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C. F. Baes, Jr.

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ABSTRACT

The spectrophotometric investigation of uranium(VI) - orthophosphate complex formation in 1 M and 0.1 M perchloric acid solutions has been continued. Detailed analysis of the results indicates that 1:1 and also 2:1 phosphate-uranium complexes are formed. The acidity dependence of the formation quotients $K_1 = C_1/C_U C_P$ and $K_2 = C_2/C_U C_P^2$ (in which C_1 and C_2 are the total concentrations of 1:1 and 2:1 complexes, C_U and C_P are the concentrations of uncomplexed uranium(VI) and phosphoric acid) can be accounted for in terms of the complex species $UO_2H_2PO_4^+$, $UO_2H_3PO_4^{++}$, $UO_2(H_2PO_4)_2$ and $UO_2(H_2PO_4)(H_3PO_4)^+$.

INTRODUCTION

In a previous spectrophotometric investigation[1] Job's method of continuous variations was applied to uranyl-phosphate-perchloric acid solutions. The results gave clear evidence, both in 1 M and 0.1 M acid, of complex species for which the mole ratio, PO_4/UO_2, is unity. In subsequent reports,[2,3] solubility measurements were presented which generally confirm a 1:1 complex species and also indicate the formation of 2:1 and 3:1 complexes in solutions of relatively high phosphoric acid concentration.

In the present spectrophotometric investigation the complexity of these uranyl phosphate solutions is examined in greater detail than was possible in the continuous variation measurements. The results have been interpreted in terms of the formation of 1:1 and 2:1 complexes, the corresponding formation quotients being estimated for both 1 M $HClO_4$ and 0.1 M $HClO_4$ - 0.9 M $NaClO_4$ solutions.

THEORETICAL

In general, the convention regarding notation which has been used previously will be continued. Accordingly, $K_{n,x}$ denotes the equilibrium quotient of formation for the complex $UO_2H_x(PO_4)_n$, resulting from the reaction of uranyl ion and undissociated phosphoric acid.

$$UO_2^{++} + nH_3PO_4 = UO_2H_x(PO_4)_n^{+(2-3n+x)} + (3n-x)H^+ \qquad (1)$$

The molar concentrations of these reactants and products will be represented by C_U, C_P, $C_{n,x}$ and C_H, respectively. Thus, the expression for $K_{n,x}$ is

$$K_{n,x} = \frac{C_{n,x}C_H^{3n-x}}{C_U C_P^n} \qquad (2)$$

From the present measurements, which were performed at constant acidity, complex formation quotients

$$K_n = \frac{C_n}{C_U C_P^n} \qquad (3)$$

were determined in which C_n is the total molarity of all complexes with a PO_4/UO_2 ratio of n,

$$C_n = C_{n,0} + C_{n,1} + C_{n,2} \cdots\cdots = \sum_{x=0}^{x} C_{n,x} \, . \qquad (4)$$

K_n is related to the individual formation quotients $K_{n,x}$ by

$$K_n = \frac{K_{n,0}}{C_H^{3n}} + \frac{K_{n,1}}{C_H^{3n-1}} + \frac{K_{n,2}}{C_H^{3n-2}} + \cdots\cdots = \sum_{x=0}^{x} \frac{K_{n,x}}{C_H^{3n-x}} \qquad (5)$$

The observed absorbency difference D (corrected for any phosphoric acid absorption) between an acidic uranium(VI) phosphate solution and a reference solution of the same composition, except that it contains no phosphoric acid, may be related to C_U, C_n and the corresponding molar extinction coefficients ϵ_U, ϵ_n by

$$D = \epsilon_U C_U + \sum_{n=1}^{n} \epsilon_n C_n - \epsilon_U \sum C_U \qquad (6)$$

In this equation $\sum C_U$ denotes the total concentration of uranium(VI) in solution. The molar extinction coefficient term ϵ_n is equal to $\sum_{x=0}^{x} \epsilon_{n,x} C_{n,x} / C_n$; i.e., the sum of the absorbencies of all complex species of the same PO_4^{-3}/UO_2^{++} mole ratio n, divided by their total molarity. Upon introducing the material balance relation, $\sum C_U = C_U + \sum_{n=1}^{n} C_n$, and combining equations (3) and (6),

$$D = \frac{\sum_{n=1}^{n} A_n K_n C_P{}^n}{1 + \sum_{n=1}^{n} K_n C_P{}^n} \qquad (7)$$

wherein $A_n = (\epsilon_n - \epsilon_U) \sum C_U$. This equation provides a relationship between the observed absorbency difference and the phosphoric acid concentration in terms of a set of extinction coefficient parameters A_n and a set of K_n values.

