The pH of the solutions in Table I does not change when the tetragermanate is formed. As can be seen from equation 3 the concentration of $(H_3GeO_4)^-$ would be small at this pH. Removal of $(HGe_7O_{16})^{3-}$ from the equilibrium then would produce little shift to the right and a corresponding rise in pH. Also the small amount of GeO_2 produced according to equation 1 would be of much greater importance.

There was no evidence of $(Ge_4O_9)^{2-}$ ions in solution. The precipitate from the run solutions contained a very small amount of birefringent material which could not be the acid germanate. Infrared and X-ray analyses indicated another compound present in small amount; however, it was unidentifiable with known patterns.

Since both the hydrogen germanates and tetragermanates prepared showed no noticeable tendency to absorb moisture from the air it is presumed that the hygroscopic product described by Nowotny and Wittmann[5] contained residual metagermanate.

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YELLOW SPRINGS, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CLARKSON COLLEGE OF TECHNOLOGY]

The Molecular Weight of the Phosphotungstic Acids by Light Scattering[1]

BY MILTON KERKER, DOROTHY LEE AND ADAM CHOU

RECEIVED SEPTEMBER 3, 1957

The light scattering of 12-phosphotungstic and 9-phosphotungstic acids in a number of organic solvents and water has been determined. In the organic solvents, the molecular weight calculated for the former corresponds to the monomer, $H_3PW_{12}O_{40}$, while that of the latter corresponds to the dimer, $H_6P_2W_{18}O_{62}$. This is consistent with crystal structure studies by X-rays. The usual treatment is not adequate to interpret the data from aqueous solutions where these acids are strong.

Since the discovery of ammonium phosphomolybdate by Berzelius in 1826, the heteropoly acids and their salts have provided a fruitful testing ground for the theories of structural inorganic chemistry. The bewildering variety of species proposed in the literature and the lack of a critical evaluation of the great amount of experimental work at the turn of the century has necessitated a new look with the aid of modern structural tools.[2]

The best characterized of the phosphotungstic acids are those with empirical formulas $H_3PW_{12}O_{40}$ and $H_3PW_9O_{31}$, 12-phosphotungstic acid and 9-phosphotungstic acid. The complete structure for these in the solid state has been elucidated by Keggin[3] and Dawson.[4] Dawson found that the unit cell of 9-phosphotungstic acid consists of the dimeric ion $P_2W_{18}O_{62}^{-6}$. This agrees with the finding of Souchay[5] who proposed, on the basis of cryoscopy of the sodium salt in sodium sulfate at its transition point, that 9-phosphotungstic acid is the dimer, $H_6P_2W_{18}O_{62}$, whereas 12-phosphotungstic acid is monomeric, $H_3PW_{12}O_{40}$.

Although the structure of these acids in the solid state has been well established, the state of molecular aggregation in solution is hardly known. This knowledge constitutes the starting point for an understanding of the various aggregation, degradation and equilibrium phenomena encountered in solution. It is the purpose of this work to investigate the molecular weight of the 12- and 9-phosphotungstic acids in solution by means of light scattering in order to determine whether these species consist of monomers, dimers or higher polymers.

Experimental

Preparation and Analysis of Compounds. 1. **12-Phosphotungstic Acid.**—The reagent grade chemical, commercially available from J. T. Baker Company, was used. The purity was checked by analysis of P_2O_5 and H_2O content, assuming the difference was WO_3. After conversion to the Na salt by Na_2CO_3 fusion, the usual method of precipitation of phosphate with magnesia reagent and ignition to the pyrophosphate was used. The loss in weight at 600° was assumed to correspond to the water content. The W/P ratio was found to be 11.7 ± 0.1. Considering the errors resulting from possible coprecipitation of WO_3 with the phosphate and the volatilization of P_2O_5 above 250°, the above accuracy was considered satisfactory.

2. **9-Phosphotungstic Acid.**—The method of Souchay[6] which is a modification of that first reported by Wu[7] was used. One hundred g. of Na_2WO_4 was dissolved in 350 ml. of hot water and brought to a boil. One hundred and fifty ml. of 85% H_3PO_4 was added slowly to the boiling solution and the whole mixture was refluxed for 5 hr. or overnight

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(1) Supported in part by U. S. Atomic Energy Commission Contract Number AT(30-1)-1801.

