and Three were used to determine the order of the exchange reaction, and Groups Four and Five were used to determine the catalytic coefficients of the bisulfate ion and of oxalic acid. Group Three was again used to determine the activation energies.

At least two runs were always made at a given concentration, to check reproducibility and ensure greater reliability in the final results. In many of the earlier experiments, three runs were made at a given concentration. For future convenience, the aggregate of runs carried out at a given concentration will be called a "series".

Exchange Studies in Basic Solution

Franke and Monch (10) have reported that in alkaline solution, the undissociable hydrogens of the hypophosphite ion will exchange deuterium with deuterated water. Some experiments were conducted on this system to check this result.

The experiments were carried out by dissolving inactive thallous hypophosphite in HTO which was made basic by the addition of TlOH. At appropriate time intervals, samples of the reaction mixture were withdrawn and neutralized with HBr. The resulting solutions were filtered to remove TlBr, evaporated, washed, and counted as usual.

C. Calculations

The general theory of homogeneous isotopic exchange reactions has been developed by Wilson and Dickinson (11), Duffield and Calvin (12), and others (13). This theory will be briefly summarized here, mainly for the purpose of introducing the notation and the fundamental ideas.

We consider the homogeneous exchange reaction,

$$AX + BX^{o} \rightleftharpoons AX^{o} + BX, \qquad (11)$$

where X^{o} represents the "tagged" atom whose exchange is being studied. Let $(AX) + (AX^{o}) = a$, $(BX) + (BX^{o}) = b$, $(AX^{o}) = x'$, and $(BX^{o}) = y'$. Let the rate of exchange of <u>all</u> <u>X</u> <u>atoms</u>, whether radioactive or not, between AX and BX be denoted by R. <u>In the absence of isotope effects</u>, R will be independent of the existence of tracer atoms in the system and be a function only of the chemical concentrations and possibly some heterogeneous parameters. In the case of an exchange reaction taking place in a system which is at chemical equilibrium (and in which all heterogeneous parameters are constant during the reaction), R will be a constant during the course of the reaction. The equation for the increase of radioactivity in the species AX then becomes

$$\frac{dx'}{dt} = R\frac{y'}{b}\,\frac{(a-x')}{a} - R\frac{x'}{a}\,\frac{(b-y')}{b}, \qquad (12)$$

an equation which is derived simply by considering the rates of formation and destruction of AX^{o}.

Since R is a constant, equation 12 is very simply integrated, giving

$$x' = Ce^{-\frac{(a+b)}{ab}Rt} + \frac{a}{(a+b)}z, \tag{13}$$

where $z = x' + y'$ and C is an arbitrary constant of integration. If we now impose the boundary conditions:

at $t = 0$, $x' = 0$ (AX initially inactive),

at $t = \infty$, $x' = x'_\infty$ and $y' = y'_\infty$,

and let $x'/x'_\infty \equiv F$, equation 13 becomes

$$1 - F = e^{-\frac{(a+b)}{ab}Rt}. \tag{14}$$

13 and 14 are standard equations for a first order process. This result shows that regardless of what dependence R may have on the chemical concentrations, for a given set of concentrations, the exchange reaction will always be a first order process. This result has been confirmed in all simple exchange reactions, where all the exchanging atoms in a given molecule are equivalent and in which no large isotope effects occur. Under certain conditions, the presence of a large isotope effect will vitiate this result. This will be discussed later, where it will be shown that although large isotope effects exist in the hypophosphorous acid exchange reaction, conditions were such that their presence did not disturb the first order character of the reaction.

The quantity of interest in all such reactions is R; one wishes to know the dependence of R on the chemical concentrations in the system. To find R, one proceeds as follows: One measures x', or a quantity which is directly proportional to it, as a function of time, by withdrawing samples of the reaction mixture, isolating $AX + AX^o$ from the mixture and measuring its activity. In the same way, one then measures or calculates x'_∞ (or a quantity proportional to it). From equation 14, it is evident that a plot of -log (1 - F) versus time will have a slope of $\frac{1}{2.3}\frac{(a+b)}{ab}R$. Thus, by measuring the slope of such a plot, one can determine R from the equation

$$R = 2.3\frac{ab}{(a+b)}(\text{slope}). \qquad (15)$$

One then changes the concentrations and repeats the reaction. A different value of R will result (unless R is zero order in all the concentrations); by properly varying the concentrations, the functional dependence of R on all the concentrations can be found. The order of the exchange reaction is thus determined, and one then knows the kinetics of the reaction

$$AX + BX \rightleftharpoons AX + BX. \qquad (16)$$

In this development, the effect of isotopes has been ignored. It will be shown later that if large isotope effects are present, due to large differences in mass between X and X^o, one may expect to find the correct order but a different rate constant from the rate constant for reaction 16.

In this investigation, the procedure described above was followed. By measuring the activity of thallous hypophosphite samples isolated from the reaction mixture, the quantity x was obtained. As explained on page 10, x is proportional to the specific activity of total hypophosphite:

$$x = M(\text{sp. act. } \sum(H_3PO_2)),$$

where M is a constant of proportionality which depends on counting geometry, etc., and $\sum(H_3PO_2) \equiv (H_3PO_2)+(H_2PO_2^-)$. By measuring the activity of the thallous hypophosphite samples at "infinite" time, as described on page 15, x_∞ was obtained. x_∞ is proportional to the specific activity of total hypophosphite at infinite time:

$$x_\infty = M(\text{sp. act. } \sum(H_3PO_2) \text{ at } t = \infty).$$

In a given run, the specific activity of total hypophosphite at any time is proportional to x', or (AX^o), the concentration of active total hypophosphite in solution:

$$(\text{sp. act. of } \sum(H_3PO_2) \text{ at time } t) = D(\text{concentration of active } \sum(H_3PO_2) \text{ at time } t)$$

$$= Dx',$$

where D is a proportionality constant which depends on the acid concentration. (See page 69, equation 53). Therefore,

$$x = MDx',$$

$$x_\infty = MDx'_\infty,$$

and

$$F \equiv x'/x'_\infty = x/x_\infty . \qquad (17)$$

Thus F could be calculated from the measured values of x and x_{∞}.

-Log(1-F) was then plotted versus the time at which the sample had been neutralized. Typical plots of this kind are shown in Figure 2. The linearity of these plots, observed in all runs, is a good check on the experimental method and shows that the required kinetics are being obeyed. It also shows that the two exchanging H atoms on the H_3PO_2 molecule are equivalent, in the exchange sense (13b), and that a phenomenon known as "separation induced exchange" (14) is not occurring. The slope of the straight line was determined both graphically and analytically, and R was then calculated from equation 18 below. The concentrations were then changed in an appropriate manner to determine the functional dependence of R on the concentrations of all the species in the system.

The quantity measured in all of these experiments was the rate at which <u>both</u> undissociable hydrogens of <u>total</u> hypophosphite, $\sum(H_3PO_2)$, become radioactive by exchange with active water. The quantity of interest, however, was the rate at which <u>one</u> of the two hydrogens exchanged. This rate can be calculated from the experimental data if one modifies 15 by multiplying a and b by two* (13c):

$$R = 2.3\,(\text{slope})\left[\frac{2(H_2O)\cdot 2\sum(H_3PO_2)}{2(H_2O)+2\sum(H_3PO_2)}\right],$$

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[*] Since both $\sum(H_3PO_2)$ and H_2O have two exchangeable hydrogens per molecule (neglecting, as usual, the dissociable hydrogen of H_3PO_2).

or

$$R = 2.3\,(\text{slope})\,2\left[\frac{(H_2O)\cdot\sum(H_3PO_2)}{(H_2O)+\sum(H_3PO_2)}\right]. \tag{18}$$

Equation 18 was always used to calculate R. For this reason, all the rate constants derived in this work apply to the exchange reaction,

$$\text{HHPOOH} + \text{THO} \rightleftharpoons \text{THPOOH} + \text{HOH} \tag{19}$$

The concentrations of all the ionic and molecular species present in the reaction mixtures were calculated in the usual way from the acid dissociation constants and the known stoichiometric concentrations of the acids in the mixtures.

Values for the dissociation constant of hypophosphorous acid,

$$K_c = (H+)(H_2PO_2^-)/(H_3PO_2),$$

were taken from the work of Griffith, McKeown, and Taylor (1c). The dissociation constant of the bisulfate ion,

$$K^{HSO_4^-} = (H+)(SO_4^{--})/(HSO_4^-),$$

was determined by Griffith and McKeown (15) and Noyes and Sherrill (16). The dissociation constant of oxalic acid,

$$K^{H_2Ox} = (H+)(HOx^-)/(H_2Ox),^*$$

has been determined by Dawson, Hoskins, and Smith (17). These investigators determined the values of these constants

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* Hereafter, H_2Ox and HOx^- will be used as a convenient notation for $(COOH)_2$ and the binoxalate ion, respectively.

over ranges of temperature and ionic strength. Plots of log K versus 1/T and k versus μ * were made to determine the values of the constants at the temperatures and ionic strengths used in this work.

The use of these constants may introduce an unknown but possibly large systematic error into the values of the rate constants. This error is probably not larger than 10%, and may be much smaller than this. However, since the values of the rate constants obtained in this research will eventually be compared to Griffith, McKeown, and Taylor's rate constants, and since Griffith, et. al. used the same dissociation constants to calculate their rate constants, this unknown systematic error will be relatively unimportant.

The actual values used for these dissociation constants were, in units of moles per liter:

at 27.23° and $\mu = 0.218$,

$$K_c = 0.080,$$

$$K^{HSO_4^-} = 0.047,$$

$$K^{H_2Ox} = 0.078;$$

at 35.30° and $\mu = 0.218$,

$$K_c = 0.069.$$

The assumption was made throughout that these constants were functions of ionic strength alone and independent of the chemical nature of the system.

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* μ = ionic strength.

The determination of the rate law for the exchange reaction from the measured values of R and the known concentrations was straightforward. Several different methods were used. If the rate expression consists of only one term in the concentrations,

$$R = k(H+)^m(H_3PO_2)^n(H_2PO_2^-)^p,$$

where m, n, and p may take on any integral, non-integral, positive, or negative values, one can set up a table of $R/(H+)^m(H_3PO_2)^n(H_2PO_2^-)^p$ quotients, where m, n, and p are assigned different values, and see which one of these quotients remains constant as R and the concentrations vary. If the rate expression consists of more than one term, one can use various graphical methods, which are best described in the next section.

D. Results

Determination of Order

Sixteen different series of experiments (39 runs) were carried out at 27.23° to determine the order of the exchange reaction,

$$\mathrm{HHPOOH} + \mathrm{THO} \rightleftharpoons \mathrm{THPOOH} + \mathrm{HOH} \qquad (19)$$

For purposes of illustration, the values of x and x_∞ obtained in typical runs are presented in table 3.

The rate expression for reaction 19 was found to be

$$R = k_1(H^+)(H_3PO_2) + k_2(H_3PO_2)^2. \qquad (20)$$

k_1 is the catalytic coefficient, k_a, for H^+, and k_2 is the catalytic coefficient for free hypophosphorous acid, H_3PO_2. Since Groups One, Two and Three were used in these experiments, H^+ and H_3PO_2 were the only acids present in the system. Equation 20 is thus a special case of the general rate expression 10, which was expected if exchange proceeded via reactions 5 and 6.

It was found that at 27.23°, the two catalytic coefficients, k_1 and k_2, were equal. Thus the two rate constants and (H_3PO_2) can be factored out of equation 20, and that expression rewritten as

$$R = k_o(H_3PO_2) \sum{}'(H_3PO_2), \qquad (21)$$

where $\sum{}'(H_3PO_2) \equiv (H_3PO_2) + (H^+)$. This rearrangement is made here for the purpose of convenience in testing this order in the tables which follow. Expression 21 is, of course, valid only at 27.23°, where the two catalytic coefficients are equal. The results of the individual Groups will now be considered separately.

In Group One, seven different series of runs were made, at seven different concentrations of $\sum(H_3PO_2)$. The results are given in Tables 4 and 5. It is evident that, although the order given by 21 holds, several other orders hold with equal validity. The variation in K_c with ionic strength in this Group was taken into account in making the calculations of the concentrations.

The experiments in Group Two were designed to do three things: 1) To extend the range of concentrations. 2) To differentiate between dependence on $\sum'(H_3PO_2)$ and dependence on $\sum(H_3PO_2)$. 3) To see if some other order, possibly valid, was failing because of the variation in ionic strength in Group One. Five series of runs were carried out, in which TlH_2PO_2 was added to the reaction mixture to maintain the ionic strength constant as $\sum(H_3PO_2)$ was varied. This amounted to keeping $(H_2PO_2^-)$ constant and equal to μ, since

$$\mu = \tfrac{1}{2}\sum_i c_i z_i^{\,2},$$
$$= \tfrac{1}{2}\left[(Tl^+)+(H^+)+(H_2PO_2^-)\right] \;;$$

but $$(Tl^+)+(H^+) = (H_2PO_2^-),$$

$$\therefore\ \mu = (H_2PO_2^-).$$

$(H_2PO_2^-)$ was chosen so that Series IV could be used in plots of the results of this Group.

The results of these experiments are presented in Tables 6 and 7. It is seen that many of the possible orders allowed by Group One were eliminated, and that six reasonable orders (the first six listed in Table 7) remained, including the correct one, given by equation 21. The results can also be presented in a graphical form which sheds further light on the relationship between these six orders. Equation 20 shows that under the conditions obtaining in this Group of experiments, a plot of log R versus log (H_3PO_2) should be a straight line with a slope of 2:

$$R = k_1(H^+)(H_3PO_2) + k_2(H_3PO_2)^2,$$

$$(H+) = K_c(H_3PO_2)/(H_2PO_2^-) = K_c(H_3PO_2)/\mu ,$$

$$R = (H_3PO_2)^2 \left[k_1K_c/\mu + k_2 \right] ,$$

$$\log R = 2\log (H_3PO_2) + \log \left[k_1K_c/\mu + k_2 \right] .$$

This plot is shown in Figure 3, where it is seen that these requirements are satisfied.

Equation 20 also shows that under these conditions, a plot of $R/(H_3PO_2)$ versus (H_3PO_2) should be a straight line with zero intercept on the $R/(H_3PO_2)$ axis:

$$R = k_1(H^+)(H_3PO_2) + k_2(H_3PO_2)^2,$$

$$= (H_3PO_2)^2 (k_1K_c/\mu + k_2),$$

$$R/(H_3PO_2) = (H_3PO_2) \left[k_1K_c/\mu + k_2 \right] .$$

This plot is shown in Figure 4, where it is seen that the requirements of linearity and zero intercept are satisfied.

The reason for the apparent validity of the other five orders under these conditions now becomes obvious, since the algebraic form of any one of them leads to the same requirements for the plots in Figures 3 and 4. It was thus impossible for this Group of experiments to distinguish between them. In a sense, these other orders were "forced" to hold when the correct one did, under the conditions in this Group, namely, $(H_2PO_2^-)$ constant.

The experiments in Group Three were designed to eliminate this ambiguity. In this Group, HBr was added as needed to maintain the ionic strength constant and equal to (H^+). (H^+) was chosen so that Series IV could be used in plots of the results of this Group. Tables 8 and 9 show that this set of experiments accomplished the desired effect.

The five spurious orders are further eliminated graphically in Figure 5. Equation 20 predicts that for (H^+) constant, a plot of $R/(H_3PO_2)$ versus (H_3PO_2) will be a straight line with non-zero slope and a non-zero intercept on the $R/(H_3PO_2)$ axis:

$$\begin{aligned} R &= k_1(H^+)(H_3PO_2) + k_2(H_3PO_2)^2, \\ R/(H_3PO_2) &= k_1(H^+) + k_2(H_3PO_2), \\ &= k_1\mu + k_2(H_3PO_2), \\ &= \text{const.} + k_2(H_3PO_2). \end{aligned}$$

Figure 5 shows that these requirements are fulfilled. The other five orders, on the other hand, predict forms for this plot which are not actually observed:

1) $R = k(H^+)^2$ predicts a hyperbola.

2) $R = k(H^+)(H_3PO_2)$ predicts a horizontal straight line.

3) $R = k(H^+) \sum'(H_3PO_2)$, or $R = k(H^+) + k'(H^+)(H_3PO_2)$, predicts a hyperbola.

4) $R = k(\sum'(H_3PO_2))^2$, or $R = k(H^+)^2 + k'(H^+)(H_3PO_2) + k''(H_3PO_2)^2$, predicts a more complicated, non-linear curve.

5) $R = k(H_3PO_2)^2$ predicts a straight line with zero intercept on the $R/(H_3PO_2)$ axis.

Thus these three Groups of experiments, which covered a 10-fold range in (H_3PO_2) and a 10-fold range in (H^+), serve to eliminate completely some thirty-odd possible rate equations, leaving only equation 20. Elimination of other possible orders was made in several ways:

1) A general consideration was made of all rate equations up to and including three term polynomials, each term containing as many as three factors, each factor of the form $(H^+)^m$, $(H_3PO_2)^n$, or $(H_2PO_2^-)^p$, where the numbers m,n and p were allowed to assume any value from $+\infty$ to $-\infty$, and the rate constants preceding each such term were allowed to take on any value. (This took care of possible orders depending on $\sum(H_3PO_2)$ or $\sum'(H_3PO_2)$ which might have failed in Tables 5,7 and 9 because of the inequality of the several rate constants in the rate expression). It was found that the

only rate expressions which satisfied the conditions imposed (the observed linearity of the plots in Figures 3,4, and 5, and the observed non-linearity of certain other plots) were those of the form $R = k_1(H^+)(H_3PO_2) + k_2(H_3PO_2)^2$, or of a form reducible to that by the proper substitution of the dissociation constant, $(H^+)(H_2PO_2^-)/(H_3PO_2)$.

2) As stated above, one can also invoke the observed facts and derive from them the correct rate expression. The observed facts are as follows:

1. A plot of $R/(H_3PO_2)$ versus (H_3PO_2) for runs in which $(H_2PO_2^-)$ is constant is linear with zero intercept.
2. A plot of log R versus log (H_3PO_2) for runs at constant $(H_2PO_2^-)$ is linear with slope = 2 and a finite intercept on the log R axis.
3. A plot of $R/(H_3PO_2)$ versus (H_3PO_2) for runs at constant (H^+) is linear with a finite intercept on the $R/(H_3PO_2)$ axis.

The derivation proceeds as follows:

Let k denote any constant which is not a function of any of the three variables, (H^+), (H_3PO_2), or $(H_2PO_2^-)$.

a. From fact 3,

$$R/(H_3PO_2) = (H_3PO_2)\left[f_1 \left[(H^+) \text{ and/or a constant} \right] \right] + f_2 \left[(H^+) \text{ and/or a constant} \right]. \quad (I)$$

b. From fact 1,

$$R/(H_3PO_2) = (H_3PO_2)\ f_3 \left[(H_2PO_2^-) \text{ and/or a constant} \right]. \quad (II)$$

c. From fact 2,

$$\log R = 2\log (H_3PO_2) + \left[\log f_4(H_2PO_2^-) \text{ and/or } \log k \right]. \quad (III)$$

We now assume that the rate expression is some unique function of the concentrations in the system, and that its algebraic form does not vary with concentration over the range studied in these experiments. Here, "unique" is used with the understanding that the presence of the maintained equilibrium, $H_3PO_2 \rightleftharpoons H^+ + H_2PO_2^-$, with $(H^+)(H_2PO_2)/(H_3PO_2) = K_c$, may make some rate expressions experimentally indistinguishable from others.

d. Following this assumption, we see that equations I and II must be made identical in form. Hence, $f_3\left[(H_2PO_2^-) \text{ and/or a constant}\right]$ in II must contain <u>at least</u> two terms, and be expressible as

$$f_5\left[(H^+) \text{ and/or a constant}\right] + \frac{1}{(H_3PO_2)} f_6(H^+). \qquad \text{(IV)}$$

It should be especially noted that $f_6(H^+)$ in equation IV cannot be a constant alone, else the second term of IV would be $k/(H_3PO_2)$, which is not a function of ((H^+) alone and/or a constant), as required by I.

e. II can be rewritten as

$$\log R = 2\log(H_3PO_2) + \log\ f_3\left((H_2PO_2^-) \text{ and/or a const}\right). \text{(V)}$$

f. Now compare V with III, after substituting IV into V:

$$\text{III: } \log R = 2\log(H_3PO_2) + \log f_4\left[(H_2PO_2^-) \text{ and/or a } k\right].$$

$$\text{V': } \log R = 2\log(H_3PO_2) + \log\left[f_5\left[(H^+) \text{ and/or } k\right] + \frac{1}{(H_3PO_2)} f_6(H^+)\right].$$

g. Obviously, $f_5\left[(H^+) \text{ and/or } k\right] + \frac{1}{(H_3PO_2)} f_6(H^+)$ must be a function of $(H_2PO_2^-)$ alone, and/or a constant. Thus:

$$f_5\left[(H^+) \text{ and/or } k\right] = k_2,$$

since the only way a function of (H+) and/or a k can also be a function of $(H_2PO_2^-)$ and/or k is for the function to be a constant;

$$f_6(H+) = k_1(H+),$$

since $(H+)/(H_3PO_2) = K_c/(H_2PO_2^-)$ is a function of $(H_2PO_2^-)$ alone. Substituting these conclusions into equation V$'$and taking antilogs, the rate expression becomes

$$R/(H_3PO_2) = (H_3PO_2)(k_2 + k_1(H+)/(H_3PO_2)),$$

or $$R = k_2(H_3PO_2)^2 + k_1(H+)(H_3PO_2),$$

which is equation 20, the rate expression found by the more standard procedure described in the above paragraphs.

Additional proof that equation 20 is the correct rate expression was obtained from the experiments on ionic strength dependence conducted in Group One. Since 20 contains terms corresponding to reaction between ions and neutral molecules, or reaction between neutral molecules only, the Brønsted Debye-Hückel (18) salt-effect theory would predict no dependence of these rate constants on ionic strength. As Table 4 shows, this is what was actually observed. Conversely, orders such as $k(H+)\sum{}'(H_3PO_2)$ predict an ionic strength dependence, yet no such dependence was shown by orders such as these in Group One. Taken by itself, this is not a very convincing argument, since the ionic strengths in this work are much too high for the Brønsted Debye-Hückel theory in its simple form to be applicable. However, in conjunction with the other methods of proof used above, it strengthens the proof that equation 20 is the correct rate expression.

Summary of Experimental Results at 27.23°.

Discussion of Error.

The values found at 27.23° for the rate constants k_1 and k_2 in equation 20 are:

$$k_1 = 2.28 \pm .03$$
$$k_2 = 2.28 \pm .03$$

in units of liters per mole hour. The word "mole" in these units refers to moles of H atoms exchanging, or moles of H_3PO_2 exchanging one of their two moles of H atoms, or moles of H_3PO_2 going through one of the cycles given in equations 5 and 6, all of these forms being equivalent (assuming that equations 5 and 6 correctly represent the exchange mechanism). Throughout this paper the k_a's for the exchange reaction will be expressed in these units.

These values were derived by assuming that k_1 and k_2 were equal, within experimental error, at this temperature, an assumption that is justified by the constancy of these constants with varying concentrations. The experimentally determined value of R in each series was then divided by the value of $(H_3PO_2)\sum'(H_3PO_2)$ in that series. The limits of error given above represent the average deviation of the values of the constants from the mean. Thus the standard deviation of these figures is .038, and the "99% confidence interval"* (19) is .033.