In applying equation (7) to each series of measurements in which ΣC_U, the ionic strength and the acidity were constant, it was assumed that the A_n and K_n terms were constant.

EXPERIMENTAL

A uranium(VI) perchlorate stock solution was prepared by first dissolving nitrate-free UO_3, obtained by the previously described procedure,[1] in slightly less than the equivalent amount of perchloric acid, performing a uranyl analysis[1] on an aliquot of the resulting solution, and then adding the required amount of acid to produce stoichiometric $UO_2(ClO_4)_2$. G. Frederick Smith's reagent grade perchloric acid and sodium perchlorate were used in preparing the other stock solutions used.

All absorbencies were measured at 25 ± 1°C with a Beckman Model DU spectrophotometer, using 1 cm and 5 cm silica cells in the ultraviolet, and 1 cm corex cells in the visible range. Cell blank determinations were made in all cases, and the results were corrected accordingly. A hydrogen discharge lamp was used in all ultraviolet measurements.

In the ultraviolet, the absorbency of phosphoric acid in 1 M perchlorate solutions was found to be large enough to require correction of some of the measurements. The observed molar extinction coefficients at 290, 300, 310 and 318 mμ were, respectively, 0.058, 0.037, 0.021 and 0.014.

The absorbencies of two series of solutions, 0.000943 M in uranium(VI) perchlorate, 1 M and 0.1 M in perchloric acid, and containing various amounts of phosphoric acid, were determined in the ultraviolet. The ionic strength of the

0.1 M acid solutions was adjusted to 1 M by the addition of sodium perchlorate. A third series, 0.0377 M in uranium(VI) perchlorate and 1 M in perchloric acid, was run in the visible range. The absorbency, D, of each sample was measured against a reference solution otherwise of the same composition, but free of phosphoric acid. Care was taken to keep the slit width the same for all measurements at a single wavelength.

RESULTS

The absorbency measurements are summarized in Tables I and II. All D values have been normalized to a path length of 1.00 cm. Log-log plots of D vs. phosphoric acid concentration are presented in Fig. 1 and 2. The C_P values plotted in Fig. 1 represent the molarity of free, undissociated phosphoric acid. In the case of the 1 M acid data, C_P was assumed to be equal to the formal concentration of phosphoric acid ΣC_P since the amount consumed in complex formation may be neglected and the primary dissociation

$$H_3PO_4 = H^+ + H_2PO_4^- \quad , \quad K_a = 0.021 \text{ mole/liter*} \qquad (8)$$

is only about 2%. In the case of the 0.1 M acid data, however, the dissociation of phosphoric acid becomes appreciable, not only decreasing C_P, but also increasing the hydrogen ion concentration, C_H. To correct for these two effects C_P and C_H were first calculated from the

---

*This value is estimated from as yet unpublished potentiometric data in which the quinhydrone electrode was employed. It may be compared with 0.016 mole/liter (30°, μ = 0.56), R. Griffith and A. McKeown, Trans. Faraday Soc. 36, 776 (1940); 0.030 mole/liter (30°, μ = 0.665), O. Lanford and S. Kiehl, J.A.C.S. 64, 292 (1942); 0.020 (30°, μ = 1.0 - 1.1), M. Cher and N. Davidson, J.A.C.S. 77, 793 (1955).