(2) The standard treatises such as J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., London, 1927–1937; J. Newton Friend, "Textbook of Inorganic Chemistry," Charles Griffin and Company, London, 1924–1930; and "Gmelins Handbuch der Anorganische Chemie," Verlag Chemie, Berlin, from 1926, summarize the literature to the early 1930's. The structural problem is stated in modern terms in such textbooks as W. Hückel, "Structural Chemistry of Inorganic Compounds," by Elsevier, New York, N. Y., 1950, p. 179; H. B. Jonassen in Bailar's "Chemistry of the Coördination Compounds," Reinhold Publ. Corp., New York, N. Y., 1956, Chapter 14; and A. F. Wells, "Structural Inorganic Chemistry," Oxford, 1950, p. 348. For present directions in research in this field see the preprints of papers read at the symposium on "Structure and Properties of Heteropoly Anions," at the National Meeting of the A.C.S., Division of Physical and Inorganic Chemistry, Atlantic City, N. J., September 17, 1956.

(3) J. F. Keggin, *Nature*, **131**, 908 (1933); **132**, 351 (1933); *Proc. Roy. Soc.* (*London*), **A144,** 75 (1934); J. W. Illingworth and J. F. Keggin, *J. Chem. Soc.*, 575 (1935); A. J. Bradley and J. W. Illingworth, *Proc. Roy. Soc.* (*London*), **A157**, 113 (1936).

(4) B. Dawson, *Acta Cryst.*, **6**, 113 (1953).

(5) P. Souchay, *Ann. Chim.*, [12] **2**, 203 (1947).

(6) P. Souchay, *Bull. soc. chim.*, 365 (1951).

(7) H. Wu, *J. Biol. Chem.*, **43**, 189 (1920).

whichever was convenient. The ammonium salt was precipitated with 100 g. of NH_4Cl. This salt was then purified by dissolving and reprecipitating with NH_4Cl several times. The free acid was obtained by dissolving the salt in 1:1 HCl and water and then extracting with ether. The ether-water phase remaining after the heavy ether phase was removed was treated with more concentrated HCl and more 9-acid–ether solution was thrown down. The ether solution of the 9-acid was vacuum dried for several days.

Two observations were made during the synthesis which are of interest. Firstly, only solid NH_4Cl will precipitate the ammonium salt of the 9-acid. Even a hot saturated solution of NH_4Cl does not precipitate the ammonium phosphotungstate after cooling overnight unless an NH_4Cl crystal is added, indicating supersaturation.

Secondly, reduction of the tungsten (indicated by the green-blue color) proceeded rather rapidly in the first precipitate, but with successive recrystallizations the compound became progressively more stable. This may indicate that the purer the acid, the less easily reduced. Perhaps also, it may be that the 12-acid (always an impurity in the synthesis of the 9-acid) is the reducible substance. With successive recrystallizations, the 12-acid is separated completely and no reduction occurs.

We were not successful in analyzing the 9-acid directly, but, as previous workers also found, had to analyze the ammonium salt from which the acid was derived. The ratio W/P was found to be 9.02 ± 0.02, using the same technique as for the 12-acid.

Preparation of Solutions.—All solvents were distilled, filtered under nitrogen pressure through a fine fritted glass filter apparatus and stored. Prior to a run the solvent was refiltered into a light scattering cell and its turbidity measured. This solvent was used to make up the solution by pouring directly into a 25-ml. volumetric flask containing a weighed amount of acid. The solution was then filtered directly into the light scattering cell, using the first 5 ml. of filtrate for rinsing. The cell was covered at all times except while emptying the rinse solution.

The ethanol solutions of the 12-phosphotungstic acid tended to undergo photoreduction. In order to avoid this a trace of nitric acid was added. In the case of the aqueous solutions, elimination of dust was the most difficult problem. We found that adding a few crystals of common alum, $KAl(SO_4)_2$, to the solution and then filtering twice eliminated most of the dust. Any effects of the added nitric acid or alum was incorporated in the properties of the solvent.