In taking the average, five values were rejected (those from Series VI, IX, X, XII, and XIII). There is no good statistical reason for the rejection of these values; the "2.5d test" (20) would allow their rejection, but it has been shown (21) that the 2.5d test is invalid for small numbers of observations. The "Q test" of Dean and Dixon (19) does not allow their rejection, but this test is so stringent that it is subject to "errors of the second kind" (21). Examination of the runs which produced these doubtful values reveals that there are fairly good chemical reasons for rejecting them. In any case, this rejection makes no serious difference, since if these five values were retained, the average would fall to 2.24, with an average deviation of .07, standard deviation of .08, and a 99% confidence interval of .08. The final limits of error assigned to these constants was ± 5%,** or ± 0.11; these limits of error include all the confidence interval of the 2.28 value and 94% of the confidence interval of the 2.24 value. Thus the only real difference the rejection makes is to assign to the value of 2.28 a misleadingly good precision.

k_1 and k_2 can also be derived from the slope and the

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* Defined as the interval in which the true value lies with a probability of 0.99. Equal to 1/3 x the range.

** See page 29.

intercept of the plot in Figure 5.[*] Values so obtained are less accurate, due to inherent uncertainties in such a derivation. In this way, one obtains $k_1 = 2.3_6$ and $k_2 = 2.2_5$. The average deviation of these two constants from their mean is certainly smaller than the estimated experimental error plus the error in the graphical derivation. The assumption that $k_1 = k_2$ within the experimental error is therefore independently justified. The maximum deviation between the arithmetically derived values of the constants, after rejection of the five series mentioned above, is 5%.

The reproducibility of the runs within a series was remarkably good, considering the various errors which might be expected to appear. The average reproducibility of the runs within a given series was 2% in Groups One, Two and Three, and in only two series was it as bad as 5%.[**] The average reproducibility of x_∞ values within a given series in these three Groups was 1.2%.

There are several schools of thought on the question of how the limits of error should be assigned to experimentally determined rate constants. In order to assign a "maximum error" [***] to k_1 and k_2, the reproducibility of sample counting, the reproducibility of the x_∞ values,

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[*] See the development on page 31.

[**] See Table 3 for typical examples.

[***] Defined by stating that 99% of the measured values should fall within the limits of this error.

the reproducibility of runs within a series, and the average and maximum deviations in the values of the rate constants were all considered; it was concluded that a maximum error of about 5% would probably be a realistic figure. This value was used in estimating the error in all quantities derived from the rate constants. The fact that this error is about $2\frac{1}{2}$ times the 99% confidence interval shows that either this estimate is pessimistic or that the results of the application of statistics to a small number of observations should sometimes be taken cum grano salis. It should be emphasized that this estimate of 5% does <u>not</u> include the possibly large error in the value of K_c, the concentration dissociation constant of hypophosphorous acid. Lack of the necessary data rendered an intelligent estimate of this error impossible; it is therefore not included explicitly in the error estimate given above.

The Catalytic Effect of Added Acids.

In order to establish with certainty that equation 20 was a special case of equation 10, the catalytic effect of other acids was investigated. Two groups of experiments were undertaken: Group Four, in which sulfuric acid was added to the hypophosphorous acid-tritiated water reaction mixture, and Group Five, in which oxalic acid was added to the H_3PO_2 - HTO reaction mixture. In all cases, H_3PO_2 and the catalytic acid were premixed and thermostatted before mixing them with the tritiated water.

The ionic strength was kept constant and equal to that in Groups Two and Three by appropriate choice of the acid concentrations. R was calculated using equation 18 in exactly the same way as in the previous Groups. Concentrations were calculated using the dissociation constants discussed in Section C.

The results of these experiments were not all that could be desired, from the standpoint of reproducibility and probable accuracy. Some representative plots are shown in Figure 6. The average deviation of the individual points from the straight line plot was much greater, running about 6-8% in some cases, and on the average the reproducibility within a given series was poorer.* Much of this difficulty was due to the nature of the method used to remove SO_4^{--} and Ox^{--} from solution; barium sulfate and calcium oxalate have a notorious tendency to remain in solution colloidally, and the conditions of precipitation which were used here (reagents mixed rapidly in the cold) were not designed to overcome this difficulty. Furthermore, the concentrations of the calcium bromide and barium bromide solutions were not accurately known. In the oxalic acid runs, definite evidence was obtained that the

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* One of the best of these series is displayed in Table 3; the limits of error quoted for the slope values in Tables 10 and 11 give a good indication of the reproducibility within a series.

calcium bromide concentration was too low, and that for that reason, thallous oxalate was appearing in the evaporated thallous hypophosphite. This, along with the presence of $BaSO_4$ or CaOx, would conspire to lower the counting rates by diluting the specific activity, and that is indeed the effect that was observed.

Regardless of these difficulties, however, clear cut cases of catalysis by both the bisulfate ion and undissociated oxalic acid were observed. The results of these experiments are presented in Tables 10 and 11.

Catalytic coefficients for these two acids were calculated by assuming a value of 2.28 for k_1 and k_2, and substituting the experimentally determined values of R and the concentrations into the expressions

$$R = k_1(H^+)(H_3PO_2) + k_2(H_3PO_2)^2 + k_3(HSO_4^-)(H_3PO_2), \quad (22)$$

(in the case of the runs with added sulfuric acid), and

$$R = k_1(H^+)(H_3PO_2) + k_2(H_3PO_2)^2 + k_4(H_2Ox)(H_3PO_2), \quad (23)$$

(in the case of runs with added oxalic acid).

In principle, equation 23 should contain a fourth term, of the form $k_5(HOx^-)(H_3PO_2)$. However, the accuracy of the results and the method of calculation were such as to preclude "seeing" this extra term. It is of interest to note in this connection that Griffith, McKeown, and Taylor (1c) found the catalytic coefficient for HOx^- in the iodine reaction to be undetectable. This result is in accord with the Brønsted equation (22), which relates catalytic activity to acid dissociation constants.

The catalytic coefficients found for these two acid catalysts at 27.23° are:

for HSO_4^-, $k_3 = 3.4 \pm 1.2$;

for free oxalic acid, $k_4 = 3.0 \pm 0.7$,

in units of liters per mole hour. The limits of error assigned to these constants are those which arise from the method of calculation, wherein one must necessarily subtract two numbers of almost equal magnitude from one another, thereby magnifying the error in the result. The poor experimental character of these runs, however, justifies such an assignment, and the values of these constants should probably be considered valid as orders of magnitude only.

The lack of "separation induced exchange" (14) noted in Groups Three, Four and Five is interesting, since it has been the experience of other investigators that if a precipitate appears in the course of quenching an exchange reaction or separating the exchanging species, a spuriously large figure for x may be obtained. This has the effect of making the -log(1-F) versus time plots straight lines with a finite intercept on the log axis, indicating that some "exchange" takes place at zero time. Figures 2 and 6 show that this effect was not observed here, even though precipitates appeared in the course of quenching the reaction and separating interfering ions.

The question of whether or not to continue with more acids and extend the list of catalysts was raised at this point, and was decided in the negative. In principle, one can never prove general acid catalysis; all one can do is investigate so many acids that no reasonable doubt can exist. Furthermore, the experimental procedure was tedious, to say the least, and the relatively unreproducible character of runs in which ions had to be removed by precipitation was very annoying, since all runs had to be carried out at least in triplicate in order to obtain results which seemed meaningful. In addition, the variety of acids that could be added to the reaction mixture was limited by the necessity for removing the acid anion and the anion of the removing agent. I feel that in view of the above results and the good correlations which can be established with the work of Griffith, McKeown, Taylor, and others, that a reasonable doubt as to the question of the "generality" of the acid catalysis does not exist. The final rate expression is then:

$$R = (H_3PO_2) \sum_{a} k_a (HA)_a, \qquad (24)$$

where the sum is taken over all Brønsted acids which may be present in the system.

Experiments at 35.30°. Activation Energy and Pre-exponential Factor.

To obtain the temperature coefficient of this reaction, runs of the Group Three type were carried out at 35.30°. In these runs, the withdrawn sample was discharged directly into a solution of thallous hydroxide which was a few drops short of an equivalent amount. This procedure was necessary because the half times were such that the time of stopping the reaction had to be known more accurately than in the runs at 27.23°.

The results of these experiments are presented in Table 12, some typical plots of -log (1-F) versus time appear in Figure 7, and an $R/(H_3PO_2)$ versus (H_3PO_2) plot of the data is presented in Figure 8.

Both graphical and arithmetical methods were used to obtain the numerical values of k_1 and k_2. In the graphical method, both of the constants were obtained from the plot in Figure 8, in which the slope of the line is equal to k_2, and the intercept on the $R/(H_3PO_2)$ axis is equal to $k_1(H^+)$. The arithmetical method involvet setting up six pairs of equations of the form of equation 20, putting in the experimentally determined values of R and the concentrations, solving them in pairs, and averaging the results. (Since the values of the two constants were no longer equal at this temperature, the simple method used for the runs at 27.23° was no longer applicable.) The values obtained by these two methods agree very well, as they should, and are,

$$k_1 = 7.0 \pm 0.4,$$

$$k_2 = 4.5 \pm 0.2,$$

in units of liters per mole hour.

The limits of error assigned to these constants are the same as those assigned to k_1 and k_2 at 27.23° (± 5%), for the same reasons. If anything, the experiments at this higher temperature were more reproducible than those at the lower temperature.*

The value for x_∞ given by theory (Section E) indicates that this quantity may or may not be temperature dependent. For this reason, several measurements of x_∞ were made at 35.30°, and are given in Table 13. The mean of these values was found to agree within 1% with the Group Three values at 27.23°, indicating that in this temperature range, x_∞ was independent of temperature.

Using the results for k_1 and k_2 at the two temperatures, the activation energies for these two constants can be determined from the integrated form of the Arrhenius equation,

$$\ln \frac{k_i^{T_1}}{k_i^{T_2}} = \frac{E_i}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right], \quad i = 1, 2; \qquad (25)$$

where $k_i^{T_1}$ and $k_i^{T_2}$ are the rate constants at the two temperatures T_1 and T_2, E_i is the Arrhenius activation energy for k_i, and R is the gas constant. This calculation gives:

for k_1, $E_1 = 25.6 \pm 1.3$ kcal. per mole,

for k_2, $E_2 = 15.5 \pm 1.0$ kcal. per mole.

The error in the activation energies was assigned by assuming a 5% error in the k_i's and using standard formulae (23) for the compounding of errors in quotients and products.

Having these values, the pre-exponential or "frequency" factor, A, in the Arrhenius equation,

---

* See Table 3 for a typical example.

$$k_i = A_i e^{-E_i/RT}, \qquad (26)$$

may now be calculated. This calculation gives:

for k_1, $A_1 \sim 10^{19}$ liters per mole hour,

for k_2, $A_2 \sim 10^{12}$ liters per mole hour.

The error in these quantities is at least of a factor of 10.

Summary of Results in Acid Solution.

At 27.23°: $k_1 = 2.28 \pm .11$ liters per mole hour

$k_2 = 2.28 \pm .11$ " " " "

$k_3 = 3.4 \pm 1.2$ " " " "

$k_4 = 3.0 \pm 0.7$ " " " "

at 35.30°: $k_1 = 7.0 \pm 0.4$ " " " "

$k_2 = 4.5 \pm 0.2$ " " " "

These rate constants apply to the rate expression,

$$R = k_1(H^+)(H_3PO_2) + k_2(H_3PO_2)^2 + k_3(HSO_4^-)(H_3PO_2) + k_4(H_2Ox)(H_3PO_2).$$

The complete rate expression is:

$$R = (H_3PO_2) \sum_a k_a(HA)_a. \qquad (24)$$

The Arrhenius activation energies and frequency factors are:

$E_1 = 25.6 \pm 1.3$ kcal. per mole

$E_2 = 15.5 \pm 1.0$ " " "

$A_1 \sim 10^{19}$ liters per mole hour

$A_2 \sim 10^{12}$ " " " "

Results of Experiments in Basic Solution.

The results of the experiments in basic solution are presented in Table 14. Interpretation of these results is rendered extremely difficult by the fact that the hypophosphite ion undergoes slow decomposition in basic solution via the reaction (lf)

$$H_2PO_2^- + OH^- \longrightarrow HPO_3^{--} + H_2.$$

It was immediately apparent that this reaction was taking place to an appreciable extent at room temperature within the reaction mixtures. The solid material appearing on evaporation was almost always wet and sticky. There was some evidence that a gas was being evolved from the reaction mixture. The melting point of the solid obtained by evaporation of a sample from a reaction mixture that had stood for forty-eight hours was taken; the solid melted over a 45° range, with most pronounced liquefaction taking place at 65-70°, 90-95°, and 105-110°. The melting point of thallous hypophosphite is 114°*, and the melting points of some of the thallous phosphites are somewhat lower.*

It appears, then, that although some exchange may have taken place by the reaction,

$$H_2PO_2^- + HTO \rightleftharpoons HTPO_2^- + H_2O, \qquad (27)$$

most of the observed exchange <u>may</u> have been due to the reactions,

$$H_2PO_3^- + HTO \rightleftharpoons HTPO_3^- + H_2O, \text{ and} \qquad (28)$$

$$HPO_3^{--} + HTO \rightleftharpoons TPO_3^{--} + H_2O. \qquad (29)$$

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* See Part II.

A large number of very careful experiments would have been necessary to assay accurately the contributions of reactions 27, 28 and 29 to the observed result. Furthermore, the first set of experiments show that some separation induced exchange is taking place.

In view of these difficulties, these experiments were abandoned.

E. Discussion

Correlation with Previous Work

In Section A, it was pointed out that in acid solution, the rate law for reaction 1, the oxidation of hypophosphorous acid to phosphorous acid by certain oxidising agents, could be expressed as

$$-d(H_3PO_2)/dt = (H_3PO_2) \sum_a k_a^o(HA)_a, \qquad (4)$$

if the pH was low and concentration of the oxidising agent was about 0.01f. or greater. The mechanism proposed to explain this rate law was given in equations 5,6 and 7. Equation 4 is identical with equation 24, the rate expression found for the acid solution exchange reaction in this work.

The values for the catalytic coefficients found by Griffith, McKeown, and Taylor (1c) for the iodine oxidation reaction at 30.0° and μ = 0.2- 0.5 are:

$k_1^o = 21$,*

$k_2^o = 7.6$,*

$k_3^o = 14 \pm 1.5$,

$k_4^o = 15 \pm 1.7$,

in units of liters per mole of H_3PO_2 oxidized per hour. These catalytic coefficients are defined by the rate equation,

$$-d(H_3PO_2)/dt = k_1^o(H^+)(H_3PO_2) + k_2^o(H_3PO_2)^2 + k_3^o(HSO_4^-)(H_3PO_2) + k_4^o(H_2Ox)(H_3PO_2). \qquad (30)$$

---

* The data necessary for the evaluation of the limits of error in these constants are not given in their paper.

The corresponding catalytic coefficients for the exchange reaction, k_1 and k_2, can be determined at 30.0° by graphical interpolation on plots of log k_i versus $1/T$. This method gives

$$k_1 = 3.3 \pm .17,$$

$$k_2 = 2.9 \pm .15,$$

in units of liters per mole hour. Although the values of k_3 and k_4 for the exchange reaction cannot be determined in this way, since their activation energies are not known, it is evident from their values at 27.23° that they will be about 4 and 3.6 or so, respectively; of the same order of magnitude as k_1 and k_2 and larger than k_2.

Comparison of these exchange reaction constants with the oxidation reaction* constants now shows that except for a drop in all the values, amounting to a factor of $6.4 \pm .45$** for k_1, $2.6 \pm .18$** for k_2, and about 3 for k_3 and k_4, the two sets of constants are the same. This drop is of the correct order of magnitude for a tritium isotope effect, a question which will be dealt with in detail later. Assuming such an isotope effect for the present, the identity of the two rate expressions, 4 and 24, and the good correlation between the two sets of values for the rate constants leaves no doubt that both the exchange reaction

---

* In all that follows, the term "oxidation reaction (s)" will refer to the reactions given by equations 1 and 2.

** The limits of error in these ratios are derived by assuming a 5% error in k_1^0 and k_2^0.

and the oxidation reactions proceed in acid solution via the same mechanism. Furthermore, it is almost certain that the mechanism common to these reactions is:

$$(H_3PO_2)_I \xrightarrow{k_a} (H_3PO_2)_{II}, \qquad \text{slow} \qquad (5)$$

and

$$(H_3PO_2)_{II} \xrightarrow{k_a'} (H_3PO_2)_I, \qquad \text{rapid} \qquad (6)$$

for the exchange reaction, and

$$(H_3PO_2)_I \xrightarrow{k_a^o} (H_3PO_2)_{II}, \qquad \text{slow} \qquad (5)$$

$$(H_3PO_2)_{II} \xrightarrow{k_a^{o\prime}} (H_3PO_2)_I, \qquad \text{rapid} \qquad (6)$$

and

$$(H_3PO_2)_{II} + Ox \xrightarrow{k_{ox}^o} H_3PO_3 + Red \qquad \text{rapid} \qquad (7)$$

for the oxidation reactions. When the concentration of the oxidising agent is high, reaction 7 disappears from the oxidation rate law, equation 4 becomes valid, and the two rate laws become identical. This mechanism will be discussed in greater detail in the next section.

The correlation between the two reactions is further strengthened by the fact that the lack of ionic strength dependence noted in this work was also noted by Griffith, et. al., and by Hayward and Yost (1d).

It should be noted, parenthetically, that the rate constants found by Griffith, et. al. are used here for comparison instead of a mean of constants found by all investigators because the constants determined by Griffith are unquestionably more accurate than those found by Hayward and Yost or by Mitchell. This difference is due to the fact that Mitchell and Hayward and Yost did not take into account the existence of general acid catalysis in their reactions.

The isotope effect found in the rate constants also appears in the activation energies, when one compares the exchange and oxidation reactions. Griffith, et. al. found a value of 20 kcal. per mole for E_1^o, the activation energy for the hydrogen ion catalytic coefficient, k_1^o, in the iodine reaction. This is to be compared to a value of 25 kcal. per mole found for E_1 in this research. Unfortunately, Griffith, McKeown, and Taylor did not determine E_2^o, the activation energy for the H_3PO_2 catalytic coefficient. The rather low value found for E_2 in this research would have made a comparison interesting.

From Griffith's values for k_1^o and E_1^o, one can calculate a value for A_1^o, the frequency factor for the hydrogen ion coefficient using equation 26. The result of this calculation is $A_1^o \sim 10^{16}$ liters per mole hour. The apparent discrepancy between this value and the value found for A_1 in this research should not be taken too seriously, since both values are uncertain by at least a factor of 10.

The collision theory of reaction rates relates the frequency factors, A_1 and A_2, to the collision frequencies, Z_1 and Z_2, by the expression (24)

$$A_i = P_i Z_i , \quad i = 1,2, \qquad (31)$$

where P_1 and P_2 are the so-called steric factors. If one assumes that Z_1 and Z_2 are approximately the same, and that the Z's can be calculated from the formula which applies to collisions in the gas phase (24),

$$Z = \sigma^{-2}\left[\frac{8\pi RT}{M}\right]^{1/2} \times 6.02 \times 10^{20} \times 3.6 \times 10^{3} \ \frac{\text{liters}}{\text{mole-hour}}, \qquad (32)$$

one obtains a number which is of the order of 10^{14} for Z. If correct, this means that P_1 and P_2 must have values of the order of 10^5 and 10^{-2}, respectively.

Although the magnitudes of the P's given by the above treatment are very uncertain, the large difference between them may be significant. If we assume only that the Z's are approximately the same, the two values of P differ by about seven orders of magnitude. This may be due to the fact that H_3PO_2 is a relatively "long" molecule, compared to H_3O^+. If one visualizes H_3O^+ as consisting essentially of a sphere of H atoms surrounding an oxygen atom, and H_3PO_2 as a long rod with only one useful H atom tacked onto one end, one can understand, ad hoc, why the steric factor for H_3PO_2 is smaller than that for H_3O^+.

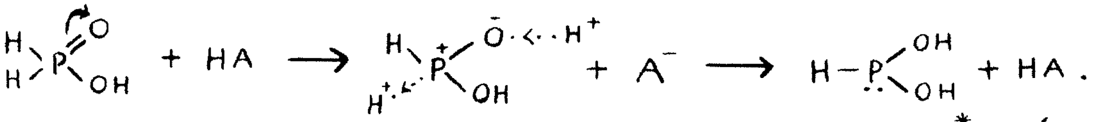
This, however, is a highly speculative argument; it may be that the values of Z_1 and Z_2 are very different, and that the use of gas kinetic theory formulae is entirely inappropriate in solution. In any case, it is a little difficult to understand a value of P_1 greater than one, since P is defined as a probability. For these reasons, this argument should probably not be taken too seriously.

Mechanisms

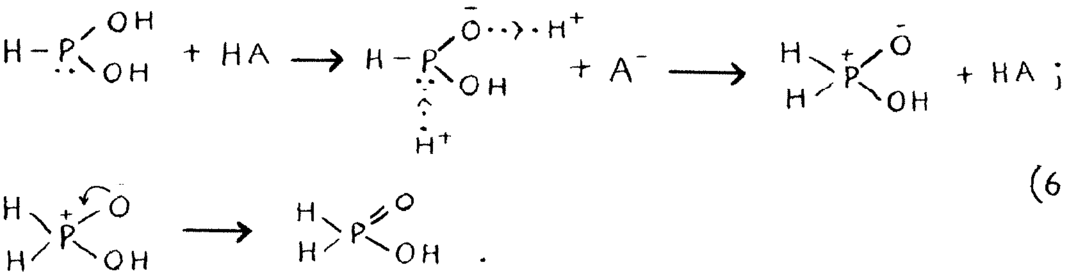
In this section, it will be demonstrated that plausible mechanisms can be written for all the steps in the exchange and oxidation reactions, if one assumes the existence of reactions 5,6 and 7 and a reasonable structure for $(H_3PO_2)_{II}$.

Reactions 5 and 6 probably take place as follows:

Reaction 5



Form I Form II[*] (5M)



(6M)

The curved arrow written over the P=O bond denotes the tendency of an electron pair to shift onto the oxygen atom. This situation is analogous to the "tautomeric shift" pictured by organic chemists for the electrons in the C=O double bond in carbonyl compounds (25). This tendency is abetted by the presence of the acid catalyst, as in many organic cases.[**] Dotted lines drawn in place of bonds are used to indicate a bond in the process of scission or formation, and have pictorial significance only.

The mechanism also explains why reaction 5 is so much

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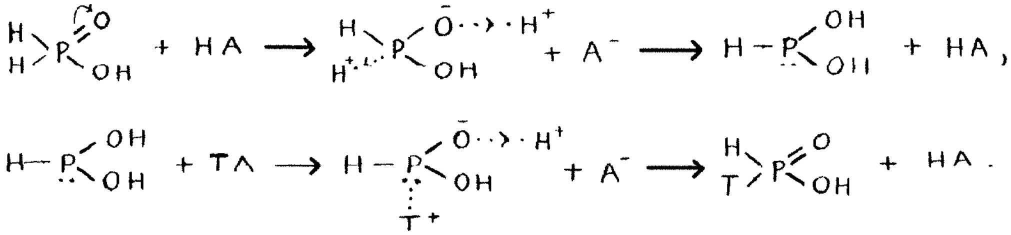
[*] This structure for form II has also been proposed by Mitchell (1a).

[**] The acid-catalyzed enol-keto shift in ketones, for instance.

slower than reaction 6 ($k_1^0/k_1^{0'}$ has been estimated (1b) as being of the order of 10^{-12}). The scission of a P—H bond, undoubtedly the rate determining step in reaction 5, is more difficult than the scission of an O—H bond, which may be rate determining in reaction 6.