Table I

ABSORBENCY MEASUREMENTS IN 0.000943 M $UO_2(ClO_4)_2$, $HClO_4$ SOLUTIONS AT 25°C

Total H_3PO_4 Molarity $\sum C_p$	Calc'd. H_3PO_4 Molarity C_p[b]	λ = 290 mμ		λ = 300 mμ		λ = 310 mμ		λ = 318 mμ	
		D_o[a]	D	D_o[a]	D	D_o[a]	D	D_o[a]	D
			Part A: Results in 1 M $HClO_4$						
0.00522		0.0044	0.0041	0.0027	0.0025	0.0025	0.0024	0.0028	0.0027
0.01043		0.0078	0.0072	0.0050	0.00465	0.0048	0.0046	0.0050	0.0049
0.01564		0.0120	0.0111	0.00806	0.0068	0.00715	0.0068	0.0074	0.0072
0.02086		0.0156	0.0144	0.0096	0.0088	0.00905	0.0086	0.0094	0.0091
0.0313		0.0218	0.0200	0.0135	0.0123	0.0126	0.0119	0.0122	0.0126
0.0522		0.0312	0.0282	0.0192	0.0173	0.0172	0.0161	0.0180	0.0173
0.0730		0.0430	0.0388	0.0271	0.0244	0.0236	0.0220	0.0244	0.0234
0.1043		0.0540	0.0480	0.0324	0.0285	0.0276	0.0254	0.0286	0.0271
0.1564		0.0686	0.0596	0.0240	0.0346	0.0340	0.0306	0.0346	0.0324
0.2086		0.0804	0.0682	0.0466	0.0396	0.0384	0.0339	0.0386	0.0356
0.313		0.0990	0.0808	0.0578	0.0462	0.0446	0.0379	0.0436	0.0392
0.438		0.1142	0.0886	0.0658	0.0495	0.0486	0.0392	0.0466	0.0404
0.626		0.1342	0.0978	0.0752	0.0520	0.0542	0.0408	0.0496	0.0408
			Part B: Results in 0.1 M $HClO_4$ - 0.9 M $NaClO_4$						
0.00313	0.00258	0.0154	0.0152	0.0091	0.0090	0.0079	0.0078	0.0082	0.0081
0.00417	0.00343	0.0208	0.0205	0.0125	0.0123	0.0109	0.0108	0.0110	0.0109
0.00626	0.00512	0.0296	0.0288	0.0178	0.0175	0.0152	0.0150	0.0158	0.0157
0.01043	0.00849	0.0430	0.0424	0.0259	0.0255	0.0219	0.0216	0.0222	0.0220
0.01564	0.01264	0.0592	0.0582	0.0356	0.0350	0.0298	0.0294	0.0300	0.0298
0.02086	0.01675	0.0710	0.0696	0.0426	0.0417	0.0352	0.0346	0.0354	0.0350
0.0313	0.02479	0.0862	0.0842	0.0508	0.0495	0.0410	0.0402	0.0408	0.0402
0.0522	0.0403	0.1066	0.1032	0.0616	0.0594	0.0478	0.0466	0.0472	0.0464
0.0730	0.0551	0.1198	0.1152	0.0682	0.0652	0.0518	0.0500	0.0508	0.0496
0.1043	0.0761	0.1358	0.1292	0.0760	0.0716	0.0562	0.0536	0.0542	0.0524
0.1564	0.1088	0.1510	0.1410	0.0840	0.0776	0.0598	0.0560	0.0562	0.0534
0.2086	0.1389	0.1612	0.1480	0.0886	0.0800	0.0616	0.0564	0.0570	0.0536

a) The observed absorbency, which has been corrected for phosphoric acid absorption to give the corresponding D values.

b) These values are equal to 0.1 (C_P/C_H) which values in turn were calculated allowing for the dissociation of H_3PO_4 (cf. p. 12).

Table II

ABSORBENCY MEASUREMENTS IN 1 M $HClO_4$,

0.0377 M $UO_2(ClO_4)_2$ AT 25°C

Total H_2PO_4 Molarity ΣC_P	H_3PO_4 Molarity C_P*	D		
		λ = 410 mμ	λ = 420 mμ	λ = 424 mμ
0.0209	0.0152	0.0485	0.0515	0.054
0.0417	0.0310	0.089	0.096	0.105
0.0626	0.0475	0.127	0.1315	0.151
0.0834	0.0644	0.152	0.159	0.183
0.1043	0.0820	0.171	0.174	0.2075
0.1460	0.1177	0.1945	0.202	0.241
0.2086	0.1736	0.220	0.221	0.279
0.2712	0.2312	0.234	0.234	0.297
0.334	0.2898	0.239	0.242	0.307
0.417	0.369	0.244	0.241	0.321
0.501	0.449	0.247	0.242	0.326
0.626	0.571	0.243	0.238	0.333

*This quantity was calculated according to equation (14), p. 22.