Optical Measurements.—Light scattering measurements were made with the American Instrument Company light scattering microphotometer, using the 4360 Å. line of the mercury spectrum. The scattering cell was 2.4 × 2.4 × 7.0 cm. The instrument was calibrated with Ludox by the method of Maron and Lou.[8] Maron and Lou[9] have given factors for correcting the turbidity for solvents with refractive index different from water. These factors depend upon the design of the light scattering instrument. Our instrument was the same as theirs and we have used their expression for C_n' which corrects for the spreading of the light rays on leaving the scattering cell. We disagree slightly with their expression for C_v' which corrects for the volume of the solution observed by the phototube and have used equation (1) instead

$$C_{v'} = \frac{[1 + 2r_2/r_3 + 2r_1/n_w(\sqrt{r_3^2 + l^2})]^2 + 1}{[1 + 2r_2/r_3 + 2r_1/n(\sqrt{r_3^2 + l^2})]^2 + 1} \quad (1)$$

The refractive index of water and the solvent for which the correction is to be applied are n_w and n, respectively. The distances r_1, r_2, r_3 and l, shown in Fig. 1, are 1.4, 2.0, 1.5 and 0.28 cm., respectively. The correction factors for the solvents we have used are presented in Table I.

None of the solutions investigated showed any depolarization beyond that exhibited by the solvent itself.

The difference in refractive index between solution and solvent was measured with a Brice–Phoenix Differential Refractometer at 4360 Å. In all cases the differential refractive index remained constant with concentration. The values of the differential refracture index, dn/dc, are listed in Table II.

TABLE I

FACTORS FOR CORRECTING THE TURBIDITY IN NON-AQUEOUS SOLVENTS

	C_n'	C_v'	$C_n'C_v'$
Acetic acid	1.04	1.01	1.05
Allyl alcohol	1.09	1.03	1.13
Ethanol	1.03	1.01	1.04
1-Propanol	1.04	1.03	1.07

TABLE II

VALUES OF n, dn/dc AND H AT 436 mμ

Acid	Solvent	n	dn/dc	$H \times 10^6$
12	Acetic acid	1.372	0.125	4.49
12	Allyl alcohol	1.413	.102	3.18
12	Ethanol	1.365	.112	3.56
12	Water	1.334	.103	2.87
9	Ethanol	1.365	.128	4.62
9	1-Propanol	1.385	.122	4.33
9	Water	1.334	.119	3.82

The solutions of 9-phosphotungstic acid were light yellow so that it was necessary to correct for the attenuation of both incident and scattered radiation due to absorption. Since the loss due to true absorption was large compared to scattering, the absorption coefficient could be obtained by determining the optical density in a Beckman spectrophotometer and the attenuation of the beam in the light scattering cell was calculated from this. The Beer–Lambert law held over the range of concentration and path lengths applicable.

The pH of the various aqueous solutions was adjusted by addition of HCl.

For Rayleigh scatterers, the excess turbidity due to concentration fluctuations is given by[10]

$$\tau_e = \frac{32\pi^3 M_1 c n^2 (dn/dc)^2}{3\lambda^4 N_0 \rho_1 (-\ d\ \ln f_1/dc)} \quad (2)$$

where

λ = wave length of light *in vacuo*
N_0 = Avogadro's number
M_1 = molecular weight of solvent
c = weight concn. (g./ml.)
n = refractive index of soln.
ρ_1 = density of solvent
f_1 = fugacity of solvent

In dilute solutions of non-electrolytes for which the extended van't Hoff law is obeyed

$$\ln f_1 = -\frac{M_1 c}{M_2 \rho_1} - \frac{M_1 A c^2}{\rho_1} \quad (3)$$

leading to

$$\frac{Hc}{\tau_e} = \frac{1}{M_2} + 2Ac \quad (4)$$

where for a given solvent and wave length, H is a lumped constant. Values of H are listed in Table II.

The procedure used to determine the molecular weight of the solute was to plot the quantity Hc/τ_e against the concentration c. The intercept at $c = 0$ gives the reciprocal of the molecular weight.

Results

In Figs. 2 and 3 is plotted Hc/τ_e against concentration for 12-phosphotungstic acid and 9-phosphotungstic acid in various solvents. According to equation 4, the intercept at zero concentration is the reciprocal of the molecular weight.

There is a definite difference between the results in organic solvents from those in water. We will discuss the latter shortly.

In ethanol and allyl alcohol, the molecular weight of 12-phosphotungstic acid is 2600 and 2900, re-

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[8] S. H. Maron and R. Lou, *J. Poly. Sci.*, **14**, 29 (1954).