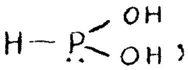
The mechanism by which H_3PO_2 becomes radioactive in the exchange reaction follows naturally from 5M and 6M:

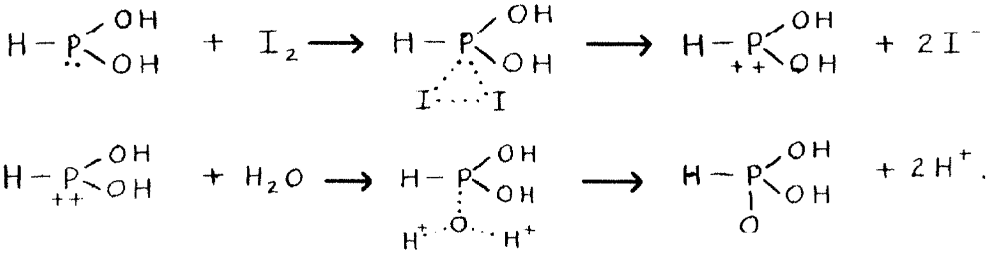


(5M)

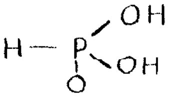
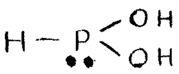
(6'M)

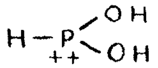
The acid catalyst thus acts as an intermediate in carrying the tritium from the water to the hypophosphorous acid.

Assuming the structure given above for the active form,  $\mathrm{H-\ddot{P}}\genfrac{}{}{0pt}{}{\mathrm{OH}}{\mathrm{OH}}$ we can write what seems like a plausible mechanism for the reaction of the active form with the halogens (reaction 7):

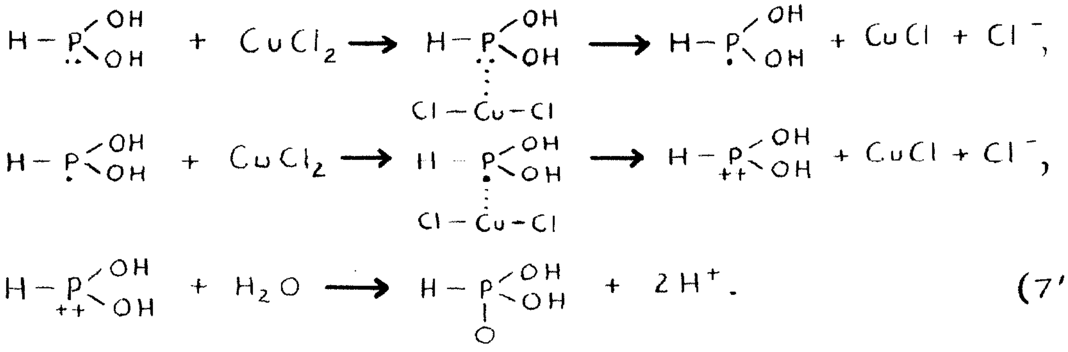


(7M)

 $\mathrm{H-\underset{O}{P}}\genfrac{}{}{0pt}{}{\mathrm{OH}}{\mathrm{OH}}$ is the accepted structure (1f) for phosphorous acid. I_2 has been used here for the sake of specificity, but this mechanism would apply to the other halogens equally well. This mechanism is to a great extent schematic, as are all the others in this section, and should not be taken too literally. For instance,  $\mathrm{H-\ddot{P}}\genfrac{}{}{0pt}{}{\mathrm{OH}}{\mathrm{OH}}$ and I_2 probably

collide in the presence of a water molecule, so that the intermediate  $H-\underset{++}{P}\langle{}^{OH}_{OH}$ is probably never present as such for any length of time. The removal of electrons from, and the transfer of an oxygen atom to the active form have been written as separate steps merely to increase the clarity of the picture.

The mechanism of reaction of the active form with $CuCl_2$ is somewhat complex, and its kinetics have not been clearly elucidated. It is probably bimolecular, and may proceed via the following free radical mechanism:



$$H-\underset{..}{P}\langle{}^{OH}_{OH} + CuCl_2 \longrightarrow \underset{Cl-Cu-Cl}{H-\underset{..}{P}\langle{}^{OH}_{OH}} \longrightarrow H-\underset{\cdot}{P}\langle{}^{OH}_{OH} + CuCl + Cl^-,$$

$$H-\underset{\cdot}{P}\langle{}^{OH}_{OH} + CuCl_2 \longrightarrow \underset{Cl-Cu-Cl}{H-\underset{\cdot}{P}\langle{}^{OH}_{OH}} \longrightarrow H-\underset{++}{P}\langle{}^{OH}_{OH} + CuCl + Cl^-,$$

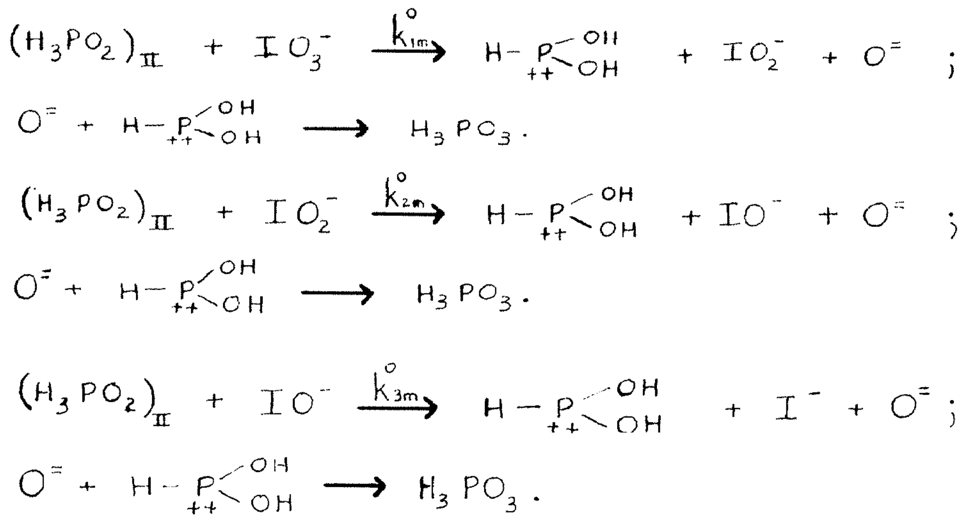
$$H-\underset{++}{P}\langle{}^{OH}_{OH} + H_2O \longrightarrow H-\underset{O}{P}\langle{}^{OH}_{OH} + 2H^+. \qquad (7'M)$$

The existence of free radicals similar to these has been suggested by Kornblum (26) to explain his results on the reduction of diazonium salts with hypophosphorous acid. This fact, however, should not be cited as additional support for mechanism 7'M, since most of Kornblum's experiments were valueless, from a kinetic standpoint, and his conclusions reveal a lack of knowledge of the fundamentals of hypophosphorous acid chemistry.

The details of the reaction of the active form with $HgCl_2$ are obscure; Mitchell (1a) finds that it may be termolecular, but this seems unlikely. At any rate, there is some question about whether or not the rate of the overall reaction between $HgCl_2$ and H_3PO_2 at low concentrations of $HgCl_2$ can be fitted to equation 3, although there is no doubt that at high concentrations of $HgCl_2$, equation 4 is rigorously obeyed. It is possible that $HgCl_2$ reacts with the active form via a free radical mechanism similar to that pictured in equation 7'M.

The reaction between mercuric ion (as mercuric nitrate) and H_3PO_2 has been investigated very recently by Gerfer (27). The mechanism of the reaction is rather complex, but it seems clear that in this case, the reaction of Hg^{++} with $H_2PO_2^-$ is so rapid that it completely conceals any reaction which may be taking place between Hg^{++} and H_3PO_2 molecules. It is interesting to note that in the $HgCl_2$ reaction, just the opposite is found - the reaction between $HgCl_2$ and $H_2PO_2^-$ is undetectable. Gerfer also finds that the relatively slow reaction between Hg_2^{++} and H_3PO_2 proceeds via the mechanism given in equations 5, 6, and 7, and obeys rate law 4 at high concentrations of Hg_2^{++}. He did not detect any reaction between Hg_2^{++} and $H_2PO_2^-$.

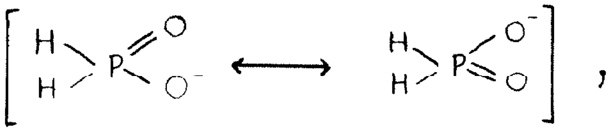
The reaction of the active form with iodate ion is about 1/35 as fast as the reaction of the active form with iodine (1d); the iodate mechanism is undoubtedly more involved. At first sight, a mechanism such as the following seems attractive:



(7''M)

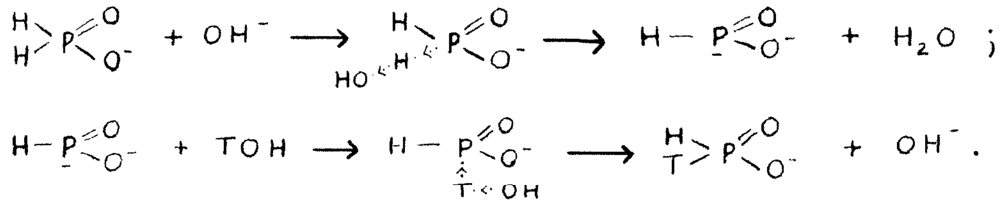
Further consideration, however, shows that this mechanism is probably not correct, for the following reason. In the iodine reaction (1a,c) the reaction of IO^- with the active form is undetectable, showing that $\overset{o}{k}_{3m}$ must be $\leqslant$ 1/10 of $\overset{o}{k}_{I_2}$. If the above mechanism is to give the correct rate law, i.e., rate = $k_{IO_3^-}(IO_3^-)(H_3PO_2)_{II}$, then it must be true that $k_{1m} \ll k_{2m}$ and k_{3m}. Yet, as stated above, $k_{IO_3^-}$ (or k_{1m}) is only 1/35 of k_{I_2}. Thus we are led to the conclusion that $k_{3m} \cong 3k_{1m}$, a condition which would not lead to the correct rate expression if it were used in conjunction with mechanism 7''M. It is unfortunate that this mechanism is untenable, since it is very difficult to think of other kinds of mechanisms which would lead to the observed second order rate law.

Tables 1 and 2 show that the exchange of hydrogens between water and the hypophosphite ion in neutral solution is very slow, if it takes place at all. The lack of a term containing $(H_2PO_2^-)$ in equation 24, and the theory to be developed later show that the ion, as such, will not exchange in acid solution either. The reason for this is fairly obvious from the mechanism given above. In solution, the $H_2PO_2^-$ ion probably has the structure (28)



where the usual symbolism is used to denote resonance forms. Attachment of an H^+ ion to this molecule would have no tendency to cause scission of the P—H bond; it would only create the acid. Attachment of another H^+ ion causes scission of this bond, as pictured above in 5M, but now we are dealing with the acid molecule exchanging and not the ion. In neutral solution, the concentration of acid catalyst molecules or ions is so small that exchange via reactions 5 and 6 is inappreciable. The possibility of direct dissociation of one of the H atoms from the P atom of the ion, caused by a high concentration of OH^- ions in basic solution, is not eliminated by this mechanism; it was partly for this reason that exchange studies in basic solution were carried out.

Unfortunately, the basic solution results were inconclusive, for reasons pointed out in Section D. The difficulties encountered with this reaction were also found by Franke and Monch (10), and their experiments are inconclusive for the same reasons. All that can be said at this time is that it is possible that exchange will take place fairly rapidly in basic solution, if the concentration of OH^- ions is large enough, by a direct dissociation mechanism such as:



This would be an interesting reaction to study, if some way could be found of suppressing the decomposition reaction, since it bears on the problem of preparing dibasic salts of hypophosphorous acid, a problem which has never been successfully solved.

There are certain hypophosphorous acid oxidation reactions to which the mechanism given by reactions 5, 6 and 7 may not apply. Mitchell (29) found that he could explain the kinetics of the reaction of $Cr_2O_7^{--}$ with H_3PO_2,

$$Cr_2O_7^{--} + 3H_3PO_2 + 8H^+ \longrightarrow 2Cr^{+++} + 3H_3PO_3 + 4H_2O,$$

if he assumed that $Cr_2O_7^{--}$ first reacted with $(H_3PO_2)_{II}$ to produce $Cr_2O_6^{--}$, which would then react with $(H_3PO_2)_{II}$ or $(H_3PO_2)_I$; the reaction velocity was found to be independent of (H^+) up to $(H^+) \sim 0.2$ f. This work, although suggestive, was not entirely clear cut and should be repeated. Vodizhenskii and Gerasimov (30) investigated the kinetics of the oxidation of H_3PO_2 by As(III), and claim that a free radical mechanism is involved. The abstract (31) of their work is almost incoherent; a re-investigation of this reaction would be worthwhile. Other oxidizing agents (HNO_3, Ce(IV), SeO_3^{--}, NH_2Cl, O_2, MnO_4^{--}) have been investigated, but only in a qualitative way. It would be very interesting to study these reactions further to try and find clear cut cases of oxidation proceeding via some other mechanism other than that given by equations 5, 6 and 7.

In their work on the iodine reaction, Griffith, McKeown, and Taylor (1c) claim that at pH ~ 6, in addition to the I_2 - $H_2PO_2^-$ reaction, some oxidation takes place via a base catalyzed mechanism:

$$(H_3PO_2)_I + OH^- \rightleftarrows R + H_2O, \quad \text{slow} \quad (a)$$

$$R + H^+ \rightleftarrows (H_3PO_2)_{II}, \quad \text{fast} \quad (b)$$

$$(H_3PO_2)_{II} + I_2 \longrightarrow 2I^- + H_3PO_3; \quad \text{fast} \quad (c)$$

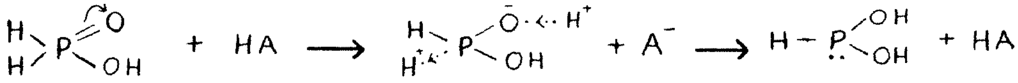
R is some combination of 2 H atoms, 2 oxygen atoms, and a P atom. They give a value of about 10^{-5} for the ratio k_R/k_1^o, where k_R is the velocity constant for reaction a. They admit, however, that these experiments were crude and subject to a great deal of uncertainty, both as to the value of k_R/k_1^o and as to the interpretation of the results in terms of the above mechanism.

If this mechanism is actually operative in neutral hypophosphite solutions, it is difficult to see why it would not lead to a slow exchange of H between H_3PO_2 and water; k_R is much too large to account for the extremely slow neutral solution exchange that may have been observed in this research. An intramolecular shift of one of the

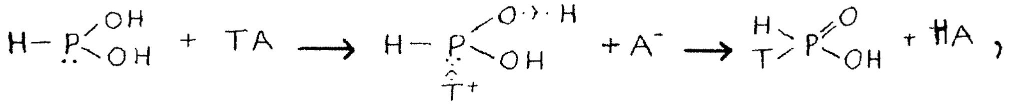
H atoms of H_3PO_2 may be involved in the slow step of the mechanism above, but it is hard to draw convincing pictures of how this process might take place. Further work on this k_R reaction would be worthwhile.

Isotope Effect

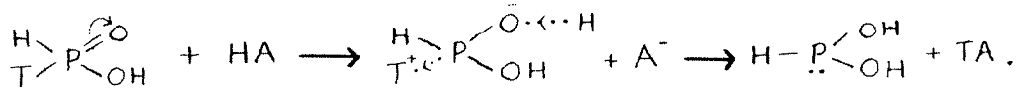
The isotope effect arises in the exchange reaction for the following reason: In the oxidation reaction, one measures the rate at which form I is converted to form II, reaction 5M:


(5M)

In the exchange reaction, on the other hand, although radioactivity gets into the molecule via reaction 6'M,


(6'M)

it turns out that the rate that one <u>measures</u> is the rate of the reaction


(5'M)

Reaction 5'M is the exact analog of reaction 5M, except that in 5'M, a P—T bond must be broken to make the reaction go, whereas in 5M, a P—H bond is broken.

The difference between the zero point energies of these two bonds (that of the P—T bond being the lower of the two), means that more energy will be required to raise the P—T bond up to the point where scission and reaction can take place. This difference is reflected in the higher value for the activation energy and the concomitantly lower value for the corresponding rate constants, when one compares the exchange reaction with the oxidation reaction. Although this explanation is greatly oversimplified, it is probably qualitatively correct.

The crucial point in the explanation is that in the exchange reaction, one measures the rate of 5'M and not the rate of 6'M or 5M. This point is readily demonstrable, as is shown in the following development:*

Assume that the mechanism of the exchange is a combination of the reactions

$$HP_I + HA \underset{\ell_2}{\overset{\ell_1}{\rightleftharpoons}} HP_{II} + HA, \qquad \text{(5M and 6M)} \qquad (33)$$

$$TP_I + HA \underset{\ell_2'}{\overset{\ell_1'}{\rightleftharpoons}} HP_{II} + TA, \qquad \text{(5'M and 6'M)} \qquad (34)$$

where HP_I represents $(H_3PO_2)_I$, HP_{II} represents $(H_3PO_2)_{II}$, TP_I represents $(HTPOOH)_I$ and the l's are rate constants.

From 34,

$$\frac{d}{dt}(TP_I) = l_2'(HP_{II})(TA) - l_1'(HA)(TP_I). \qquad (35)$$

The quantity that is actually measured in this reaction, after the insertion of the factors of two into equation 18, is the rate at which one of the two hydrogen atoms in <u>total hypophosphite</u> becomes radioactive, $\frac{d}{dt}(\sum(HTPOOH)_I)$. Since

$$\sum(H_3PO_2) = (H_3PO_2)\left[1 + K_c/(H^+)\right] = B(H_3PO_2), \qquad (36)$$

and since, for any given run, all the chemical concentra-

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* I am indebted to Dr. Norman Davidson for many helpful discussions concerning this theory.

tions in the system remain constant, B is a constant in any given run.

We now assume that $H_2PO_2^-$ does not participate in the exchange reaction as such. Then the rate at which total hypophosphite becomes radioactive, $\frac{d}{dt}(BHTPOOH)_I$, will be 1/B times the rate at which H_3PO_2 becomes radioactive. This is understandable when one realizes that if one is putting radioactivity at a given rate into a larger reservoir (BHP_I) than one originally though one had, (HP_I), then the rate at which the reservoir fills up with radioactivity[*] must necessarily be slower than it would be if the reservoir contained only HP_I to be filled up. This involves the assumption that the additional material in the reservoir, $H_2PO_2^-$, doesn't aid in the filling process (i.e., doesn't react).

Thus:

$$\frac{d}{dt}(BTP_I) = \frac{l_2'}{B}(HP_{II})(TA) - \frac{l_1'}{B}(HA)(TP_I). \qquad (37)$$

We now note that:

a) The rapid equilibrium

$$HA + HTO \rightleftharpoons TA + H_2O, \qquad (38)$$

is maintained throughout the reaction, and hence,

$$(TA) = K_a^* (HA)(HTO)/(H_2O) \qquad (39)$$

where K_a^* is the concentration equilibrium constant for reaction 38.

b) The water concentration in these experiments is so

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[*] expressed as the rate of approach to "completely full".

high compared to the concentration of total hypophosphite that the decrease in the concentration of HTO during a reaction, due to tritium leaving the water and entering the H_3PO_2 molecule, is negligible. Thus, for a given (HA), which remains constant throughout a run, (TA) = const. = T_o.

37 now becomes:

$$\frac{d}{dt}(BTP_I) + \frac{l_1'}{B}(HA)(TP_I) = \frac{l_2'}{B}(HP_{II})T_o \ ; \qquad (40)$$

integrating,

$$(BTP_I) = Ce^{-[\ell_1'(HA)/B]t} + \frac{\ell_2'(HP_{II})T_o}{\ell_1'(HA)} \ ; \qquad (41)$$

at t = 0, $(BTP_I) = 0$, hence,

$$C = -l_2'\ (HP_{II})\ T_o/l_1'\ (HA)\ ;$$

at $t = \infty$, $(BTP_I) = (BTP_I)_\infty = l_2'\ (HP_{II})T_o/l_1'(HA)$. (42)

We now assume that the experimentally measured thallous hypophosphite activity, x, is proportional to $B(TP_I)$,* and we note that $x' = (BTP_I)$.

Thus, measured activity of $TlHTPO_2 = LB(TP_I) = x$. (43)

L is a proportionality constant which includes counting geometry, counting efficiency, total acid concentration, etc., but which is a constant in any given run.

Then

$$F \equiv \frac{x'}{x'_\infty} = \frac{x}{x_\infty} = \frac{LB\ (TP_I)}{LB\ (TP_I)_\infty}\ , \qquad (44)$$

and $(1 - F) = e^{-(l_1'\ (HA)/B)t}$.

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* See page 23.

Thus the slope of a plot of $-\log(1 - F)$ versus time is

$$\text{slope} = \frac{1}{2.3}\, l_1' \,(\text{HA})/B. \tag{45}$$

In the calculation of R, we use the expression,

$$R = 2.3 \times \text{slope} \times \left[\frac{(H_2O) \times \sum (H_3PO_2)}{(H_2O) + \sum (H_3PO_2)}\right], \tag{46}$$

where the factors of 2 have been left out for the present, and will be taken care of later.

Since in this reaction, $(H_2O) >> \sum(H_3PO_2)$, 46 becomes

$$\begin{aligned} R &= 2.3 \times \text{slope} \times \sum (H_3PO_2), \\ &= 2.3 \times \text{slope} \times B(H_3PO_2). \end{aligned} \tag{47}$$

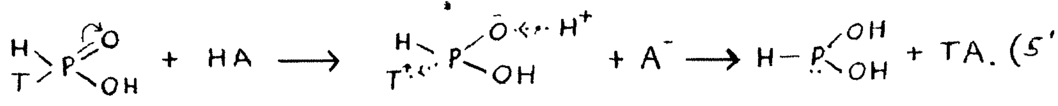
For any given acid catalyst, HA, experiment shows that

$$R = k_a \,(\text{HA})(H_3PO_2). \tag{48}$$

If we now combine 45, 47 and 48, we have

$$k_a = l_1' \tag{49}$$

This is the desired result, and it shows that the experimentally measured rate constants, k_a, are the rate constants *for the forward step in reaction 34, in which* P—T bond is broken:



(5'M)

Having established this, the reasons given in the above paragraphs for the existence of the isotope effect now appear to be valid.

It should be noted that the explicit assumption was made in this development that the hypophosphite ion did not participate as such in the exchange reaction. The correct result obtained as a consequence of this assumption seems to justify it. Furthermore, the reason for use of the quantity $\sum(H_3PO_2)$ in expression 16 becomes clearer.

The explicit introduction into this theory of the factors of two which appear in equation 18 can be made in a straightforward way. In the case of an equilibrium exchange reaction where one of the reactants is present in great excess (such as the one under consideration here, where $\sum(H_3PO_2) \ll (H_2O)$), the necessity for the factor of two can be easily visualized, since it is evident that the rate at which both H atoms of the hypophosphorous acid become radioactive is <u>half</u> of the rate at which only one becomes radioactive. If one <u>measures</u> the rate at which both become radioactive, and one wishes to <u>calculate</u> the rate at which only one becomes radioactive, one multiplies the observed rate by two. In this case, the rate at which only one H becomes radioactive is the rate in which one is interested, since that rate is a measure of the rate at which <u>one</u> of the cycles

$$(H_3PO_2)_I \longrightarrow (H_3PO_2)_{II},$$
$$(H_3PO_2)_{II} \longrightarrow (H_3PO_2)_I,$$

is being carried out in solution.

As it stands, equation 37 gives the rate at which one hydrogen of total hypophosphite becomes radioactive. If one divides the right hand side of that equation by 2, and replaces the left hand side by $\frac{d}{dt}\left[B\left[(HTPOOH_I) + (T_2POOH_I)\right]\right]$, one then has an equation which represents the rate at which both hydrogens exchange, which was the rate which was actually measured. The remainder of the development proceeds as before, and in the end, the two which remains in the denominator of the slope expression cancels the two which should be in the numerator of 46. The twos were left out of the development above in an attempt to increase the clarity. This shows, however, why it was necessary to put the two into equation 18 when using it for calculation.