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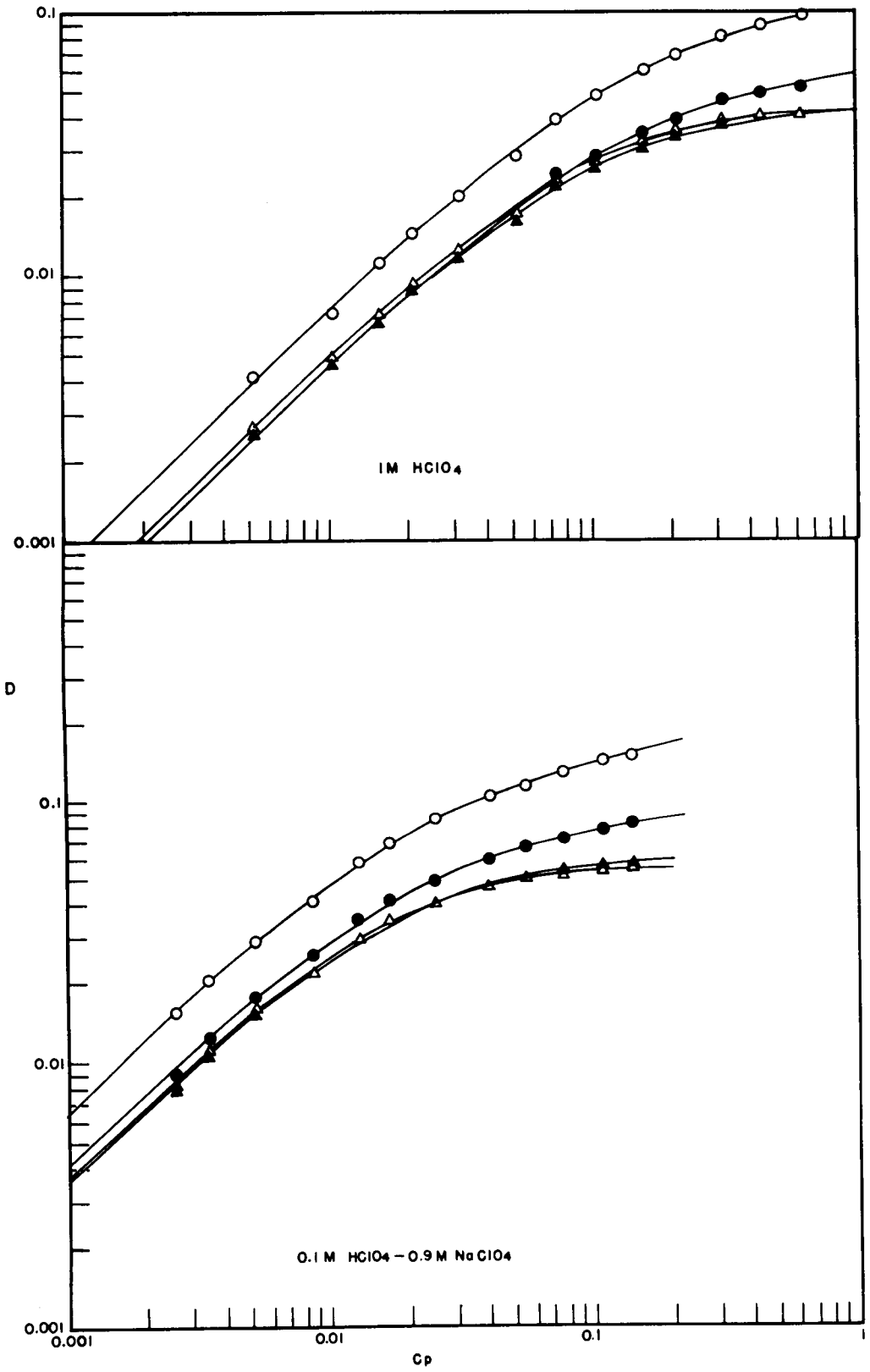

Fig. 1. Absorbency Results at $\Sigma C_U = 0.000943$ *M*: O, 290 mμ; ●, 300 mμ; ▲, 310 mμ; Δ, 318 mμ.