[9] S. H. Maron and R. Lou, *ibid.*, **14**, 273 (1954).

[10] G. Oster, *Chem. Revs.*, **43**, 319 (1948).

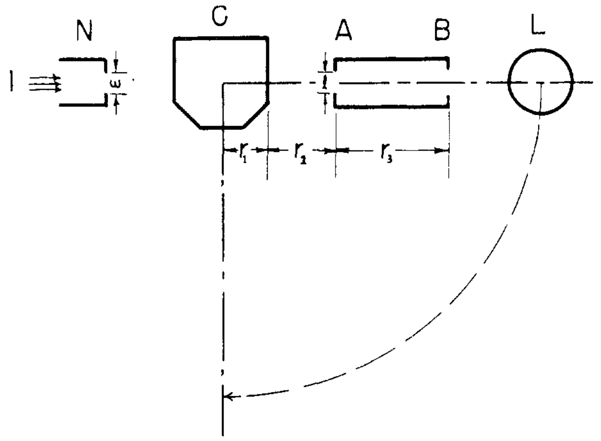

Fig. 1.—Schematic diagram of optical path in light scattering photometer showing the distances r_1, r_2, r_3 and l. N, incident nose piece; C, scattering cell; I, collimated incident light beam; AB, receiving nose piece; L, photomultiplier tube.

spectively, which compares reasonably well with the empirical formula weight of 2880 for the monomer, $H_3PW_{12}O_{40}$. We estimate the uncertainty in our experimental values of the molecular weight to be about 10%.

We did not extrapolate the Hc/τ_e curve for acetic acid to zero concentration because, due to the steepness of the curve at low concentrations, relatively small errors in the turbidity produce considerable uncertainty in the intercept. Of course, the light scattering data are also least precise in this low concentration range. However, it is apparent from Fig. 2 that the acetic acid data are consistent with the results obtained in ethanol and allyl alcohol.

The molecular weight of the 9-phosphotungstic acid in ethanol and propanol was determined to be 4700 and 4400, respectively, which agrees with a formula weight of 4370 for the dimer, $H_6P_2W_{18}O_{65}$.

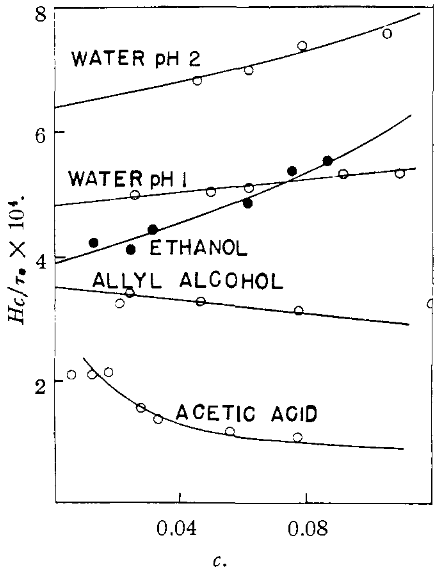

Fig. 2.—Hc/τ_e for 12-phosphotungstic acid *vs.* concentration c (g./ml. solution).

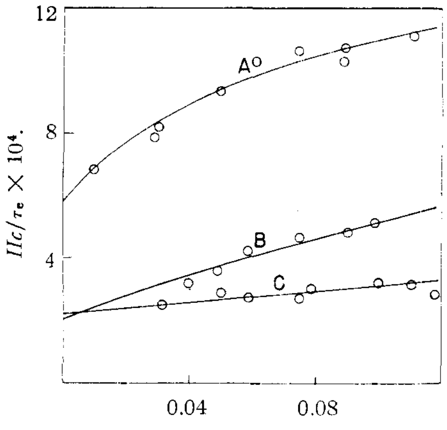

Fig. 3.—Hc/τ_e for 9-phosphotungstic acid *vs.* concentration c (g./ml. solution) in water (A), ethanol (B) and 1-propanol (C).

The aqueous solutions of the 12-phosphotungstic acid were only stable when the *p*H was maintained in the neighborhood of from 1 to 2. Figure 4 depicts the increase in turbidity with time of a solution containing 0.152 g. of 12-phosphotungstic acid per ml. of distilled water. This suggests light scattering as a sensitive tool with which to investigate the kinetics of this decomposition. Aqueous solutions of 9-phosphotungstic acid were stable both in neutral and moderately acid solutions.