The explicit introduction of general acid catalysis is also simple. Equation 35 should actually be written

$$\frac{d}{dt}(TP_I) = (HP_{II}) \sum_a l'_{2a}(TA)_a - (TP_I) \sum_a l'_{1a}(HA)_a . \qquad (35G)$$

The development then proceeds as before; we find

$$\text{slope} = \frac{1}{2.3B} \sum_a l'_{1a}(HA)_a . \qquad (45G)$$

Since the true rate law is

$$R = (H_3PO_2) \sum_a k_a(HA)_a , \qquad (48G)$$

combination of 45G, 47 and 48G then gives

$$\sum_a k_a(HA)_a = \sum_a l'_{1a} (HA)_a , \qquad (49G)$$

the same result that was obtained in simplified treatment.

The theory developed above leads to an interesting expression for x_∞:

After the introduction of general acid catalysis into the theory, equation 42 becomes

$$(BTP_I)_\infty = \frac{(HP_{II}) \sum_a l'_{2a}(T_{oa})_a}{\sum_a l'_{1a}(HA)_a} , \qquad (42G)$$

where T_{oa} is now defined as

$$T_{oa} = (TA) = \frac{(HA)(HTO)K_a^*}{(H_2O)} . \qquad (50)$$

Since chemical equilibrium is always preserved during a reaction,

$$(HP_{II}) = \frac{l_1}{l_2} (HP_I). \qquad (51)$$

Inserting 50 and 51 into 42G, we have

$$(BTP_I)_\infty = \frac{\ell_1}{\ell_2} \frac{(HP_I)(HTO)}{(H_2O)} \left[\sum_a \ell'_{2a} (HA)_a K_a^* \Big/ \sum_a \ell'_{1a} (HA)_a \right] \qquad (52)$$

The measured value of the activity of total hypophosphite at infinite time, x_∞, is given by

$$x_\infty = M \frac{(BTP_I)_\infty}{(BHP_I)+(BTP_I)} \cong M \frac{(BTP_I)_\infty}{(BHP_I)}. \qquad (53)$$

Equation 53 represents the facts because the activity measured in the assay apparatus is proportional to the <u>specific</u> activity of total hypophosphite, which is the activity per mole of total hypophosphite. This point was brought out on pages 10 and 23. Substituting 53 into 52,

$$x_\infty = \frac{M}{B} \frac{(HTO)}{(H_2O)} \frac{\ell_1}{\ell_2} \left[\sum_a \ell'_{2a} (HA)_a K_a^* \Big/ \sum_a \ell'_{1a} (HA)_a \right] ,$$

$$= M \left[\frac{(H^+)}{(H^+) + K_c} \right] \frac{(HTO)}{(H_2O)} \frac{\ell_1}{\ell_2} \left[\frac{\sum_a \ell'_{2a} (HA)_a K_a^*}{\sum_a \ell'_{1a} (HA)_a} \right] . \qquad (54)$$

When H^+ and H_3PO_2 are the only acids present in the system, 54 becomes

$$x_\infty = M\left[\frac{(H^+)}{(H^+)+K_c}\right]\frac{(HTO)}{(H_2O)}\,\frac{\ell_1}{\ell_2}\underbrace{\left[\frac{\frac{(H^+)}{(H_3PO_2)}K^*_{H^+}\,\ell'_{2H^+}+K^*_{H_3PO_2}\,\ell'_{2H_3PO_2}}{\frac{(H^+)}{(H_3PO_2)}\,\ell'_{1H^+}+\ell'_{1H_3PO_2}}\right]}_{C} \cdot \qquad (55)$$

It is difficult to predict how the quantity C will vary with changes in the concentrations of H^+ and H_3PO_2, since the values of $K^*_{H^+}$, $K^*_{H_3PO_2}$, l'_{2H^+}, and $l'_{2H_3PO_2}$ are not known. It is possible that C might stay constant over the range of concentrations of H^+ and H_3PO_2 used in this work; in that case, x_∞ would be a function of (H^+) and the extent to which the stock HTO was diluted in making up a reaction mixture. Therefore, if (H^+) is kept constant from series to series and the HTO is always diluted by the same amount, x_∞ should stay constant. Table 13 shows that this is, indeed, the case; x_∞ was constant, within experimental error, for all the runs in Group Three, in which (H^+) was constant and in which all the reaction mixtures were made up by a 1:1 mixture of HTO and acid. In Groups One and Two, x_∞ varied from series to series in a way that would be predicted from equation 55; i.e., x_∞ increased as (H^+) increased, the rate of increase falling off at higher (H^+).

The lack of temperature dependence shown by x_∞ in the temperature range 27-35° is believable but not predictable. Of the quantities in 55, all the rate constants and equilibrium constants should be temperature dependent, and it is conceivable that their temperature coefficients might cancel out, at least in this small temperature range. Table 13 shows that this is the case.

The magnitude of the isotope effect found here is by no means unreasonable. Turkevich and Smith (32) report, in a study of the relative rates of scission of C—H and C—T bonds in the isomerization of butene-1 to butene-2, a 25% increase in the activation energy when tritium is substituted for hydrogen. Much of their discussion about the relative rate constants seems contradictory, but it is clear that they too have found a large effect. Jones (33) has found a factor of 3.5 between the rates at which H_2 and HT react photochemically with chlorine; the activation energy difference in this case is 550 cal., which is about a 10% increase over the activation energy for the non-isotopic reaction. Unfortunately, very few other cases of tritium isotope effects on rates have been reported.

Most of the experimental work that has been done to date in this field has concerned itself with the carbon isotopes, where the effect is naturally much smaller (characteristically about 2-4%), and with deuterium. Much work has been done with deuterium, and rate ratios of 3 (34) (C—H versus C—D in the mass spectrograph), 2.5 (35) (relative rates of hydrogenation and deutrogenation of ethylene), and 10 (36) (hydrogen and deuterium competing photochemically with carbon monoxide for chlorine) have been found. This list could be extended ad infinitum, but to no good purpose; it suffices to show that isotope effects as large as those found in this work are not at all uncommon when one works with isotopes of the very light elements, such as hydrogen.

It is unfortunate that data are not available to enable one to make a theoretical calculation of the ratios k_1^o/k_1 and k_2^o/k_2. Such a calculation (37) requires a knowledge of molecular frequencies, partition functions for activated complexes, transmission coefficients, etc., in aqueous solution, and is at this time a well nigh impossible task.

The values for E_1 and E_2 found in this work can be used, in conjunction with other data, to estimate the magnitude of the activation energy of reaction 6 and the magnitude of $k_a^o/k_a^{'o}$. Griffith and McKeown (1b), noting that the ratio $k_a^{o'}/k_{0x}^o$ was practically temperature independent and very nearly the same for the three halogen reactions, suggested that reaction 7 might have a zero activation energy and proceed upon every collision between the active form and the oxidizing agent. Knowing the (small) temperature coefficient for $k_a^{o'}/k_{0x}^o$, and assuming that the frequency factor for reaction 6 is equal to the collision number, they calculated a value of 2700 cal. for the activation energy of reaction 6 and a value of 10^{-12} for $k_a^o/k_a^{o'}$.

Aside from the uncertainties in the explicit assumptions made in this calculation, an additional large uncertainty arises from the fact that Griffith and McKeown, when they calculated this value in 1934, did not realize that their reaction was subject to general acid catalysis. Thus their rate constants and activation energies are "lumped" values of k_1^o, k_2^o, E_1^o, and E_2^o. The calculation can be cleaned up a bit if one uses the value of E_1^o that they determined in 1940, when they realized that general acid catalysis was present. Such a recalculation, using 20 kcal. for E_1^o, gives $k_a^o/k_a^{o\prime} \sim 10^{-12.5}$.

In this research, a value of 15.5 kcal. was found for E_2, the activation energy of reaction 5'M catalyzed by H_3PO_2. This means that the activation energy of reaction 5M catalyzed by H_3PO_2 must be $\leqslant$ 15.5 kcal., since, as was explained on page 41, the presence of the isotope effect raises the values of the observed activation energies. As a matter of fact, we can get a rough idea of the magnitude of E_2^o by assuming that $A_2 = A_2^o$ and equating k_2^o/k_2 to $e^{+\frac{(E_2-E_2^o)}{RT}}$ This calculation gives $E_2^o \sim 15$ kcal. Thus ΔE_{int}, the internal energy change for reaction 5, must be $\leqslant$ 15 kcal., the "less than" sign applying if reaction 6 catalyzed by H_3PO_2 has an activation energy greater than zero, a possibility which is actually very likely. Thus the activation energy for reaction 6 catalyzed by H^+ must be $\geqslant$ (20-15) = 5 kcal., and $k_a^o/k_a^{o\prime} \geqslant 10^{-\frac{15000}{2.3RT}} = 10^{-11}$, assuming, with Griffith and McKeown, that the frequency factors for reactions 5 and 6 are the same.

If we now discard the unlikely assumption that reaction 6 catalyzed by H_3PO_2 has a zero activation energy, and assume a value of about 2 kcal. for that reaction, ΔE_{int} becomes $\sim$ 13 kcal., the activation energy for reaction 6 catalyzed by H^+ becomes $\sim$ 7 kcal., and $k_a^o/k_a^{o\prime}$ becomes $\sim 10^{-10}$.

Using a different line of reasoning, and ignoring general acid catalysis, Hayward (1g) estimated that reaction 6 had an activation energy of about 6.5 kcal., and that $k_a^o/k_a^{o\prime} \sim 10^{-9}$. The agreement between this estimate and the one given in the preceding paragraph is probably fortuitious.

The main reason for the disagreement between the estimates made above and those made by Griffith and McKeown is simply that Griffith and McKeown did not measure E_2^o. Had they done so, they would have found that their assumption of a value of 2.7 for the activation energy of reaction 6 catalyzed by H^+ was much too small, since it leads to a value of 17.3 for ΔE_{int}, the internal energy change for reaction 5, a value which is greater than the observed value for E_2. This implies that reaction 6 catalyzed by H_3PO_2 has a negative activation energy, a situation which is very seldom realized, to say the least. Thus the only real contribution made here is that an upper limit is provided for E_2^o and ΔE_{int}, and a lower limit is set for $k_a^o/k_a^{o\prime}$.

General Theory of Isotope Effects in Exchange Reactions

Before the detailed theory of the isotope effect in this reaction was formulated, a general kinetic theory of the isotope effect in any exchange reaction was worked out. This theory has several rather interesting consequences which warrant its inclusion here.

Consider the homogeneous isotopic exchange reaction,

$$AX + BX^{o} \rightleftharpoons AX^{o} + BX,$$

where X^{o} denotes the radioactive* isotope used to follow the reaction. Let R be the rate at which exchange of <u>non</u>-radioactive X atoms takes place. As on page 15, let $(AX) = a$, $(BX) = b$, $(AX^{o}) = x'$, $(BX^{o}) = y'$, $x'+y' = z$. Then the usual expression for dx'/dt is

$$\frac{dx'}{dt} = R\frac{y'}{b}\,\frac{a-x'}{a} - R\frac{x'}{a}\,\frac{b-y'}{b}\,. \qquad (12)$$

However, this equation assumes that the ratio of the probabilities for exchange of radioactive atoms and non-radioactive atoms is equal to the ratio of the concentrations of these atoms in the system. This assumption may be invalid if the masses of the isotopic atoms are different enough to appreciably affect the zero point energy of the isotopic bond; if this occurs, an isotope effect may result. To take this possibility into account, we assume that the ratio of exchange probabilities is equal to the concentration ratio multiplied by a factor which may depend on the structure of the exchanging molecules and the mechanism of exchange. This factor may be different for forward and back

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* Radioactive isotopes are used here for the sake of specificity. The discussion applies equally well to reactions in which stable isotopes (C^{13},O^{18}) are used as tracers.

reactions, but will be independent of the chemical concentrations in the system. Then,

$$\frac{dx'}{dt} = R\,\frac{y'}{b}\,\frac{a-x'}{a}\,\alpha \;-\; R\,\frac{x'}{a}\,\frac{b-y'}{b}\,\beta \qquad (56)$$

where α is the factor for the forward reaction, and β is the factor for the back reaction. Rearranging 56,

$$\frac{dx'}{dt} = \frac{R}{ab}\left[\alpha a y' - \beta b x'\right] + \frac{Rx'y'}{ab}\left[\beta - \alpha\right],$$

$$= \frac{R}{ab}\left(\alpha a z - \alpha a x' - \beta b x'\right) + \frac{R}{ab}\left(\beta - \alpha\right)\left(x'z - (x')^2\right).$$

We note that in general, the exchange will not follow a first order course if α and/or β are not equal to one and if the concentration of the radioactive isotope is of the same order of magnitude as the concentration of non-radioactive atoms. We now assume that the concentration of radioactive atoms in the system is very low, so that the terms in $(x')^2$ and $x'z$ will be negligible compared to first order terms in x' and z. (This is the situation in the H_3PO_2-HTO reaction, where $(T)/(H) \sim 10^{-6}$). Then

$$\frac{dx'}{dt} = x'\left(-\frac{R\alpha a}{ab} - \frac{R\beta b}{ab}\right) + \frac{R\alpha a z}{ab},$$

$$= \left[\frac{\alpha a + \beta b}{ab}\right] R x' + \frac{R}{b}\alpha z .$$

Integrating,

$$x' = C e^{-(\alpha a + \beta b)\frac{Rt}{ab}} + \frac{\alpha z a}{\alpha a + \beta b} . \qquad (57)$$

At $t = \infty$, let $x' = x'_\infty$ and $y' = y'_\infty$:

$$x'_\infty = \frac{\alpha z a}{\alpha a + \beta b}, \qquad y'_\infty = \frac{\beta z b}{\alpha a + \beta b} .$$

Then 57 becomes

$$x' = C e^{-\left(\frac{\alpha a + \beta b}{ab}\right) Rt} + x'_{\infty}.$$

If x' = 0 at t = 0, (AX initially unradioactive), $C = -x'_{\infty}$. Then,

$$x' = -x'_{\infty}\, e^{-\left(\frac{\alpha a + \beta b}{ab}\right) Rt} + x'_{\infty},$$

$$2.3 \log\left(1 - x'/x'_{\infty}\right) = -\left(\frac{\alpha a + \beta b}{ab}\right) Rt.$$

Thus a plot of -log (1-F) versus t gives slope $= \frac{1}{2.3}\left(\frac{\alpha a + \beta b}{ab}\right) R$.

Hence

$$R = \left(\frac{ab}{\alpha a + \beta b}\right) \cdot 2.3 \cdot (\text{slope}).$$

In general, one will not know the values of α and β, and the experimental data will be used to "evaluate" R by the expression,

$$R' = \left(\frac{ab}{a + b}\right) \cdot 2.3 \cdot (\text{slope}).$$

(This expression may be considered as defining R'). R', however, is not the quantity of interest; the following general expression relates R and R':

$$R = \left[\frac{1/\beta\,(a+b)}{\frac{\alpha}{\beta} a + b}\right] R'. \tag{58}$$

Some consequences of equation 58 are as follows:

1) We assume that:
    a. The rate determining step in the forward reaction,

    $$AX + BX^{o} \longrightarrow BX + AX^{o},$$

    involves the scission of the BX^{o} bond.
    b. The rate determining step in the reverse reaction,

    $$AX^{o} + BX \longrightarrow BX^{o} + AX,$$

    involves the scission of the AX^{o} bond.
    c. X^{o} is heavier than X.

Then α and β will be less than one. This is due to the fact that BX^o and AX^o will be more reluctant to give up their X^o atoms than their X atoms, due to the lower zero point energy of the BX^o and AX^o bonds.* Then $R = \left(\frac{a+b}{\alpha a + \beta b}\right) R'$, and an isotope effect will appear.

2) We assume that:

  a. The rate determining step in the forward reaction does not involve the scission of a BX^o bond, but that the rate determining step in the reverse reaction involves the scission of an AX^o bond.

  b. X^o is heavier than X.

Then α will be equal to one, but β will be less than one, and an isotope effect will appear only under certain conditions, since

  i) if $a \gg b$, $R \sim R'$, and no isotope effect will appear.

  ii) if $a \ll b$, $R \sim R'/\beta$, and an isotope effect will appear.

3) We assume that:

  a. The rate determining step in the forward reaction involves the scission of a BX^o bond, but that the rate determining step in the reverse reaction does <u>not</u> involve the scission of an AX^o bond.

  b. X^o is heavier than X.

Then β will be equal to one, but α will be less than one, and, as in 2, an isotope effect will appear only under certain

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* Zero point energy = $\frac{1}{2}h\nu_0$ for $\underset{m_1}{A}\!-\!\underset{m_2}{B}$, $\nu_0 = \frac{1}{2\pi}\sqrt{k/\mu}$, $\mu = \frac{m_1 m_2}{m_1 + m_2}$.

conditions, since

i) if $a \gg b$, $R \sim R'/\alpha$, and an isotope effect will appear.

ii) if $a \ll b$, $R \sim R'$, and no isotope effect will appear.

4) We assume that:

a. Neither the forward nor the reverse reactions involve in their rate determining steps the scission of AX^o or BX^o bonds. Then $\alpha = \beta = 1$, $R = R'$, and no isotope effect will appear, regardless of the concentration conditions. This last case could conceivably be realized in the case of an exchange reaction proceeding via an atomic mechanism in the rate determining step.

(The case of the H_3PO_2 - HTO exchange reaction, where $a \ll b$, and where an isotope effect appears, could be covered by a number of the cases listed above. It is very likely, however, that case 2 ii applies to this reaction. As can be easily seen by reference to the mechanism proposed for this exchange reaction, the rate determining step in the reverse reaction, (5'M), will involve an isotope effect, but the rate determining step in the forward reaction, (5M), will not involve an isotope effect.)

The concentration equilibrium constant for the general exchange reaction, $AX + BX^o \rightleftharpoons BX + AX^o$, $K = \frac{(AX^o)(BX)}{(BX^o)(AX)}$, is easily derived:

$$\frac{(AX^o)(BX)}{(BX^o)(AX)} = \frac{b x'_\infty}{a y'_\infty} ,$$

$$x'_\infty = \frac{\alpha Z a}{\alpha a + \beta b}, \qquad y_\infty = \frac{\beta Z b}{\alpha a + \beta b},$$

$$\therefore K = \alpha/\beta .$$

The same result could have been obtained by setting $dx'/dt = 0$ in 56.

Up to this point, we have been considering the measurement of dx'/dt, the rate at which AX molecules become radioactive, with (AX^o) initially equal to zero. One might suppose that the equilibrium constant, α/β, could be evaluated if one also measured the rate of the reverse reaction, dy'/dt, with (BX^o) initially equal to zero. This, surprisingly enough, is not the case. If one sets up the analog of equation 56 for dy'/dt and integrates, using $y'=0$ at $t = 0$ for the first boundary condition, one finds that the slope is given by the expression, $\frac{1}{2.3}\left(\frac{\alpha a + \beta b}{a\,b}\right)R$. Thus one will find the same slope for the forward and reverse reactions, and R', the calculated value of R, will therefore also be the same. We see then, that the equilibrium constant cannot be evaluated by these two measurements alone.

(At first sight, it appears as though it might be possible to evaluate the equilibrium constant for the H_3PO_2-HTO exchange reaction by assuming that $\alpha = 1$, and that β is given by k_a/k_a^o. It is immediately evident, however, that such assumptions would give different values for K depending upon which acid catalyst was chosen, since, $k_1/k_1^o \neq k_2/k_2^o$.

This apparent violation of the Second Law of Thermodynamics is due to the fact that the equilibrium in the H_3PO_2-HTO system is determined by two reactions:

$$HTO + HA \rightleftharpoons TA + H_2O, \quad K_a^{*} = \frac{(TA)(H_2O)}{(HTO)(HA)},$$

and $TA + H_2POOH \rightleftharpoons HTPOOH + HA, \quad K_a' = \frac{(HA)(HTPOOH)}{(TA)(H_2POOH)}.$

Thus the equilibrium constant for the overall reaction,

$$HTO + H_2POOH \rightleftharpoons HTPOOH + H_2O, \quad K = \frac{(HTPOOH)(H_2O)}{(HTO)(H_2POOH)},$$

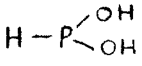
is equal to $K_a^{*}K_a'$. K_a' is probably determined by the value of β_a alone, since α is probably equal to one for that reaction, but K is determined by both β_a and K_a^{*}:

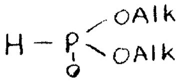
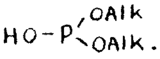
$$K = K_a^{*}/\beta_a .$$

According to this theory, K_a^{*} and β_a should vary in such a way as to keep K constant as the catalyst is varied).

A theory with essentially the same consequences as this one has been developed by Harris (38).

F. Summary

The results of the acid solution exchange experiments show that 1) the tautomeric equilibrium, reactions 5 and 6, actually does exist in hypophosphorous acid solutions, 2) the oxidation mechanism proposed by Mitchell (reactions 5,6, and 7) is, in all likelihood, correct, and 3) the structure of the active form is probably that pictured in equation 5M,  $H-P{<}^{OH}_{OH}$.

It is interesting to note that other phosphorus compounds seem to exhibit the same sort of behavior. For instance, Griffith and McKeown (39) have found that it is necessary to assume an interconversion between normal and active forms of phosphorous acid to explain their results on the acid solution oxidation of phosphorous acid to phosphoric acid by iodine. Nylen (40) has found that the rate of oxidation of the dialkyl esters of phosphorous acid is the same for iodine and bromine, and is independent of the concentration of the oxidizing agent. He therefore assumes that a "tautomeric shift" is taking place in the ester molecule, converting an inactive form,  $H-\underset{\overset{\|}{O}}{P}{<}^{OAlk}_{OAlk}$, to an active form,  $HO-P{<}^{OAlk}_{OAlk}$.

The successful verification of the analogous mechanism for hypophosphorous acid by means of exchange experiments suggests that such experiments on these systems would also be worthwhile.

II. An Investigation of Some Aspects of the Chemistry of Hypophosphorous Acid and Thallous Hypophosphite.

A. The Purification of Hypophosphorous Acid.

B. 1. The Preparation and Thermal Stability of Thallous Hypophosphite.

2. The Reaction of Hypophosphorous Acid with Persulfate and Dichromate.

A. The Purification of Hypophosphorous Acid*

Before the exchange experiments were begun, some time was devoted to the problem of preparing very pure hypophosphorous acid. The very pure material finally obtained was never used in the kinetic investigations, but its preparation is included here since, to my knowledge, no preparative method has been reported which will yield solid acid of such a high degree of purity.

Purification.

Hypophosphorous acid from almost any source will serve as a starting material, so long as it is about 10 formal. The commercial grade 50% acid (Merck), which usually contains from 2 to 3 mole percent phosphorous acid, meets this requirement and was used in all the preparations.

About 600 ml. of concentrated hypophosphorous acid is placed in a one liter filtering flask which is connected to a water aspirator. Through a two hole stopper in the top of the flask run a thermometer and a coarse gas dispersion tube, the tube being connected to a source of dry nitrogen. The flask rests on a hot plate. After all of the air has been thoroughly flushed out of the system with nitrogen, the aspirator and hot plate are turned on, the nitrogen flow is cut down, and the temperature regulated so that it remains around 40° during the evaporation, which

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* The material presented in this Section appeared as a Note in the Journal of the American Chemical Society, 74, 1353 (1952).

is continued until the volume of solution is about 300 ml. The hot plate is then turned off and the solution allowed to cool. The liquid in the flask is then poured into a wide mouthed Erlenmeyer flask and placed in a dry ice - acetone bath. After a few hours in the bath, the contents of the flask will freeze. The flask is then removed from the bath and allowed to stand in a cold room ($\sim 5^{\circ}$) for about 12 hours, after which time the flask contents should be from 30 to 40% liquid.