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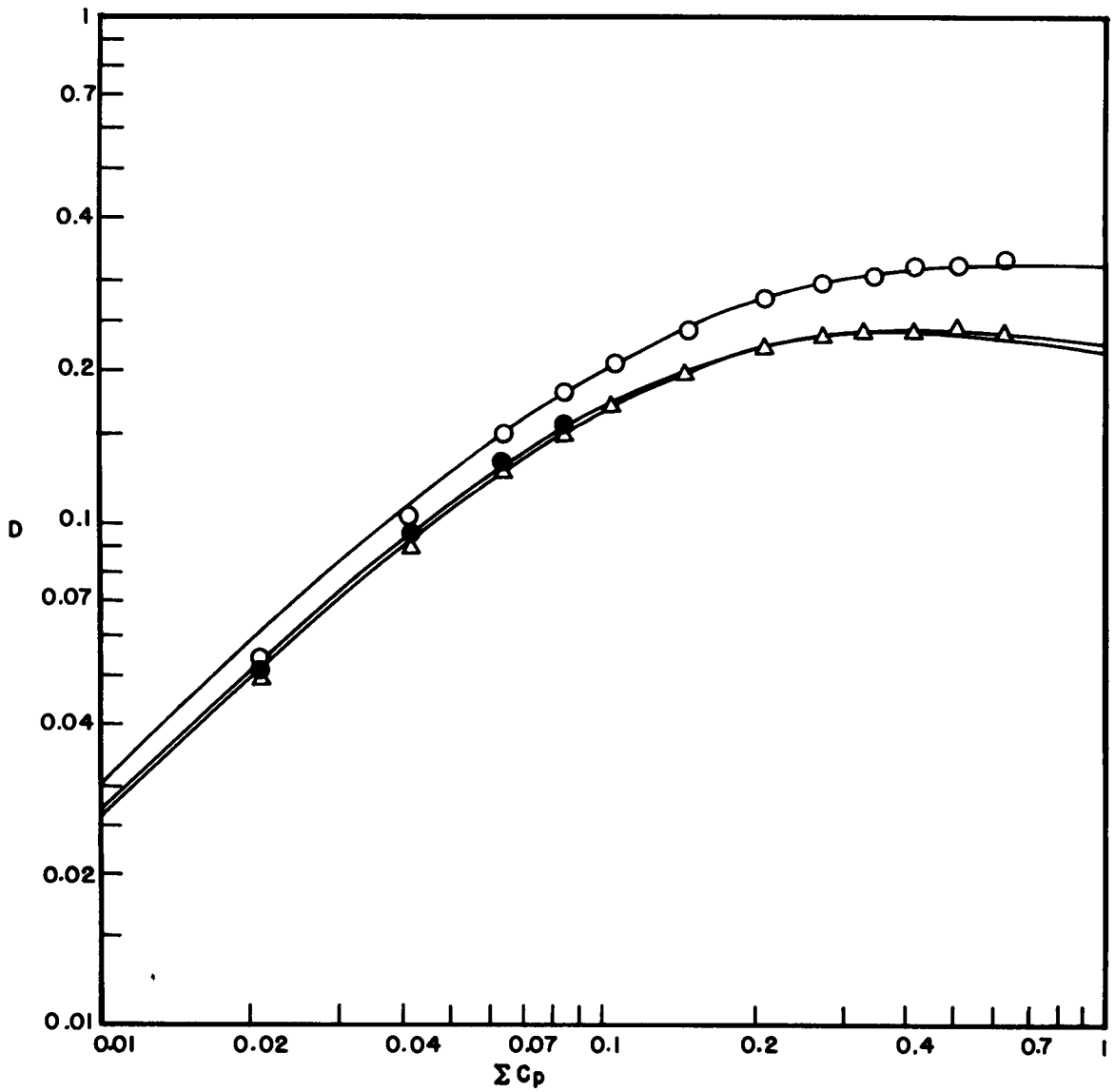

Fig. 2. Absorbency Results in 1 *M* Perchloric Acid at $\Sigma C_U = 0.0377$ *M*: Δ, 410 mμ; ●, 420 mμ; O, 424 mμ.