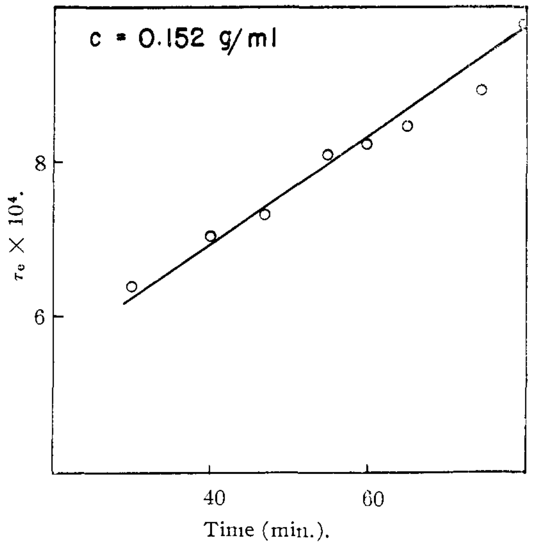

Fig. 4.—The change of excess turbidity τ_e with time for 0.152 g. of phosphotungstic acid per ml. distilled water.

The molecular weight of the acid calculated from the turbidity of the aqueous solutions was much lower than in the organic solvents and also lower than the empirical formula weights. This is not surprising in view of the fact that the procedure for calculating the molecular weight is dependent upon the solute being a nearly ideal non-electrolyte. The phosphotungstic acids are actually strong electrolytes.

In the case of the 12-phosphotungstic acid, the molecular weight obtained varied with *p*H. At *p*H of 2, it was 1700 and at *p*H of 1, it was 2100. This

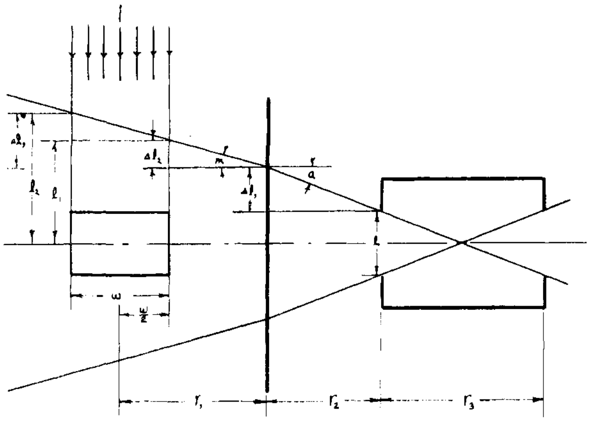

Fig. 5.—Diagram of optical system used in derivation of expression for C_V.

may be due to the common ion effect. The lower *p*H favors the formation of more undissociated acid and the system thus approaches the conditions for which the light scattering treatment is valid.

For the 9-phosphotungstic acid, the *p*H has no effect, the turbidity in pure water and at *p*H of 2 being identical. This probably is due to the fact that the 9-phosphotungstic acid is so strong that the additional hydronium ion does not produce sufficient undissociated acid to affect the turbidity.

In order to relate the light scattering of a non-ideal substance to the molecular weight, it is necessary to revert to equation 2. By utilizing the Gibbs–Duhem relation

$$N_1 \, d \ln f_1 + N_2 \, d \ln f_2 = 0 \qquad (5)$$

where N_1 and N_2 are mole fractions, it can be shown that in dilute solutions

$$\tau_e = \frac{HM_2}{d \ln f_2/dc} = \frac{HM_2}{d \ln a_2/dc} \qquad (6)$$

Thus the determination of the molecular weight requires in addition to the turbidity, knowledge of d ln a_2/dc. This relation is perfectly general in moderately dilute solutions.

We are now engaged in determining d ln a_2/dc for 12- and 9-phosphotungstic acids from measurements of cells with transference, transference number and dissociation constants. We will report on this work in a subsequent communication.