The following operations are carried out in the cold room. The mixture is filtered by suction through Whatman #44 filter paper. The filtrate is discarded, the solid pressed dry on the paper, transferred to a crystallizing dish and allowed to stand until 20 to 30% of it liquefies. It is then refiltered, and the resulting white solid stored over $Mg(ClO_4)_2$ in an evacuated desiccator in a cold room.

The yield in this preparation is about 15%.

Large crystals of this product can be prepared by recrystallizing the white solid from n-butanol. (The high solubility of hypophosphorous acid in the lower alcohols renders them impractical for recrystallization purposes.) Analysis showed that the purity of the product was not increased by recrystallization.

Analysis

Aqueous solutions of the white solid were analyzed for hypophosphorous acid and phosphorous acid by a combination acidimetric-iodometric method in which total acid was determined by titration with standard NaOH to the phenolphthalein end point, and phosphorous acid was determined by the method of Jones and Swift (6). The results of these analyses showed that the phosphite impurity had been reduced from 3% in the crude acid to about 0.2% in the purified material. This purification method was subsequently extended by Mr. R.T. Jones (7), who found that three filtration-liquefaction cycles reduced the phosphite impurity to less than 0.1 mole percent.

Qualitative tests for phosphate were run on aqueous solutions of some batches of H_3PO_2 prepared by this method, using the ammonium molybdate procedure reccommended by Swift (41). At no time was any yellow coloration or yellow precipitate noted. This test is sensitive to about 0.1 mole percent phosphate in the presence of hypophosphorous acid.

B. 1. The Preparation and Thermal Stability of Thallous Hypophosphite.*

2. The Reaction of Hypophosphorous Acid with Persulfate and Dichromate.

Introduction

Before it was realized that tritium-active samples could be assayed for activity in the solid phase, the only method available was gas-phase assay. In order to analyze total hypophosphite for activity by this method, it had to be converted to a form suitable for counting as a gas inside a Geiger-Muller tube or an ionization chamber. This conversion was to be carried out as follows: The reacting solution was to be neutralized with TlOH and the resulting solution evaporated to dryness in vacuo. The solid TlH_2PO_2 thus obtained was to be dried by heating it in a high vacuum desiccator, dissolved in water, and oxidized to thallic phosphate. The thallic phosphate would then come to exchange equilibrium with the water. The water could then be distilled off in vacuo and converted to hydrogen by passing it over magnesium turnings at 500°. The resulting hydrogen could then be put into a counter or ionization chamber for assay.

In order to assess the feasibility of such a procedure, several questions had to be answered. Is thallous hypophos-

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* This material has been published as a Note in the Journal of the American Chemical Society, 73, 2945 (1951).

phite stable enough to be heated to 100° in vacuo for an appreciable length of time? What oxidizing agent will convert hypophosphites to phosphates quickly and without gas evolution? Can a GM tube be made to function properly when 10-20% of the filling gas is hydrogen? Two of these questions were answered satisfactorily and are of enough intrinsic interest to warrant their consideration here.

1. The Preparation and Thermal Stability of Thallous Hypophosphite

This subject was briefly touched upon by Rammelsberg (42) in the course of his research on the thermal decomposition products of hypophosphites. Some doubt is cast upon the validity of his results by the fact that he used a salt which had a melting point of 150° and which contained only 74.3% thallium. Furthermore, no quantitative thermal data are given in his paper.

The experiments described here were carried out to develop a convenient method of preparation for thallous hypophosphite and to determine to what extent it would decompose when heated under various conditions of temperature and pressure.

Preparation of Thallous Hypophosphite

Thallous hydroxide solution is prepared by shaking thin slices of thallium metal with an 80% excess of water, while bubbling oxygen through the mixture. The resulting mixture is then filtered and saturated with carbon dioxide; after partial evaporation and cooling, thallous carbonate precipitates out and can be recrystallized from water. To the crystals, an equivalent amount of approximately 10 f. hypophosphorous acid (prepared by ion exchange and concentrated by vacuum desiccation) is added, and the resulting solution is filtered and further concentrated under vacuum. After two days, about 20% of the salt will precipitate out and can be filtered off. To the remainder of the solution, a large excess of n-propyl or isopropyl alcohol is then added (about 3 liters of alcohol per 100 ml. of saturated salt solution), and the resulting mixture is refrigerated at 5° for one week. The white, needle-like crystals that form are collected and washed with fresh isopropyl alcohol. The product is then dried in a vacuum desiccator.

Samples of thallous hypophosphite prepared in this manner were analyzed for thallium by the gravimetric chromate method (43) with the following results: 1) crystals obtained directly from water, 75.8 ± 0.04%; 2) salt removed from isopropyl alcohol, 75.8 ± 0.03% (theoretical thallium, 75.89%). In a typical preparation, the over-all yield was about 70%, based on thallium.

Melting Point of Thallous Hypophosphite

Four determinations of the melting point of this product gave a value of 114 ± 0.5° (corr.), in good agreement with the value of 110° found by Ferrari and Colla (44). Slight decomposition of the salt was usually observed at and near the melting point.

Experiments on Thermal Stability

The results of these experiments are presented in Table 15.

Series I was carried out by simply heating a salt sample for successive 24 hour periods in a Fisher "Iso-Temp" electric oven, with poor ($\pm 5^{\circ}$) temperature control, and weighing after each 24 hour heating period. Under these conditions, the salt began to liquefy at 90°. This fact, coupled with the weight increase observed and the absence of the odor of phosphine, led to the supposition that under these conditions, thallous hypophosphite is slowly air oxidized to thallous phosphite, TlH_2PO_3, which has a reported melting point of 70° (45). Analysis of the heated product for thallium supported this supposition.

Each member of Series II, III, and IV was run as follows: About one gram of the salt in a small, open weighing bottle was freed of most of its adsorbed solvent (isopropyl alcohol in Series II and III, water in Series IV) by vacuum desiccation. It was then weighed and the bottle inserted in a 28 mm. Pyrex tube which was sealed off at one end and fitted at the other with a 34/45 standard taper joint. The tube and bottle were evacuated at room temperature with a mercury diffusion pump until the salt attained constant weight. At no time in this initial pumping was a weight loss greater than about 0.2 mg. noted. After weighing, the tube and bottle were re-evacuated, and a cylindrical electric heater, at the desired temperature, was placed around the tube. During each heating period, a vacuum of 10^{-5} mm. Hg was maintained. The salt, in its bottle, was removed at the end of each heating period, weighed, pulverized, stirred up well, returned to the tube, and heated under vacuum as before. Fresh salt samples were taken for each Series. The observed weight losses are given in Table 15.

Several interesting phenomena were observed during these heating experiments: (a) In all cases, the salt blackened slowly during the course of the heating period. At 95°, about six or seven hours were usually necessary to cause blackening to begin. (b) When air was excluded by evacuation or flushing with argon, neither melting nor weight <u>increase</u> was ever observed, even though the temperature ran 30° above the melting point of thallous <u>phosphite</u> for considerable periods of time. This supports the conclusion drawn above concerning the air oxidation of thallous hypophosphite at elevated temperatures. (c) In all cases, the weight loss observed in the first heating period was from four to five times that observed in subsequent periods. This can probably be attributed to the last traces of solvent disappearing from the salt.

In some cases, analyses were run on the samples after heating; no significant change in the thallium content was noted.

The small, reproducible weight losses observed after the larger initial weight losses were probably due to one or both of the reactions:

$$5TlH_2PO_2 \longrightarrow Tl_4P_2O_7 + TlPO_3 + 2H_2 \quad (42),$$

$$\text{or} \quad 2TlH_2PO_2 \longrightarrow Tl_2HPO_4 + PH_3.$$

To test this point, an attempt was made to trap out, with liquid nitrogen, any phosphine that might be produced. No phosphine was visible in the trap, but when air was rapidly admitted to the system, a green flame appeared in the trap. Such behavior is characteristic of phosphine at low pressures. Qualitative tests for phosphate were made after Series IA and II. A faint positive test was observed in IA.

It is worth noting that some thallous hypophosphite preparations seemed to be somewhat sensitive to light; that is to say, if they were allowed to stand in strong sunlight for a week or two, they began to develop the same black color noted in the heating experiments. Control samples in blackened bottles developed no color. Thallous hypophosphite is not the only thallium salt which exhibits this behavior; other salts of thallium are also photosensitive. For this reason, all experiments involving this salt at elevated temperatures were run in complete darkness, and exposure of the salt to the light while cold was minimized as much as possible.

2. The Reaction of Hypophosphorous Acid with Persulfate and Dichromate

Reaction with Persulfate

This reaction proceeds at a conveniently measurable rate with both ammonium and potassium persulfate, in solutions which are about 4 f. in perchloric acid. Because of its greater solubility, the ammonium salt was used in most of the experiments.

To ascertain the extent of reaction in a qualitative way, samples were withdrawn from the reaction mixture and a large excess of 1 f. $BaCl_2$ solution was added. The resulting precipitate of $BaSO_4$ was centrifuged down in calibrated centrifuge tubes, and the amount of precipitate served to indicate the extent of reaction. Some of the withdrawn samples were also tested for phosphate, using the ammonium molybdate procedure recommended by Swift (41), and for hypophosphorous acid, using $KMnO_4$ solutions.

The results of all these tests were considered in making an estimate of the half time of the reaction. These half times are given in Table 16, and must be considered as indicating orders of magnitude only. A large uncertainty is introduced by the fact that none of the tests used accurately differentiated between the oxidation of H_3PO_2 to phosphorous acid, $H_3PO_2 + S_2O_8^{--} + H_2O \longrightarrow 2SO_4^{--} + H_3PO_3 + 2H^+$, and the oxidation of H_3PO_2 to phosphoric acid,

$$H_3PO_2 + 2S_2O_8^{--} + 2H_2O \longrightarrow 4SO_4^{--} + H_3PO_4 + 4H^+.$$

Since only the second reaction was of interest at this time, the data given in the Table apply only to it. In Run III, the reactant solution was made about 0.0002 f. in $AgNO_3$, to see if any appreciable catalysis would occur. The difference noted in the half time is probably not significant.

The half times found in these experiments were too large to make quantitative experiments worthwhile. This method of oxidation was therefore abandoned, and the reaction between H_3PO_2 and dichromate was studied.

Reaction With Dichromate

In these experiments, the reaction under consideration is

$$3H_3PO_2 + 2Cr_2O_7^{--} + 16\ H^+ \longrightarrow 3H_3PO_4 + 4Cr^{+++} + 8H_2O.$$

The oxidation of H_3PO_2 to phosphorous acid by dichromate has been studied by Dhar (46), and by Mitchell (29); the oxidation of phosphorous acid to phosphoric acid by dichromate has been studied by Kirson (47). Since the latter reaction has a reported half time of about ten minutes at moderate concentrations, dichromate seemed like a worthwhile oxidizing agent to investigate.

In the initial experiments, the reaction was followed in a qualitative way by precipitating $Cr(OH)_3$ and centrifuging it down, as in the persulfate experiments. These preliminary runs indicated a half time of about an hour, so quantitative experiments were initiated, in which samples were withdrawn from the reaction mixture and analyzed for dichromate iodometrically (48). The stock dichromate solutions were made up from c.p. $K_2Cr_2O_7$ and standardized iodometrically. Stock H_3PO_2 solutions were prepared by ion exchange (see Part I), and analyzed for H_3PO_2 and H_3PO_3 by the Jones-Swift method (6).

The reaction, when carried out at the concentrations given in Table 17, liberates a large amount of heat, the temperature of the reaction mixture rising to about 55° in five minutes. In the first run, no heat was applied to the mixture from external sources, and the reaction was found to be 90% complete in eight hours. In all the subsequent runs, the reaction mixture was heated to about 80° under reflux until reaction was thought to be complete, then cooled and analyzed for dichromate. The results of these experiments are presented in Table 15. It is clear that at the concentrations used in Runs I-III, the reaction is complete in two hours at 80°.

These results, although they have little value from the kinetic standpoint, are worthwhile for two reasons. First, the close agreement between equivalents of dichromate consumed and equivalents of $H_3PO_2 + H_3PO_3$ added to the reaction mixture constitutes an independent verification of the Jones-Swift analytical method. Second, the relatively short reaction time gives a convenient method for the complete oxidation of H_3PO_2 to H_3PO_4.

III. A New Assay Method for Tritiated Water

Introduction

The advent of solid phase counting techniques has opened up new possibilities for the rapid radioactive assay of tritiated compounds. For experiments which involve HTO and in which an accurate value for the activity of HTO is not necessary, it would be very useful to have a method by which the tritium content of HTO could be rapidly estimated with fair accuracy. In the research described in Part I, this approximate HTO assay was made with an ionization chamber. This method is very laborious unless the chamber and the associated vacuum system are already in operating condition.

Experimental

In principle, any chemical compound which contains hydrogen can be used to develop a solid-phase assay method, but it is evident that one would like to use hydrogen - containing compounds which can be easily rendered radioactive. Given such a compound, one could develop the assay method as follows:

Given a supply of tritiated water of known activity, one would render the hydrogen - containing compound radioactive to a known extent by treating it in an appropriate way with HTO of known activity. One would then measure the activity of the resulting compound in a windowless flow counter, thereby determining the ratio

$$S = \frac{\text{activity of solid compound}}{\text{activity of HTO used to render it active}}$$

After having established that this ratio is constant for all HTO activities, one could then measure the activity of an HTO sample of unknown activity by treating the hydrogen-containing compound in the same way and measuring the resulting activity of the compound in the flow counter; the activity of the HTO could then be calculated from the known value of S.

In this work, three hydrogen - containing compounds were investigated: $CuSO_4 \cdot 5H_2O$, $Mg(ClO_4)_2 \cdot 3H_2O$, and NH_4Cl. For the two hydrates, the procedure was as follows: the salt was rendered anhydrous by heating it in an oven, weighed out into a mortar, and ground up well. A known volume of HTO of a known activity* (hereafter referred to as "standard HTO") was then added. The resulting mixture of anhydrous salt and hydrate was again ground up and mixed well in a mortar. Portions were then removed, packed into planchets, and counted as described in Part I, Section B.

It soon became apparent that copper sulfate pentahydrate and magnesium perchlorate trihydrate were not satisfactory hydrogen - containing compounds for this assay method. The rapid absorption of water vapor from the air caused a steady decrease in the activity of the portion of the solid left exposed to the air as successive samples were counted. The vapor pressure of HTO over the hydrates was high enough so that detectable amounts of HTO were liberated inside the

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* Standardized by ionization-chamber assay. See page 6.

counter while the solids were being counted. This HTO deposited on the walls of the counter and increased the background count appreciably. For these reasons, these salts were abandoned without further ado and experiments on NH_4Cl were initiated.

NH_4Cl was rendered active by exchange with standard HTO in the following manner: C.p., Baker's Analyzed ammonium chloride was ground up well and dried by vacuum desiccation. Accurately weighed portions were placed in the bottom section of the still shown in Figure 9, a known amount of standard HTO was pipetted in, and the mixture swirled to dissolve the NH_4Cl. The resulting solution was allowed to stand at room temperature 10-15 minutes to ensure exchange equilibrium (although experiments showed that exchange equilibrium was reached in less than 5 minutes at room temperature), and the HTO was then distilled off in a hood, using the apparatus shown in Figure 9. After the still had been gently flamed with an oxygen torch, it was taken apart and the bottom section, which contained most of the NT_4Cl[*], replaced on the hot plate.

Two procedures were used to remove the last traces of adsorbed water from the NT_4Cl. The first, hereafter referred to as Method 1, was to heat the solid NT_4Cl for about 10-15

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[*] The NH_4Cl which had come to exchange equilibrium was really a mixture of NT_4Cl, NHT_3Cl, NH_2T_2Cl, NH_3TCl and NH_4Cl, with the last two species predominant. However, the active salt will be referred to here as NT_4Cl for simplicity.

minutes on the hot plate in the hood until about 50% of it had sublimed away. The solid was then judged to be dry. The second procedure, hereafter referred to as Method 2, was to heat the solid NT_4Cl until dense white fumes of NT_4Cl vapor began to appear. At this point, the bottom section of the still, containing the NT_4Cl, was removed from the hot plate and allowed to cool. The salt was then scrpaed out of the still put into a mortar, ground up well, and put into a crystallizing dish. The dish was covered with a watch glass containing cold water and placed on the hot plate. In about 20 minutes, all of the NT_4Cl had sublimed out of the dish and condensed on the watch glass. The watch glass was then removed and the NT_4Cl scraped off into a mortar.

Before the NT_4Cl was counted, it was ground up and mixed up well in the mortar. The counting procedure then consisted of filling a 7.3 $cm.^2$ planchet with about 0.75 g. of the ground-up salt and measuring its activity in the windowless flow counter described on page 9, using the same Berkeley Decimal Scaler. After counting, the salt was removed from the planchet, returned to the mortar, mixed up again, repacked in the planchet, and recounted. In many cases, 10 or 15 refillings and recountings (hereafter referred to simply as countings), were made, in order to obtain a reliable value for the activity. Coincidence corrections were made on all counting rates above 1600 c/m, using a resolving time determined by the method of single paired sources (49).

Results

The first group of experiments were carried out to examine the counting characteristics of NT_4Cl. A sample of NT_4Cl was prepared, dried by Method 1, and counted. It was found that successive countings gave the same activity within about 2%, that the counter did not become contaminated with HTO or NT_4Cl vapor, and that the active salt could be left in the open overnight without its activity decreasing to any significant extent. It was also found that successive samples of NT_4Cl, prepared from the same weight of NH_4Cl and the same volume of standard HTO, gave the same observed counting rate within about 1 or 2%. It was further found that 5 minutes drying by Method 1 gave the same activity as 15 minutes drying, indicating that 5 minutes drying by Method 1 was adequate to remove all the adsorbed HTO from the active salt. At this point, the assay method looked as though it had a great deal of promise; further experiments showed this conclusion to be essentially sound, although some of the conclusions drawn from these preliminary results had to be modified somewhat.

In the second group of experiments, a "dilution curve" was run, in which successive samples of NH_4Cl were rendered active by exchange with HTO samples of varying activity. A plot of the observed NT_4Cl activity versus the activity of the HTO used to render the NT_4Cl active should be a straight line which passes through the origin, showing that the ratio

$$S = \frac{\text{activity of } NT_4Cl}{\text{activity of HTO used to make it active}} \qquad (59)$$

is a true constant. These experiments were carried out using HTO samples of varying activity which had been made up by accurate dilution of the standard HTO. All samples were prepared by dissolving 2.86 g. of NH_4Cl in 10 ml. of HTO. The NT_4Cl was dried by Method 1. A plot of the results obtained appears in Figure 10, where it is evident that S is not a true constant. If one ignores the first two points and extrapolates the curve back to zero water activity, one obtains a finite NT_4Cl activity at zero HTO activity, showing that some HTO may have been left adsorbed on the salt even after the drastic drying procedure used in Method 1. The reason for the constancy of the NT_4Cl activity after further drying, noted in the preliminary experiments, may be that the NT_4Cl was subliming away as fast as the HTO was evaporating, thereby maintaining the specific activity approximately constant. At any rate, it was evident that this method for the preparation of active NT_4Cl was not satisfactory.

A second dilution curve was then run. Again, all samples were prepared by dissolving 2.86 g. of NH_4Cl in 10.0 ml. of HTO, but this time, Method 2 was used to dry the NT_4Cl. The results of this set of experiments are presented in Figure 11 and Table 18, where two things are immediately apparent: 1) The activity of NT_4Cl prepared from HTO of a given activity is lower in every case than the corresponding NT_4Cl activities in the first set of dilution curve experiments. 2) The plot is now linear and S is constant, with the average deviation of the individual values from the mean being about 1%. This set of experiments was then repeated. The results are presented in Table 19, where it is seen that although S is still constant, all the activities are higher by about 5%.

Experiments were then conducted to see if these higher activity values were due to contamination of the apparatus. A solution of NH_4Cl in H_2O was evaporated and dried by Method 2; the resulting salt was completely inactive, showing that appreciable contamination of the apparatus had not taken place.

The next set of experiments was designed to show the effect of changing the initial concentration of NH_4Cl in the NH_4Cl - HTO equilibration mixture. Varying amounts of NH_4Cl were dissolved in 20.0 ml. portions of HTO which had an activity of 15.9×10^{-6} curies per gram. Method 2 was used to dry the salt.

Theoretically, the initial concentration of NH_4Cl should have no effect on the resultant NT_4Cl activity, since the activity of the NT_4Cl is determined by the equilibrium constants of the reactions

$$NH_4Cl + (4 - i)HTO \rightleftharpoons NH_iT_{4-i}Cl + (4 - i)H_2O,$$
$$i = 1....4,$$

at the boiling point of a saturated solution of NH_4Cl in H_2O, the concentration of NH_4Cl in a saturated solution at this temperature, and the constants of the detection apparatus. However, as is shown in Figure 12, the concentration of NH_4Cl does have an effect, when the initial concentrations of the solutions are greater than about 4 g. NH_4Cl per 10 ml. HTO. This decrease in the NT_4Cl activity at high initial (NH_4Cl) may be due to the fact that with large amounts of NH_4Cl, equilibration at the boiling point is not quite complete before all of the HTO has been evaporated off. The results of these experiments indicated that it might be better to use lower initial concentrations of NH_4Cl in the assay method, since at lower initial (NH_4Cl), the NT_4Cl activity was less sensitive to the initial (NH_4Cl).

Accordingly, another dilution curve was run, using the same HTO solutions as before but a lower initial (NH_4Cl) in the equilibration solution. In this set of experiments, the initial concentration of NH_4Cl was 1.50 g. NH_4Cl per 10 ml. HTO. After the first curve had been run, the experiments were repeated; the results of the two sets of experiments are shown in Table 20. The data in this Table show no systematic trend from run to run, such as was observed in the previous experiments.

It is evident that if this assay method is to be of use to investigators in various laboratories who might be using flow counters made by different manufacturers, some experiments should be conducted to find out how the observed activity of a given sample of NT_4Cl varied when different flow counters were used to measure its activity. Through the kindness of Professor Dan Campbell and Dr. Justine

Garvey, another Q-gas flow counter was made available. This counter, which will be called counter 2, was a product of the Nuclear Instrument and Chemical Company, and was a Model D-46A, as was counter 1, the counter used in all the above experiments. However, it differed from counter 1 in having a wider and deeper planchet holder. The bottom of the planchet holder in counter 2 was about one inch from the counter anode, whereas the bottom of the planchet holder in counter 1 was about $\frac{1}{2}$ inch from the counter anode. The planchet holder in counter 2 had an area of 11.0 cm.^{2}, whereas the area of the planchet holder in counter 1 was 8.05 cm.^{2} A sample which counted at the rate of 1970 c/m in counter 1 had an activity of 1420 c/m in counter 2. The same planchet was used in both cases, so the planchet area was the same. When the sample was propped up in counter 2 so that it was about 3/8 inch from the counter anode, the activity observed was about 1750 c/m, showing that the major difference between the two counters was the distance from the counter anode.

Unfortunately, no other flow counters were available to allow an extension of these experiments. It would have been very interesting to measure the activity of this sample in a counter which used a flow gas which had a composition different from the composition of the Q-gas used in both of the counters discussed above. It is conceivable that the counting efficiency might vary somewhat with a change in the nature of the flow gas.

Reproducibility. A Discussion of Error

Two disturbing features were noticed in the course of some of these experiments. One major source of difficulty was the fact that the observed activities of the NT_4Cl samples decreased with successive countings until they reached a point about which they oscillated with an average deviation of about 2%. Almost all of the samples showed this behavior, although it seemed to be more pronounced for samples of higher activity. A typical example is afforded by the first sample in Figure 12, which started off counting at about 2500 c/m, and slowly decreased until it reached a constant activity of 1950 ± 15 c/m. This behavior made many refillings and recountings necessary, since one had to convince oneself that the observed activity was the "true" activity, i.e., the activity that would be observed when "counting equilibrium", so to speak, had been reached. The large number of recountings that seemed to be necessary detract from the efficiency and apparent reliability of the method. In all cases, the activities quoted in the Tables and Figures are the activities found when counting equilibrium had been reached. At counting equilibrium, the overall average reproducibility of successive countings of a given sample was 2.3%.

The other difficulty is exemplified by the results of the second and third dilution curve experiments, which are compared in Table 19. As was previously pointed out, the activities observed in the third set of experiments were consistently higher than those observed in the second set. The reason for this consistent increase is not apparent, but it was felt that experiments carried out at lower (NH_4Cl) might not show this behavior. As Table 20 shows, they did not; the reproducibility of S in this set of experiments was about 2%. It was further noted that in these experiments at lower initial (NH_4Cl), the decrease in counting rate with successive countings was not so pronounced; some samples did not show a decrease at all. Thus it seems that the assay method is most reliable when carried out at initial NH_4Cl concentrations which are in the 1-2 g. NH_4Cl/10 ml. HTO.

The existence of the two difficulties mentioned above requires some conservatism in the estimate of the maximum error to be expected in the method. Until the difficulties have been completely worked out, it is probably safest to assign a maximum error of about 15% to any value of HTO activity obtained by this method. This estimate includes the uncertainty in the activity of the standard HTO, and strictly speaking, applies only to values obtained with counter 1 or other counters exactly like it.

Summary

The preceding discussion shows the feasibility of developing an assay method for HTO based on the use of the windowless flow counter. Given a dependable value for S, an investigator who wishes to know the activity of HTO which he has prepared for use in tracer experiments need only repeat the procedure outlined in the Experimental section, measure the activity of the NT_4Cl produced, and calculate the activity of the HTO from equation 59. Knowing that the planchet area used in these experiments was 7.30 $cm.^2$, the investigator can easily convert S to a value applicable to the planchet area which he may be using, since the observed activity is obviously directly proportional to the planchet area. If he is using a flow counter manufactured by a different firm, which uses a counter gas of a very different composition than that used in these experiments, then the figure that he obtains will probably be good to an order of magnitude or better.

It is evident that further work on this method should concern itself with discovering the reasons for the difficulties mentioned in the preceding section and evaluating S for different types of counters and flow gases.

Table 1

Results of Neutral Solution Exchange Experiments Using TlH_2PO_2 and HTO. Specific activity of HTO: $4.15 \times 10^{-4} \frac{\text{curies}}{\text{gram}}$.

(TlH_2PO_2)	Contact time[*]	Washing Procedure[**]	Activity of TlH_2PO_2, c/m	Apparent % exchange[***]
0.46	3 hr.	Not washed	485	4.9%
0.46	26 hr.	Not washed	360	3.6%
0.46	26 hr.	$(CH_3)_2CHOH$	237	2.4%
0.46	10 min.	1 water wash	150	1.5%
0.75	1 hr.	2 water washes	190	1.9%
1.3	1 hr.	1 water wash	145	1.5%
1.3	1 hr.	acetone	145	1.5%
0.75	5 min.	1 water wash	60	0.6%
0.75	5 min.	2 water washes	60	0.6%
1.3	5 min.	2 water washes	34	0.4%
1.33	5 min.	3 water washes	32	0.3%
0.75	31 days	2 water washes	80	0.8%

---

[*] The time of evaporation and the time for washing are not included in this figure. In the first seven experiments, HTO which had been distilled twice was used. In the next two experiments, triply-distilled HTO was used. In the next three experiments, quadruply-distilled HTO was used.

[**] A "water wash" means dissolution of the sample in about 10 ml. of inactive distilled water, re-evaporating, and recounting.

[***] 100% exchange would correspond to a sample activity of about 10,000 c/m.

Table 2

Results of Neutral Solution Exchange Experiments Using $TlHTPO_2$ and H_2O.

($TlHTPO_2$)	Contact time (days)	Initial activity of $TlHTPO_2$, c/m*	Final activity of $TlHTPO_2$, c/m*
0.3	1	4600	4600
0.3	1	4600	4600
0.3	3	4600	4600
0.3	1 hour	1500	1500
0.3	1 hour	1500	1480
0.4	10	1500	1450
0.6	31	1450	1100

---

* All these activities are subject to the statistical error of counting, 1%.

Table 3

Values for x and x_{∞}, and Quantities Calculated from Them, Found in Typical Runs.

Series VI $\sum(H_3PO_2) = 0.997$, $(H^+) = 0.246$, $(H_3PO_2) = 0.751$.

	Δt,* min.	x, c/m.	$x/x_{\infty} = F$	$-\log(1-F)/\Delta t$, $min^{-1} \times 10^3$.
Run 1	30	543 ± 7	0.340	6.02
	60	895 ± 10	0.560	5.95
	90	1136 ± 11	0.711	5.98
	120	1285 ± 13	0.805	5.92
	∞ (24 hr.)	1596 ± 15	mean:	5.97 ± .03
Run 2	40	666 ± 8	0.420	5.92
	80	1057 ± 10	0.666	5.96
	120	1287 ± 13	0.810	6.00
	∞ (24 hr.)	1586 ± 15	mean:	5.96 ± .03

Series XI $\sum(H_3PO_2) = 0.508$, $(H^+) = 0.106$, $(H_3PO_2) = 0.290$.

	Δt, hr.	x, c/m.	$x/x_{\infty} = F$	$-\log(1-F)/\Delta t$, $hr^{-1} \times 10^1$.
Run 1	1.5	430 ± 7	0.320	1.12
	3.0	713 ± 8	0.530	1.09
	4.5	974 ± 10	0.724	1.15
	6.0	1074 ± 11	0.800	1.17
	∞ (48 hr.)	1344 ± 13	mean:	1.13 ± .02

---

* $\Delta t \equiv$ time between start of reaction and time sample was withdrawn and neutralized.

Table 3 (continued)

Series XI (continued from previous page)

	Δt, hr.	x, c/m.	$x/x_\infty = F$	$-\log(1-F)/\Delta t$, $hr^{-1} \times 10^1$.
Run 2	1.5	300 ± 8	0.219	0.71
	3.0	707 ± 8	0.516	1.05
	4.5	937 ± 10	0.696	1.15
	6.0	1058 ± 10	0.772	1.07
	∞ (27 hr.)	1370 ± 13	mean:	1.09 ± .04

Series XX $\sum(H_3PO_2) = 0.600$, $\sum(H_2Ox) = 0.216$, $(H^+) = 0.218$, $(H_3PO_2) = 0.439$.

	Δt, min.	x, c/m.	$x/x_\infty = F$	$-\log(1-F)/\Delta t$, $min^{-1} \times 10^3$.
Run 1	30	445 ± 10	0.281	4.76
	60	810 ± 15	0.512	5.19
	90	1060 ± 15	0.671	5.36
	120	1200 ± 15	0.760	5.17
	∞ (24 hr.)	1580 ± 15	mean:	5.12 ± .18
Run 2	30	455 ± 10	0.288	4.93
	60	790 ± 15	0.500	5.02
	90	1025 ± 14	0.649	5.07
	120	1210 ± 16	0.765	5.23
	∞ (24 hr.)	1580 ± 20	mean:	5.06 ± .09

Table 3 (continued)

Series XXIV $\sum(H_3PO_2) = 0.660$, $(H^+) = 0.218$, $(H_3PO_2) = 0.501$, $T = 35.30^\circ$.

	Δt, min.	x, c/m.	$x/x_{\infty} = F$		$-\log(1-F)/\Delta t$, $\text{min}^{-1} \times 10^2$.
Run 1	12	370 ± 4	0.238		0.98*
	24	690 ± 10	0.445		1.06
	36	900 ± 10	0.580		1.05
	48	1050 ± 15	0.678		1.03
	∞ (24 hr.)	1550 ± 10		mean:	1.05 ± .01
Run 2	12	370 ± 2	0.238		0.98*
	24	680 ± 35	0.439		1.05
	36	910 ± 10	0.587		1.07
	48	1080 ± 20	0.696		1.08
	∞ (24 hr.)	1550 ± 30**		mean:	1.06 ± .01

---

* These values were rejected, both by the Q test (19), and because the time error was large and tended to be high at the first sample, due to the short reaction times. These first numbers were systematically low in both Series XXIV and XXV, and were rejected in both Series.

** This value of x_{∞} was not obtained in this run. A value of 1450 ± 70 was obtained, and was rejected as being a bad sample, since it showed poor counting characteristics and imparted pronounced curvature to the $-\log(1-F)$ vs. t plot. The value used here is a mean of the values obtained at 35.30°. See Table 13.

Table 4

Results of Experiments in Group One.

$\mu = (H^+) = (H_2PO_2^-)$. $\sum(H_3PO_2) = \sum'(H_3PO_2)$. T = 27.23°.

Series	$\sum(H_3PO_2)$	(H_3PO_2)	(H^+)	slope, hr^{-1}*	R, moles per liter hour
I	0.490	0.329	0.161	0.163	0.368
II	0.572	0.395	0.177	0.199	0.520
III	0.700	0.500	0.199	0.256	0.815
IV	0.795	0.580	0.215	0.284	1.03
V	0.891	0.661	0.230	0.337	1.37
VI	0.997	0.751	0.246	0.355	1.60
VII	0.300	0.182	0.118	0.091	0.125

---

* Here, and in succeeding tables, "slope" refers to the mean of the slopes of the -log(1-F) vs. t plots for each run. R is calculated from this mean slope.

Table 5

Test of Possible Orders in Group One.

Let $(H^+) = A$, $\sum(H_3PO_2) = \sum'(H_3PO_2) = B$, $(H_3PO_2) = C$.

Series	R/BC	R/B^2	R/AB	R/C^2	R/A^2	R/AC	R/C	R/B	R/A
VII	2.29	1.39	3.52	3.76	8.92	5.79	.686	.416	1.05
I	2.28	1.53	4.66	3.40	14.2	6.94	1.12	.750	2.28
II	2.30	1.59	5.14	3.33	16.6	7.43	1.32	.910	2.94
III	2.32	1.66	5.83	3.25	20.5	8.15	1.63	1.16	4.08
IV	2.23	1.63	6.01	3.05	22.2	8.22	1.77	1.29	4.78
V	2.32	1.72	6.66	3.12	25.8	8.97	2.07	1.53	5.94
VI	2.13	1.61	6.52	2.80	27.5	8.65	2.13	1.60	6.50

Series	R/A^2C	R/C^2A	R/A^2B	R/B^2A	R/ABC	R/C^2B	R/B^2C
VII	48.4	31.8	29.7	11.7	19.3	12.6	7.62
I	43.2	21.1	29.0	9.52	14.2	6.93	4.67
II	42.0	18.6	29.0	8.98	13.0	5.82	4.03
III	40.8	16.3	28.3	8.35	11.6	4.64	3.32
IV	38.2	14.2	27.9	7.56	10.4	3.84	2.80
V	39.0	13.6	28.9	7.47	10.1	3.51	2.60
VI	36.6	11.4	27.5	6.53	8.67	2.81	2.14

Table 6

Results of Experiments in Group Two. $\mu = 0.218$, $T = 27.23^{\circ}$.

Series	$\sum(H_3PO_2)$	$\sum'(H_3PO_2)$	(H_3PO_2)	(H^+)	slope, hr^{-1}	R, moles per liter hour.
VIII	0.289	0.0971	0.0712	0.0259	0.0116	0.0153
IX	0.356	0.194	0.141	0.0528	0.0355	0.0579
X	0.434	0.300	0.219	0.0809	0.0708	0.140
XI	0.508	0.396	0.290	0.106	0.112	0.258
XII	0.593	0.513	0.376	0.137	0.152	0.410

Table 7

Test of Possible Orders in Group Two.

Let $(H^+) = A$, $\sum'(H_3PO_2) = B$, $\sum(H_3PO_2) = C$, $(H_3PO_2) = D$.

Series	R/BD	R/B^2	R/AB	R/D^2	R/A^2	R/AD	R/D	R/B	R/A
VIII	2.22	1.63	6.10	3.02	22.0	8.31	.215	.158	.592
IX	2.11	1.54	5.65	2.90	20.8	7.75	.409	.298	1.09
X	2.13	1.56	5.78	2.92	21.4	7.91	.640	.467	1.73
XI	2.22	1.63	6.09	3.05	22.8	8.39	.882	.646	2.42
XII	2.12	1.56	5.82	2.90	21.7	7.95	1.09	.798	2.98

Series	R/A^2D	R/D^2A	R/A^2B	R/B^2A	R/ABD	R/D^2B	R/B^2D	R/C^2	R/AC
VIII	309	117	226	62.7	85.6	31.1	22.8	.184	2.05
IX	147	55	107	29.2	56.5	15.0	10.9	.693	3.08
X	97.7	36.1	71.3	19.3	26.4	9.73	7.12	.745	4.00
XI	78.5	28.7	57.5	15.4	21.0	7.70	5.63	.992	4.75
XII	57.9	21.2	42.4	11.3	15.5	5.65	4.15	1.16	5.02

Series	R/C	R/A^2C	R/C^2A	R/CD	R/ACD	R/D^2C	R/C^2D	R/BC
VIII	.053	75.4	7.1	.745	28.7	10.5	2.58	.546
IX	.163	64.3	8.68	1.15	21.8	8.06	3.24	.838
X	.323	49.2	9.25	1.47	18.2	6.73	3.41	1.07
XI	.504	44.9	9.36	1.74	16.4	6.00	3.42	1.27
XII	.690	36.6	8.48	1.84	13.4	4.90	3.09	1.35

Table 8

Results of Experiments in Group Three. $\mu = (H^+)$, $T = 27.23^\circ$.

Series	$\sum(H_3PO_2)$	$\sum'(H_3PO_2)$	(H_3PO_2)	(H^+)	slope, hr^{-1}	R, moles per liter hour
XIII	0.250	0.397	0.182	0.215	0.150	0.172
XIV	0.350	0.468	0.255	0.213	0.171	0.274
XV	0.450	0.547	0.329	0.218	0.201	0.413
XVI	0.554	0.624	0.406	0.218	0.230	0.583

Table 9

Test of Possible Orders in Group Three.

Let $(H^+) = A$, $\sum'(H_3PO_2) = B$, $\sum(H_3PO_2) = C$, $(H_3PO_2) = D$.

Series	R/BD	R/B^2	R/AB	R/D^2	R/A^2	R/AD
XIII	2.37	1.09	2.01	5.17	3.72	4.38
XIV	2.30	1.25	2.75	4.21	6.04	5.05
XV	2.30	1.38	3.46	3.82	8.80	5.50
XVI	2.29	1.50	4.28	3.53	12.3	6.55

Table 10

Results of Runs in Group Four (added H_2SO_4). μ = 0.218, T = 27.23°.

Series	$\sum(H_3PO_2)$	$\sum(H_2SO_4)$*	(H^+)	(H_3PO_2)	(HSO_4^-)	slope, hr^{-1}	R, moles per liter hour	k_3
XVII	0.256	0.104	0.198	0.182	0.0843	.20 ± .03**	0.23	4.4 ± 2
XVIII	0.3545	0.0855	0.202	0.254	0.0695	.19 ± .02	0.31	2.7 ± .9
XIX	0.512	0.0554	0.208	0.370	0.0453	.23 ± .01	0.54	3.2 ± .6

* $\sum(H_2SO_4) = (HSO_4^-) + (SO_4^{--})$.

** Average deviations given here and in the next Table indicate the reproducibility of the slope values in a Series.

Table 11

Results of Runs in Group Five (added H_2Ox). = 0.218, T = 27.23°.

Series	$\sum(H_3PO_2)$	$\sum(H_2Ox)$*	(H^+)	(H_3PO_2)	(H_2Ox)	slope, hr^{-1}	R, moles per liter hour	k_4
XX	0.600	0.216	0.218	0.439	0.159	.30 ± .02	0.83	2.5 ± .7**
XXI	0.700	0.115	0.218	0.512	0.0844	.32 ± .04	1.03	4.1 ± 1

* $\sum(H_2Ox) = (H_2Ox) + (HOx^-)$.

** For several reasons, this value of k_4 was weighted twice as heavily as the next in obtaining the final value given on page 42.

Table 12

Results of Experiments at 35.30°. $\mu = (H^+) = 0.218$.

Series	$\sum(H_3PO_2)$	(H_3PO_2)	(H^+)	slope, hr^{-1}	R, moles per liter hour
XXII	0.400	0.304	0.218	0.482	0.883
XXIII	0.530	0.403	0.218	0.564	1.36
XXIV	0.660	0.502	0.218	0.632	1.90
XXV	0.800	0.608	0.218	0.720	2.62

Values of Rate Constants at 35.30° Determined by the Arithmetic Method

Series Pair Used	k_1	k_2
22 and 23	6.7	4.8
22 and 24	7.2	4.4
22 and 25	6.9	4.6
23 and 24	7.8	4.2
23 and 25	7.2	4.5
24 and 25	6.1	4.9

Table 13

x_∞ Values in Group Three

Series	x_∞ in Run 1*	x_∞ in Run 2*	mean**
XIV	1530 ± 15	1480 ± 15	1505 ± 25
XV	1560 ± 15	1520 ± 15	1540 ± 20
XVI	1520 ± 10	1540 ± 15	1530 ± 10
XXII	1550 ± 20	1580 ± 20	1565 ± 15
XXIII	1550 ± 20	1400 ± 100****	1550
XIV	1550 ± 10	1450 ± 70****	1550
XXV	1530 ± 10	1520 ± 20	1525 ± 5

Special Experiments to Determine x_∞ at 35.30°.

Experiment	x_∞*
1	1535 ± 10
2	1600 ± 5
3	1520 ± 10

Overall average of all these x_∞ values:*** 1540 ± 20.

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* Quoted limits of error represent the average deviation of four countings of the same sample.

** Quoted limits of error represent the average deviation of the two values from the mean.

*** Quoted limits of error represent the average deviation of all the individual mean values from the overall mean value.

**** These values were rejected as bad samples, and were not used in the calculations. They showed poor counting characteristics, and when used for calculation, imparted pronounced curvature to the -log(1-F) vs. t plot. They evidently did not represent the true value of x_∞ in these runs.

Table 14

Results of Experiments on Exchange in Basic Solution. $T \sim 20^{\circ}$

Run[*]	(TlH_2PO_2)	(OH^-)	Contact time	Apparent % Exchange
I	0.27	0.25	20 hours	15%
			44 hours	20%
			104 hours	60%[**]
II	0.75	0.8	24 hours	45%[**]
			48 hours	80%[**]

[*] All samples were washed at least twice with inactive distilled water.

[**] Decomposition of $H_2PO_2^-$ obvious from the nature of the evaporated sample. See text.

Table 15

Thermal Stability Experiments on Crystalline Thallous Hypophosphite

Series	Initial weight of sample, g.	Net weight change in mg. after 24 hr. heating at the indicated temperature:								
		50°	65°	75°	80°	90° - 48 hr. heating periods				
I	0.843	-0.2	-0.4	+0.2	+2.7	+1.8[a]	+2.4	+2.4	+3.4[b]	+5.0
		Net weight change in mg. after heating[c] at the indicated temperature:								
		80°	89°	95°	95°					
IA	0.847	-0.2	-0.2	-0.2	-1.3					
		Net weight change in mg. after heating[d] at 95° for the indicated time intervals:								
		3 hours	1 hour	2 hours	3 hours	3 hours				
II	0.993	-2.0	-0.1	-0.1	-0.2	-0.1				
		Net weight change in mg. after 3 hours heating at the indicated temperature:								
		95°	95°	95°	100°	100°				
III	0.672	-0.6	-0.2	-0.2	-0.5	-0.8				

(continued on next page)

Table 15 (continued)

Series	Initial weight of sample, g.	Net weight change in mg. after heating as follows:			
		95° for 3 hr.	95° for 3 hr.	100° for 2 hr.	100° for 2 hr.
IV[e]	1.137	-0.8	-0.2	-0.3	-0.2

a. Partial melting began here.

b. Completely liquefied here.

c. Series IA was run as follows: The sample was first evacuated to a pressure of 10^{-5} mm. Hg. The system was then thoroughly flushed out with argon, re-evacuated, the sample closed off from the pump, and heated. At the end of the heating period, the system was re-evacuated, the heater removed, and the sample allowed to cool while connected to the pump.

d. In this Series, salt which had been neither ground up nor vacuum dried before putting it in the vacuum line was used.

e. In this Series, salt which had been directly crystallized from water alone was used; in all the others, salt which had been crystallized from isopropyl alcohol was used.

Table 16

Reaction of H_3PO_2 with Persulfate T ~ 20°.

Run	$\sum(H_3PO_2)$	$(HClO_4)$	$((NH_4)_2S_2O_8)$	$T_{\frac{1}{2}}$, hr.
I	0.23	2.5	1.02	5
II	0.09	2.35	1.32	12
III	0.23	2.5	1.02	4

Table 17

Reaction of H_3PO_2 with Dichromate T ~ 80°.

Run	Initial $\sum(H_3PO_2) + \sum(H_3PO_3)$	Initial $(Cr_2O_7^{--})$	Time reacted, hr.	Mole percent P(I) + P(III) left unoxidized
I	0.316	0.477	3	0.15%
II	0.316	0.477	2	0.00%
III	0.316	0.477	1	2.0%
IV	0.523	0.398	2	2.5%
V	0.523	0.398	3	1.2%

Table 18

Results of the Second Set of Dilution Curve Experiments.

Initial (NH_4Cl) = 2.86 g./10 ml.

Sample no.	NT_4Cl activity, c/m x 10^{-2}	HTO activity, curies per gram x 10^{6}	S, gram-counts per curie minutes x 10^{-7}
1	3.80	3.97	9.55
2	5.90	5.95	9.90
3	7.70	7.94	9.70
4	11.7	11.9	9.85
5	15.8	15.9	9.95
6	19.2	19.8	9.70
7	23.2	23.8	9.74
8	30.6	31.8	9.65
		mean:	9.75 ±.10

Table 19

Results of Second and Third Sets of Dilution Curve Experiments

Sample No.	Activity of NT_4Cl, c/m x 10^{-2}		Activity of HTO, curies per gram x 10^{6}	S, gram-counts per curie-minutes x 10^{-7}	
	Second Set	Third Set		Second Set	Third Set
1	3.80	4.13	3.97	9.55	10.4
2	5.90	6.23	5.95	9.90	10.5
3	7.70	8.00	7.94	9.70	10.1
4	11.7	12.0	11.9	9.85	10.1
5	15.8	17.2	15.9	9.95	10.8
6	19.2	20.3	19.8	9.70	10.3
7	23.2	25.1	23.8	9.74	10.4
8.	30.6	32.0	31.8	9.65	10.1
9	----	40.2	39.7	----	10.1
				mean: 9.75	mean: 10.3 ± .15

Mean value of S for initial (NH_4Cl) = 2.86 g./10 ml. HTO:

(10.0 ± 0.28) x 10^{7} gram-counts per curie minutes.

Table 20

Results of Dilution Curve Experiments at Lower (NH_4Cl). (NH_4Cl) = 1.5 g./10 ml.

Sample No.	Activity of NT_4Cl, c/m x 10^{-2}		Activity of HTO, curies per gram x 10^6	S, gram-counts per curie minutes x 10^{-7}.	
	First Run	Second Run		First Run	Second Run
1	5.25	5.20	3.97	13.2	13.1
2	11.3	10.7	7.94	14.2*	13.5
3	15.5	----	11.9	13.0	----
4	20.0	21.1	15.9	12.6	13.3
5	27.0	----	19.8	13.6	----
6	31.8	30.2	23.8	13.4	12.7
			mean:	13.2 ± .3	mean: 13.2 ± .2

Mean value of S for initial (NH_4Cl) = 1.5 g./10 ml. HTO:

(13.2 ± 0.2) x 10^7 gram-counts per curie minutes.