Appendix

The correction factor C_V' which is the volume seen by the photomultiplier tube in non-aqueous solvents compared to that in water may be derived with the aid of Figs. 1 and 5.

$$R_V = \frac{l^2 w}{(l_1 + l_2)^2 w} = \frac{l^2}{(l_1 + l_2)^2} \qquad (7)$$

where R_V = ratio of volume l^2w to the actual volume seen by the photomultiplier tube in the presence of a liquid with refractive index n. When the angle m is sufficiently small so that sin $m \cong$ tan m, it can be shown that

$$l_1 = l \left(\frac{1}{2} + \frac{r_2}{r_3} + \frac{r_1 - w/2}{n\sqrt{l^2 + r_3^2}} \right) \qquad (8)$$

and

$$l_2 = l \left(\frac{1}{2} + \frac{r_2}{r_3} + \frac{r_1 + w/2}{n\sqrt{l^2 + r_3^2}} \right) \qquad (9)$$

It follows that

$$R_V = \left(1 + \frac{2r_2}{r_3} + \frac{2r_1}{n\sqrt{1^2 + r_3^2}} \right)^{-2} \qquad (10)$$

The light radiated by the excess volume is only half as intense as that radiated by the volume l^2w.[11] The ratio of the light scattered by the volume l^2w to the total volume seen by the photomultiplier tube is

$$C_V = 2\left[\left(1 + \frac{2r_2}{r_3} + \frac{2r_1}{n\sqrt{l^2 + r_3^2}} \right) + 1 \right]^{-1} \qquad (11)$$

and the correction factor for non-aqueous solvents becomes

$$C_V' = \frac{\left(1 + \frac{2r_2}{r_3} + \frac{2r_1}{n_w\sqrt{1 + r_3^2}} \right)^2 + 1}{\left(1 + \frac{2r_2}{r_3} + \frac{2r_1}{n\sqrt{l^2 + r_3^2}} \right)^2 + 1} \qquad (12)$$

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(11) C. I. Carr and B. H. Zimm, *J. Chem. Phys.*, **18**, 1616 (1950).

POTSDAM, N. Y.

[CONTRIBUTION NO. 2260 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

Kinetics of the Ferrous Iron–Oxygen Reaction in Acidic Phosphate–Pyrophosphate Solutions

BY JAMES KING AND NORMAN DAVIDSON[1]

RECEIVED OCTOBER 15, 1957

The rate law for the ferrous iron–oxygen reaction in acid solutions (*p*H ~1–2) containing phosphate and pyrophosphate anions is $-$ d(Fe^{++})/dt = k_1(Fe^{++})($H_2PO_4^-$)$^2 P_{O_2}$ + k_2(Fe^{++})($H_2P_2O_7^=$)P_{O_2} where k_1 = 1.08(±0.06) × 10^{-3} atm.$^{-1}$ mole^{-2} liter^2 sec.$^{-1}$ and k_2 = 2.13(±0.05) × 10^{-2} atm.$^{-1}$ mole^{-1} liter sec.$^{-1}$ at 30° (μ = 1.0–1.1 mole/liter, NaClO$_4$). The activation energies are ΔH_1^* = 21(±1) and ΔH_2^* = 6(±1) kcal. The rate law and the values of k_1 and k_2 both show that $H_2P_2O_7^=$ and $H_2PO_4^-$ are independent catalysts and that the unusual quadratic dependence on ($H_2PO_4^-$) is not due to the equilibrium $2H_2PO_4^- \rightleftarrows H_2P_2O_7^= + H_2O$. The mechanism of the reaction presumably involves as the rate-determining step either the one electron transfer process $Fe^{II} + O_2 \rightarrow Fe^{III} + O_2^-$ or the two-electron process $Fe^{II} + O_2 \rightarrow Fe^{IV} + O_2^=$, with iron in the transition state stabilized by the complexing phosphorous anions.

Cher and Davidson[2] found that the rate law for the oxygenation of Fe^{II} in phosphoric acid solution is $-$d(Fe^{++})/dt = k_1(Fe^{++})P_{O_2}($H_2PO_4^-$)^2. The quadratic dependence on ($H_2PO_4^-$) is somewhat

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[1] We are indebted to the Atomic Energy Commission for support of this research under Contract AT(11-1)-188; and to the Danforth Foundation and the General Education Board for fellowships to one of us (J.K.). This paper was presented in part at the 129th National Meeting of the A. C. S., Dallas, April, 1956.

(2) M. Cher and N. Davidson, THIS JOURNAL, **77**, 793 (1955).