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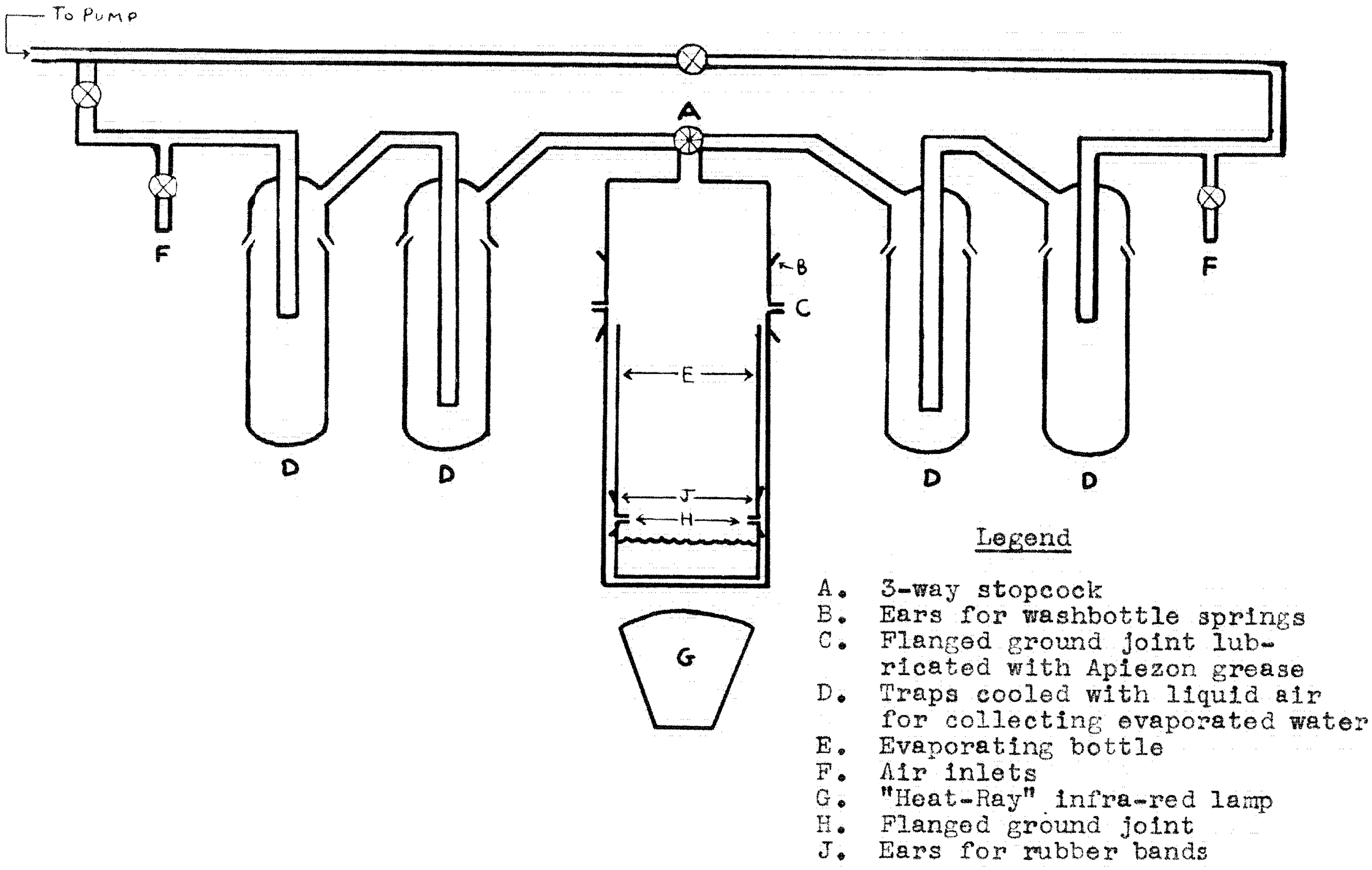
* This value was rejected before taking the average.

Figure 1.

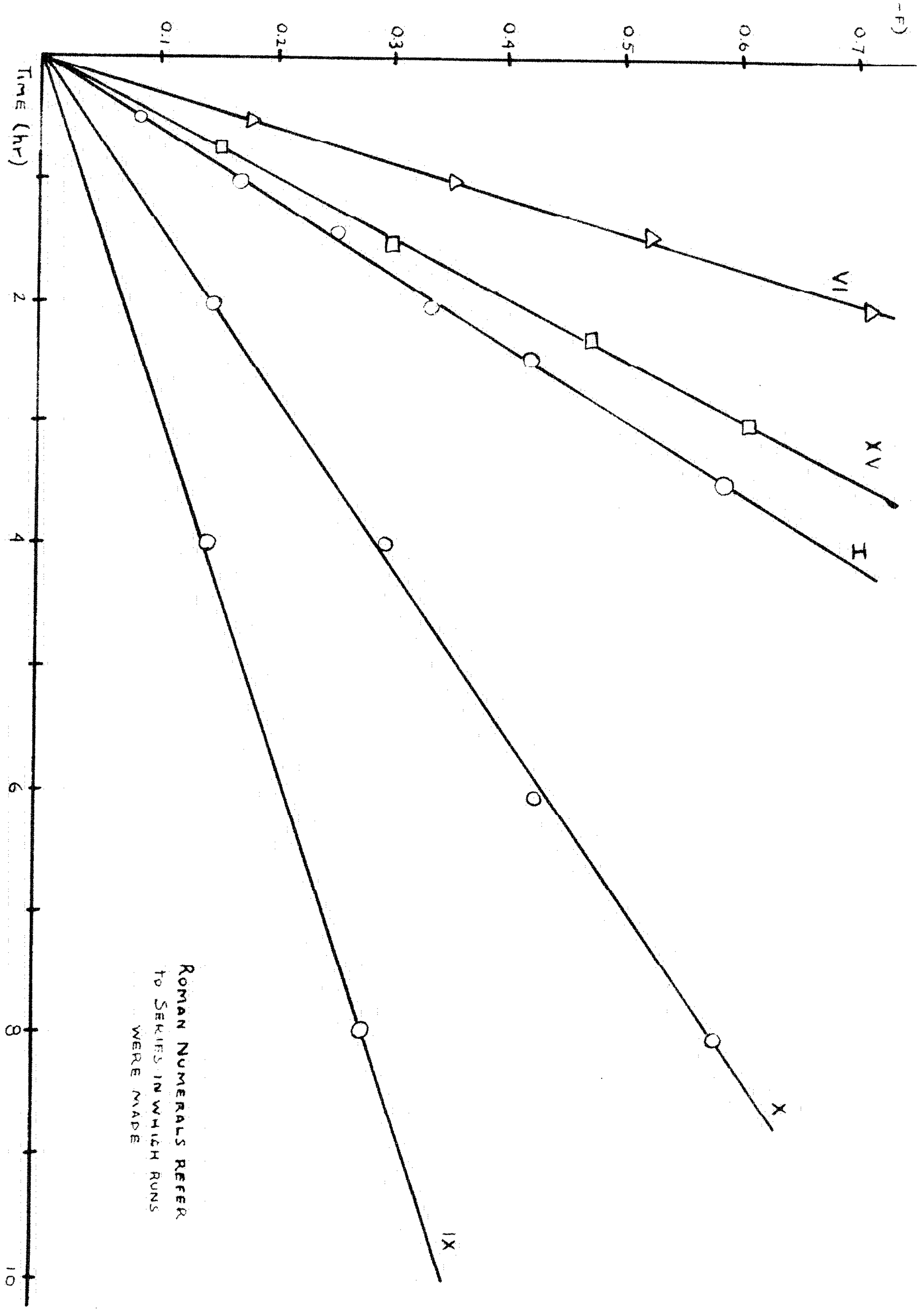
Apparatus for the vacuum evaporation of thallous hypophosphite solutions.



Legend

A. 3-way stopcock
B. Ears for washbottle springs
C. Flanged ground joint lubricated with Apiezon grease
D. Traps cooled with liquid air for collecting evaporated water
E. Evaporating bottle
F. Air inlets
G. "Heat-Ray" infra-red lamp
H. Flanged ground joint
J. Ears for rubber bands

Figure 2. Some -log(1-F) vs t plots for runs at 27.23°.



ROMAN NUMERALS REFER TO SERIES IN WHICH RUNS WERE MADE

Figure 3. Log R vs log (H_3PO_2) plot for Series VIII - XII, IV. T = 27.23°.

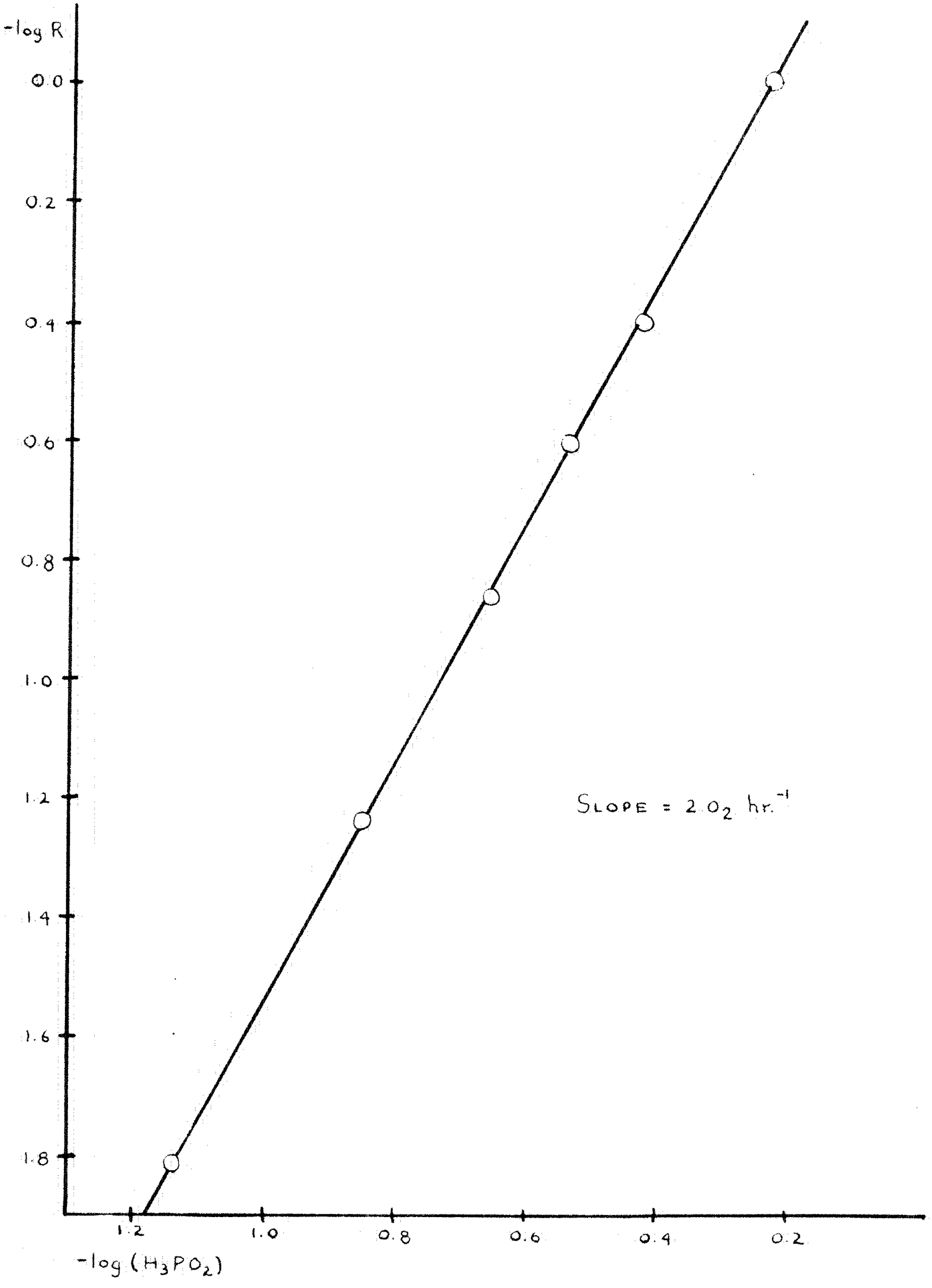


Figure 4. $R/(H_3PO_2)$ vs (H_3PO_2) plot for Series VIII - XII, IV. T = 27.23°.

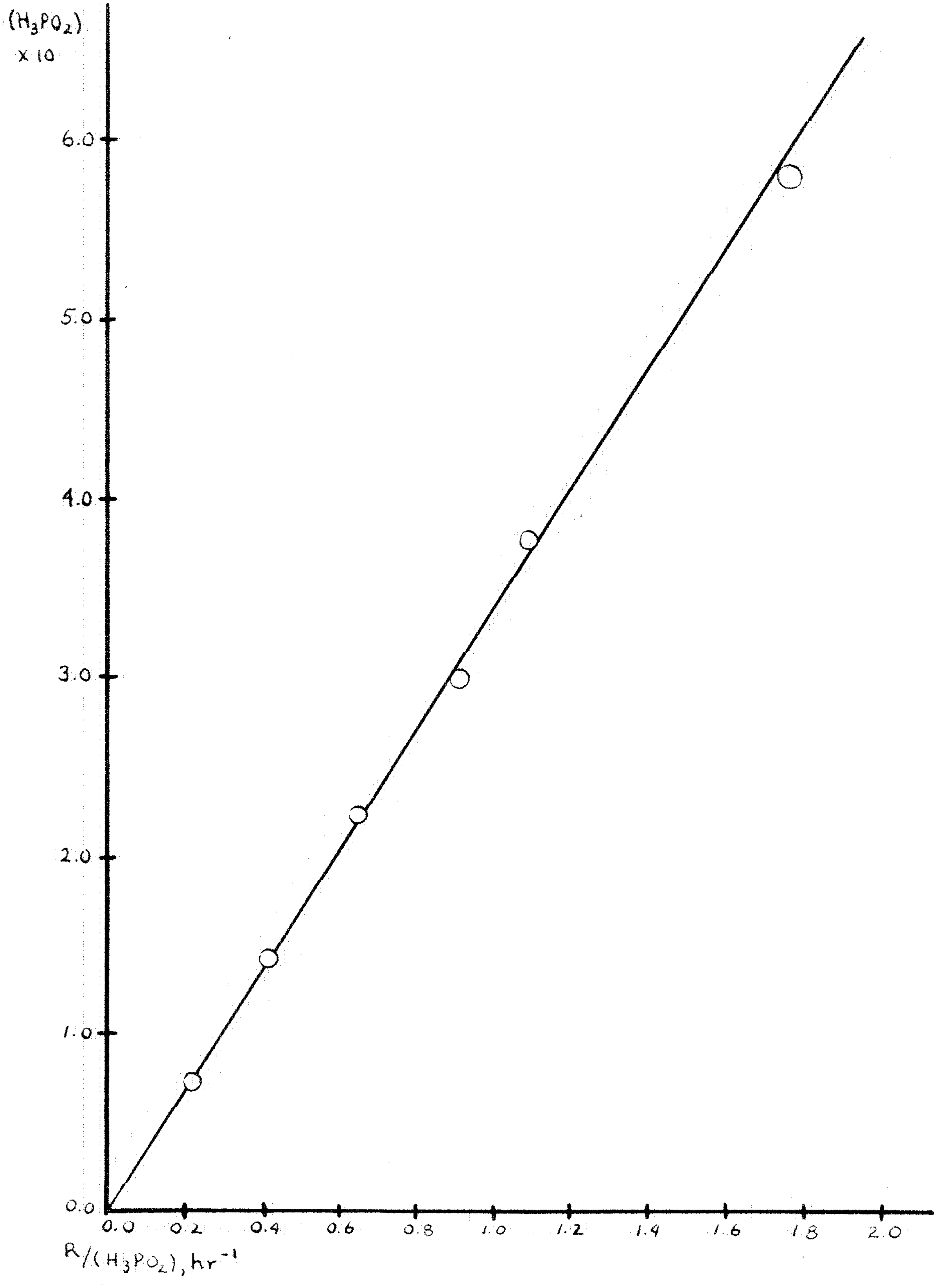


Figure 5. $R/(H_3PO_2)$ vs (H_3PO_2) plot for Series XIII - XVI, IV. T = 27.23°.

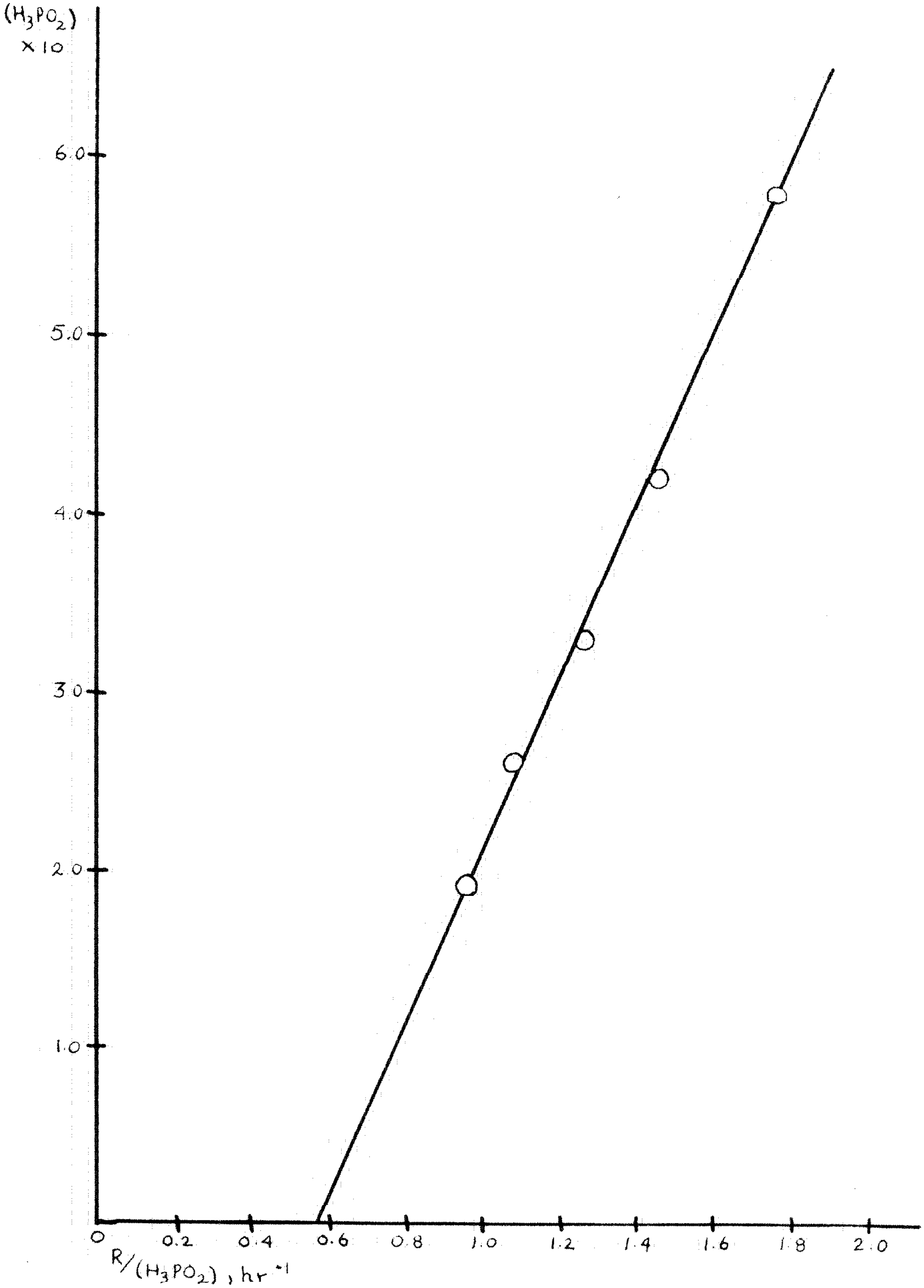


Figure 6. Some -log(1-F) vs t plots for H_2Ox and HSO_4^- runs.

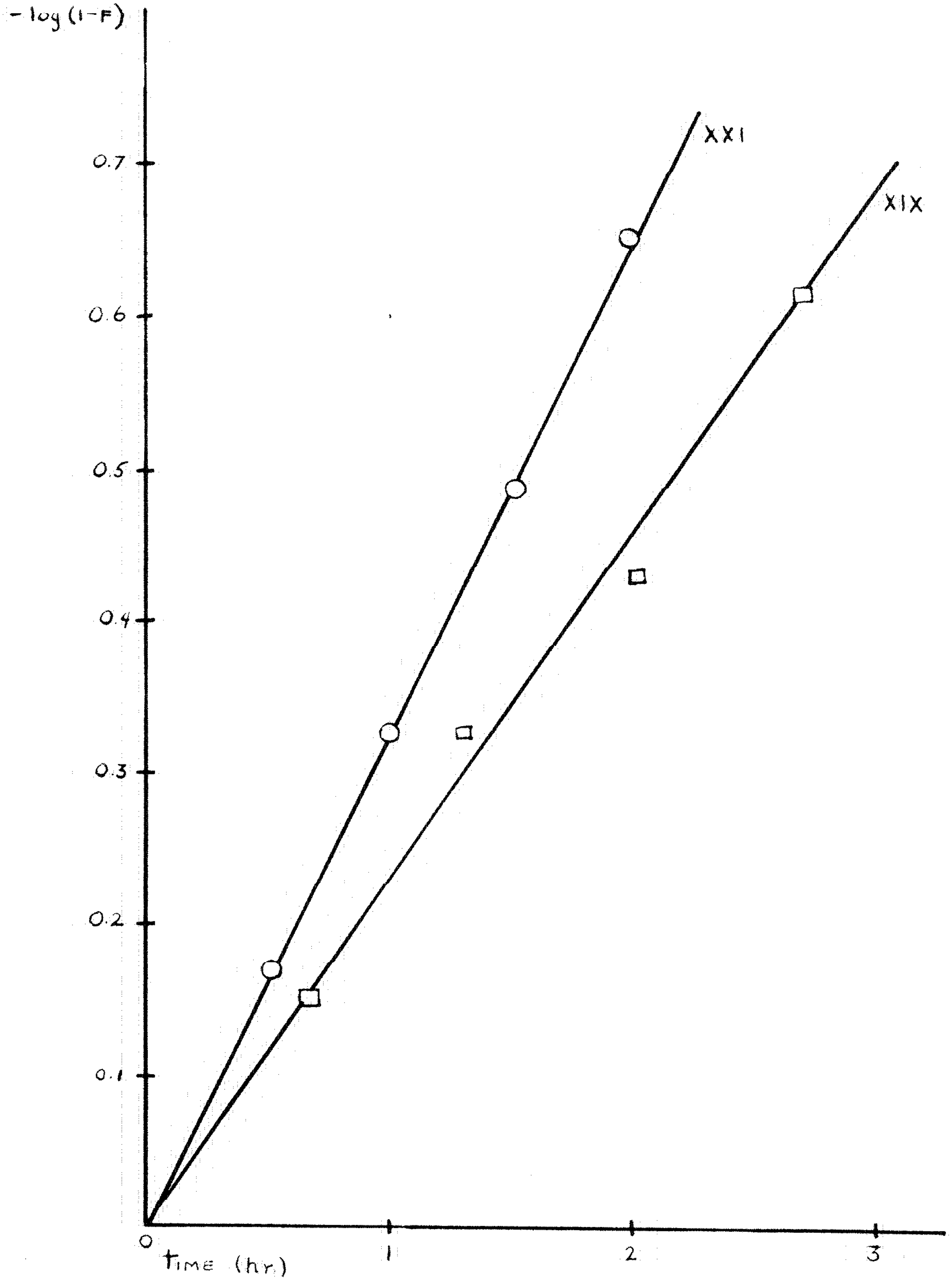


Figure 7. Typical -log(1-F) vs t plots for runs at 35.30°.

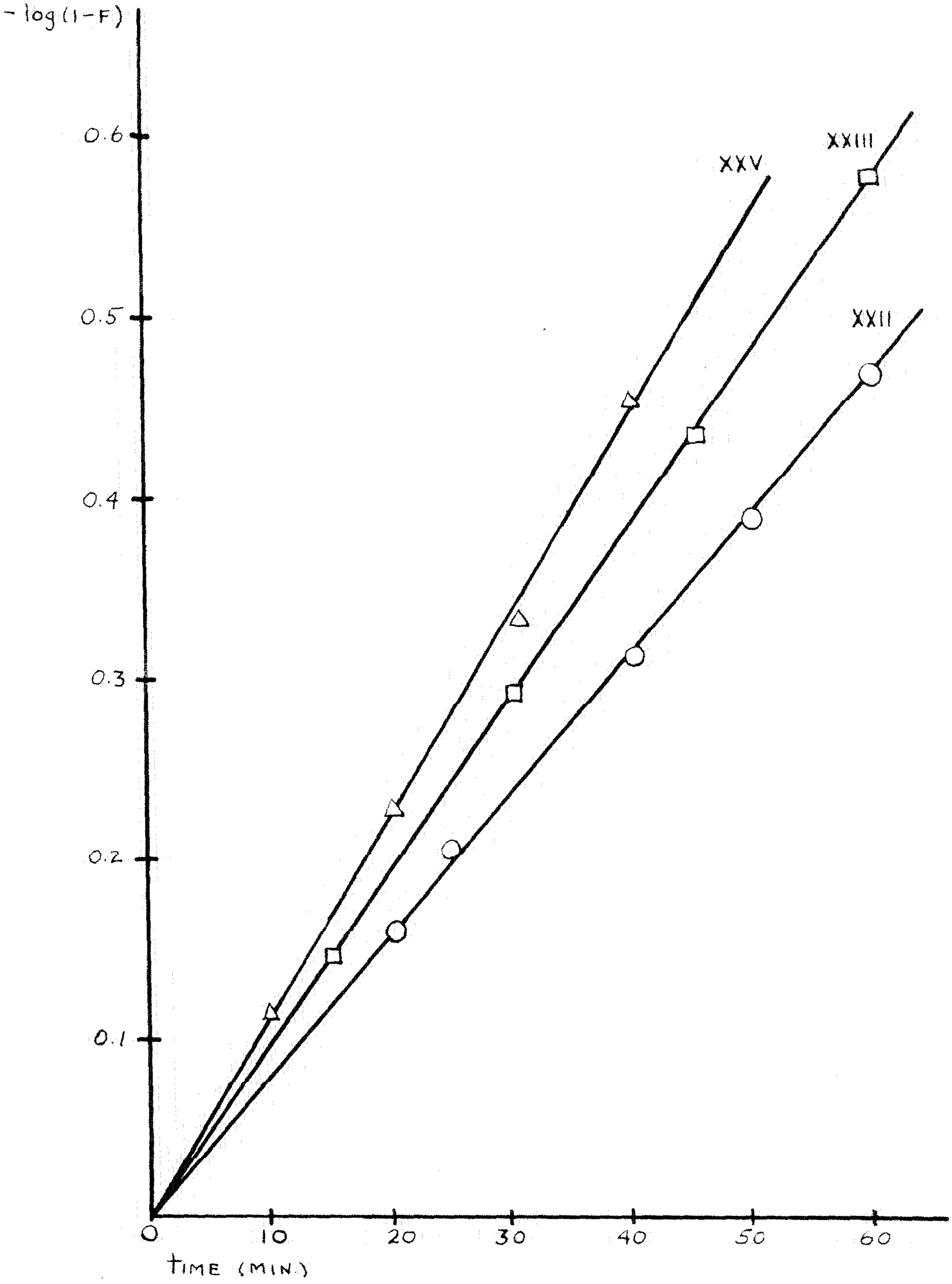


Figure 8. $R/(H_3PO_2)$ vs (H_3PO_2) plot for Series XXII - XXV.
$T = 35.30°$

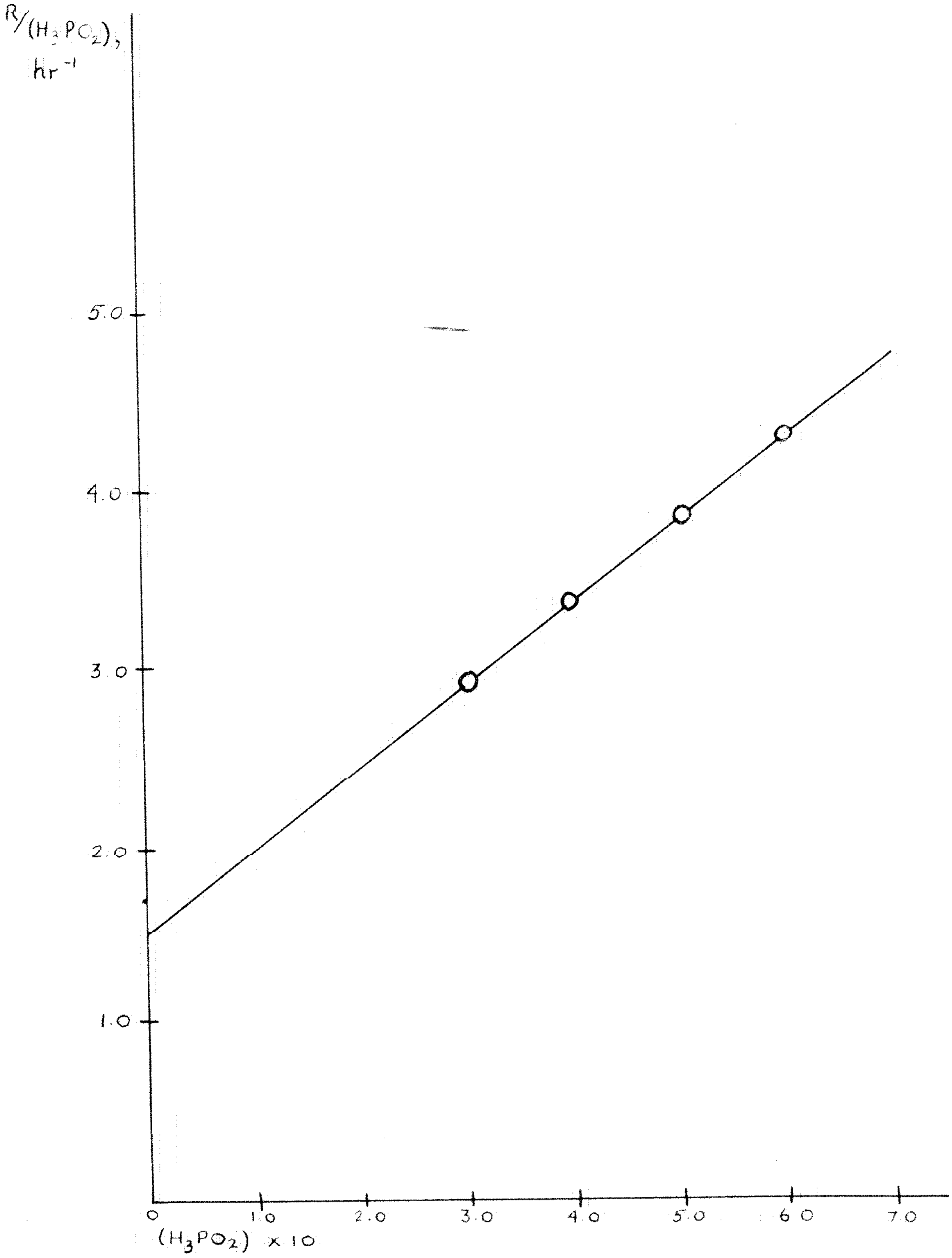
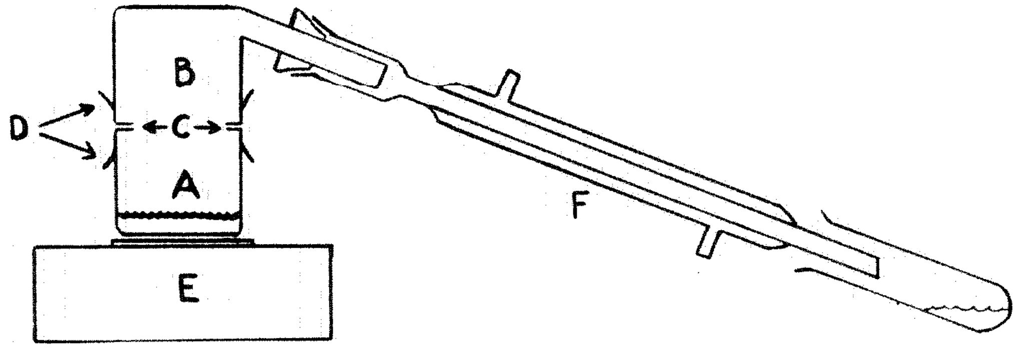


Figure 9

Apparatus for distilling off the HTO from HTO - NT_4Cl solutions.



Legend

A. Bottom section of still

B. Top section of still

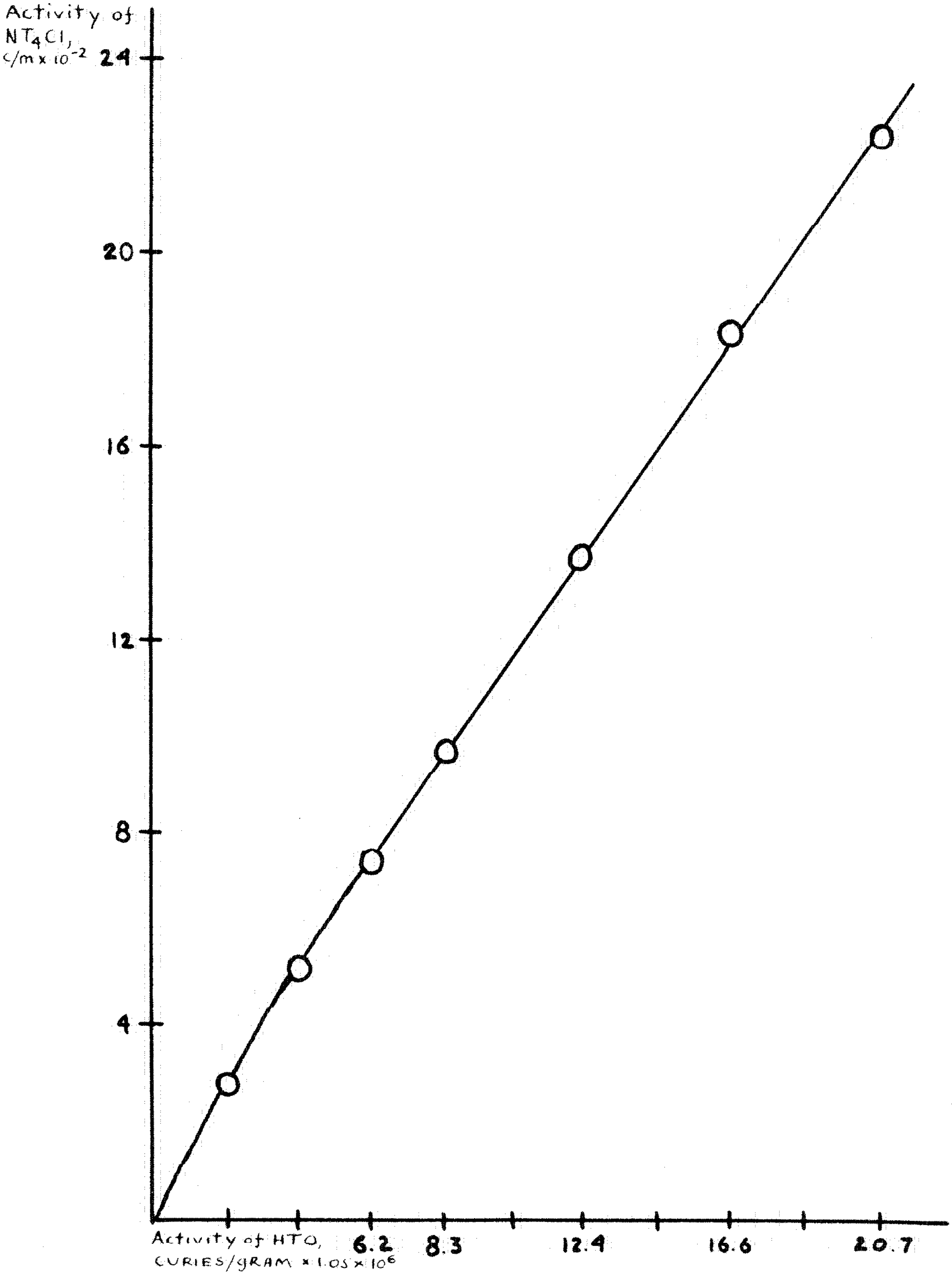
C. Flanged ground joint

D. Ears for washbottle springs

E. Hot plate

F. Condenser

Figure 10. Results of first set of dilution curve experiments



igure 11. Results of second set of dilution curve experiments.

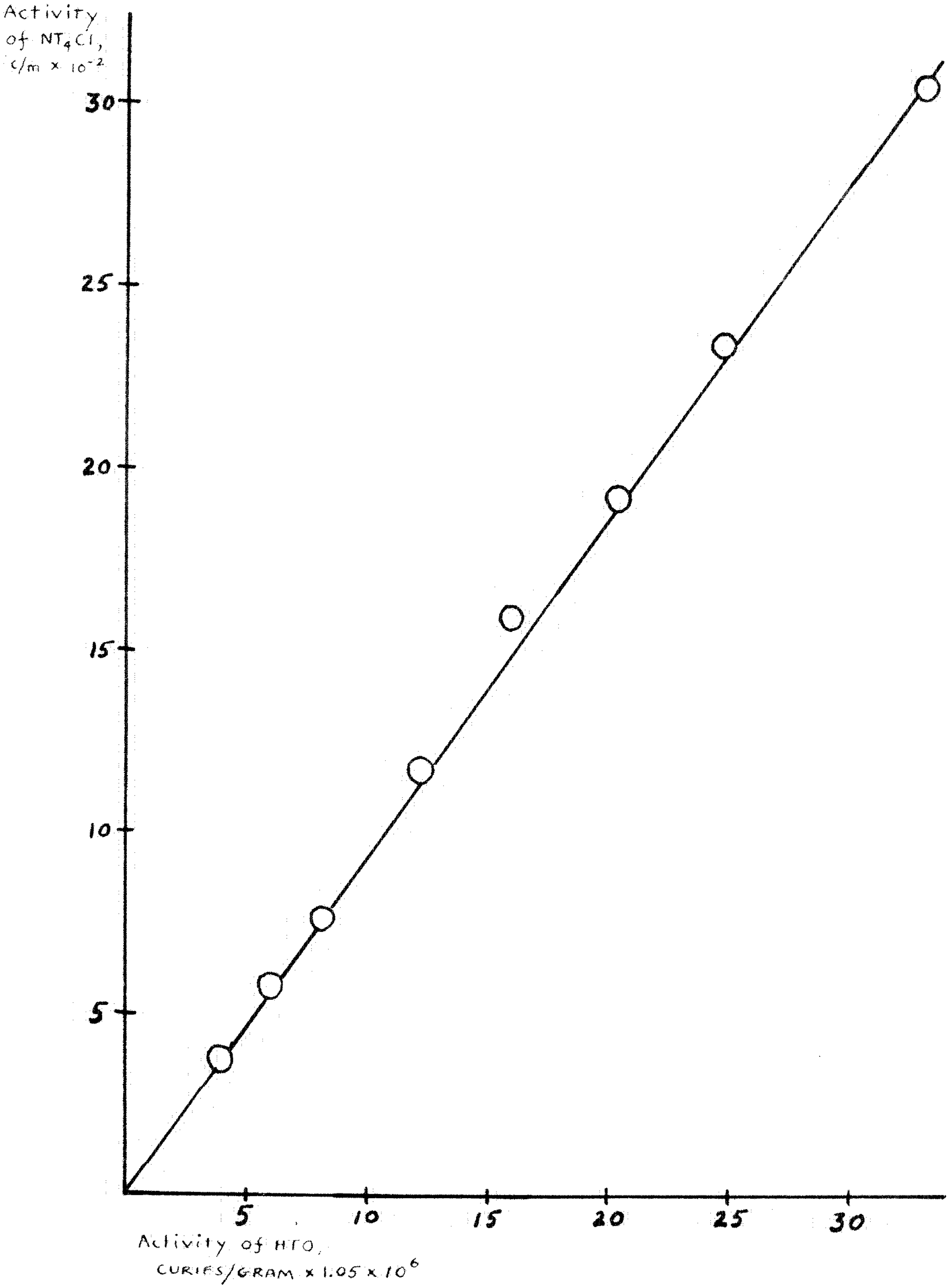
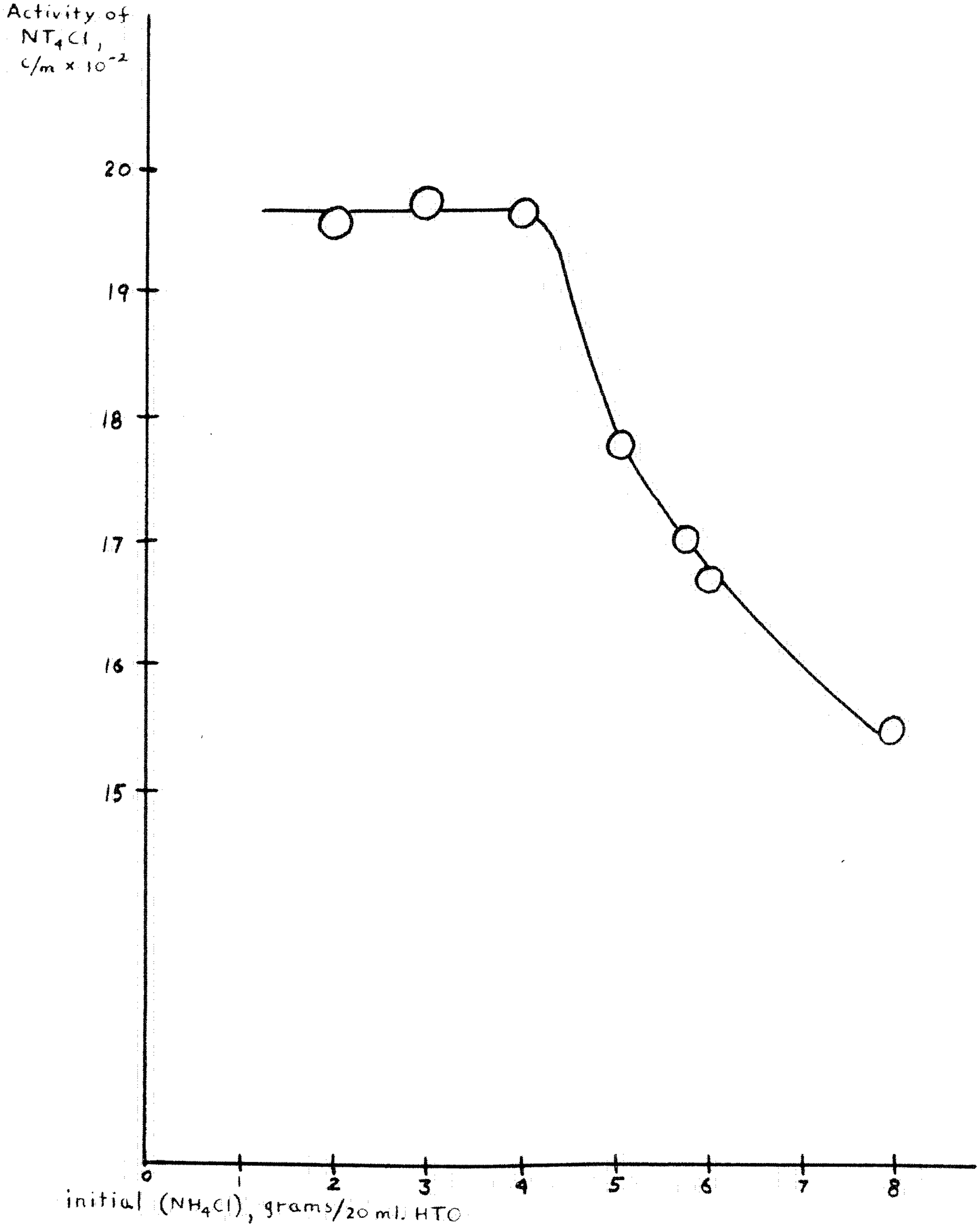


Figure 12. The effect of varying the initial (NH_4Cl).



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Propositions

1. The accurate dating of archeological and geological specimens by the carbon 14 technique is made very difficult by the low specific activities of the specimens (1). A new method for the assay of low activity C^{14} samples, which should rival the existing methods in accuracy and convenience, is suggested.

2. Although the exchange of radiobromine between sodium bromide and propyl bromide in acetone has been shown (2) to be a second order reaction, the S_N1 mechanism proposed for this reaction would lead to first order kinetics. A mechanism which satisfies the rate law is proposed.

3. A measurement of the Hall coefficient of solutions of the alkali metals in liquid ammonia might provide interesting information about the physical nature of these solutions. A rough calculation shows that the magnitude of the effect should be small but measurable.

4. A structure for difluosilicic acid, $H_2Si_2F_{10}$, is proposed. The proposed structure facilitates the explanation of some aspects of the chemical behavior of high silica fluosilicic acid solutions (3) and suggests some lines of attack for future investigation.

5. Although glycol-boric acid esters have been used for years by carbohydrate chemists (4), several interesting

features of these compounds remain unexplored. In particular, a) the esterification reaction should have rather interesting kinetics, b) analogous compounds might be useful in verifying the structure proposed in this thesis for the active form of H_3PO_2, and c) the potential value of these compounds in analytical chemistry should be investigated.

6. If the exponential absorption law for beta particles is valid, a simple derivation shows that all solid materials, rendered radioactive to the same specific activity with a given beta-emitting isotope, should show approximately the same activity to a given counting setup, if the thickness of the material is equivalent to infinite thickness; furthermore, this observed activity should be independent of the density of the material and depend only on the mass absorption coefficient. This result should have useful experimental consequences.

7. A new method for carrying out redox titrations, based on the use of the recently developed electron exchange resins (5), is proposed.

8. An investigation of complex formation in the thermodynamically unstable systems Fe(III) - H_3PO_2 and Sn(IV) - H_3PO_2 is suggested. Much of the scanty information which exists (6) on these systems is internally contradictory; furthermore, the fact that these are the only known cases

of metal ion - hypophosphite complexing would lend added interest to such an investigation.

9. Although Sanderson's empirical rule (7) which relates non-polar covalent bond stability to the covalent radius difference may be valid, his criterion of stability is uncertain and poorly defined. A better test of this rule would be provided by bond dissociation energies or average bond energies (8).

10. The mechanism which Maybury and Koski (9) have proposed to explain their data on the kinetics of the gas phase exchange of deuterium between diborane and hydrogen does not fit their rate law. An alternative mechanism, derived from the kinetics of diborane pyrolysis (10), is proposed. This alternative mechanism fits the rate law, showing that Maybury's work, if interpreted correctly, confirms the mechanism suggested for diborane pyrolysis. Further experiments on this system are proposed.

11. The interesting and unusual electrical nature of alkali metal-liquid ammonia solutions suggests that other odd electron compounds (e.g., organic free radicals) might show the same sort of behavior in appropriate solvents. Some possible lines of approach to this problem are suggested.

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