initial solution composition using K_a = 0.021 (neglecting the small effects produced by complex formation). As an approximation it was then assumed that the principle complex species in solution at this acidity and range of phosphoric acid concentration are $UO_2H_2PO_4^+$ and $UO_2(H_2PO_4)_2$.* Since the corresponding formation quotients

$$K_{1,2} = \frac{C_{1,2}C_H}{C_U C_P} \; ; \quad K_{2,4} = \frac{C_{2,4}C_H^2}{C_U C_P^2} \qquad (9)$$

contain C_P and C_H to the same power in each case, a correction factor $0.1/C_H$ was applied to C_P and the results plotted as the equilibrium C_P values at C_H = 0.100 M. The magnitude of this correction is indicated in Part B of Table I.

---

*While the $K_{n,x}$ values estimated in the discussion indicate that in 0.1 M acid three complexes - $UO_2H_2PO_4^+$, $UO_2(H_2PO_4)_2$ and $UO_2(H_2PO_4)(H_3PO_4)^+$ - should be considered, the fairly small effect of this correction procedure on K_1 and K_2 values (cf. footnote b, Table IV) suggests that no serious error is introduced by neglecting $UO_2(H_2PO_4)(H_3PO_4)^+$.

DETERMINATION OF K_1 AND K_2

Considering only the first two terms of the summations in equation (7),

$$D = \frac{A_1K_1C_P + A_2K_2C_P^2}{1 + K_1C_P + K_2C_P^2} \tag{10}$$

Rearranging,

$$K_2C_P + K_1 = \frac{A_1K_1 - A_2K_2C_P}{D} - \frac{1}{C_P} = Q \tag{11}$$

Values of the quantity Q for the data in Table I have been calculated using A_1K_1 and A_2K_2 values obtained as described below. These Q values are summarized in Table III. In accordance with the above equation, at each value of C_P, Q was found to be constant independent of wavelength within experimental error. Plots of Q vs. C_P are shown in Fig. 3. The satisfactory straight lines of slope K_2 and intercept K_1 which result indicate that these data may be accounted for satisfactorily assuming 1:1 and 2:1 phosphate-uranium complexes only. The scatter of points at low C_P values results from greater sensitivity of Q to errors in D. The resulting K_n values are listed in Table IV.

The values of A_1K_1 and A_2K_2 used in the calculation of Q as a function of C_P and D are listed in Table V. These were obtained as follows:

(1) Whiteker and Davidson have pointed out[4] that if only 1:1 complexes are formed plots of D/C_P

Table III

VALUES OF THE QUANTITY, $Q = \frac{A_1K_1 + A_2K_2C_P}{D} - \frac{1}{C_P}$,

AS A FUNCTION OF C_P, 0.000943 M $UO_2(ClO_4)_2$

H_3PO_4 Molarity C_P	Q			
	λ= 290 mμ	λ= 300 mμ	λ= 310 mμ	λ= 320 mμ
		1 M $HClO_4$		
0.00522	5.8	7.0	14.9	7.1
0.01043	20.3	12.9	13.2	14.7
0.01564	11.9	11.7	10.7	12.1
0.02086	11.6	11.4	11.6	12.8
0.0313	12.4	11.7	11.9	12.7
0.0522	14.5	13.8	14.6	14.5
0.0730	12.4	11.1	12.0	12.1
0.1043	13.5	13.3	13.9	13.8
0.1564	14.8	14.8	14.8	14.7
0.2086	16.0	15.9	15.9	15.9
0.313	18.2	18.1	18.1	18.2
0.438	21.5	21.6	21.5	21.5
0.626	25.7	26.8	25.9	26.5
		0.1 M $HClO_4$ - 0.9 M $NaClO_4$		
0.002575	77.7	94.0	89.4	86.5
0.00343	56.9	63.0	56.3	63.3
0.00512	58.8	58.4	58.5	54.7
0.00849	61.9	62.8	62.6	64.1
0.01264	58.2	57.8	57.1	58.3
0.01675	60.5	59.4	59.3	60.0
0.02479	67.6	67.3	67.4	68.4
0.0403	76.8	76.7	77.0	77.0
0.0551	84.5	84.5	84.7	83.9
0.0761	93.1	93.6	93.3	92.6
0.1088	109.1	108.2	108.4	108.5
0.1389	123.8	123.6	123.8	122.9

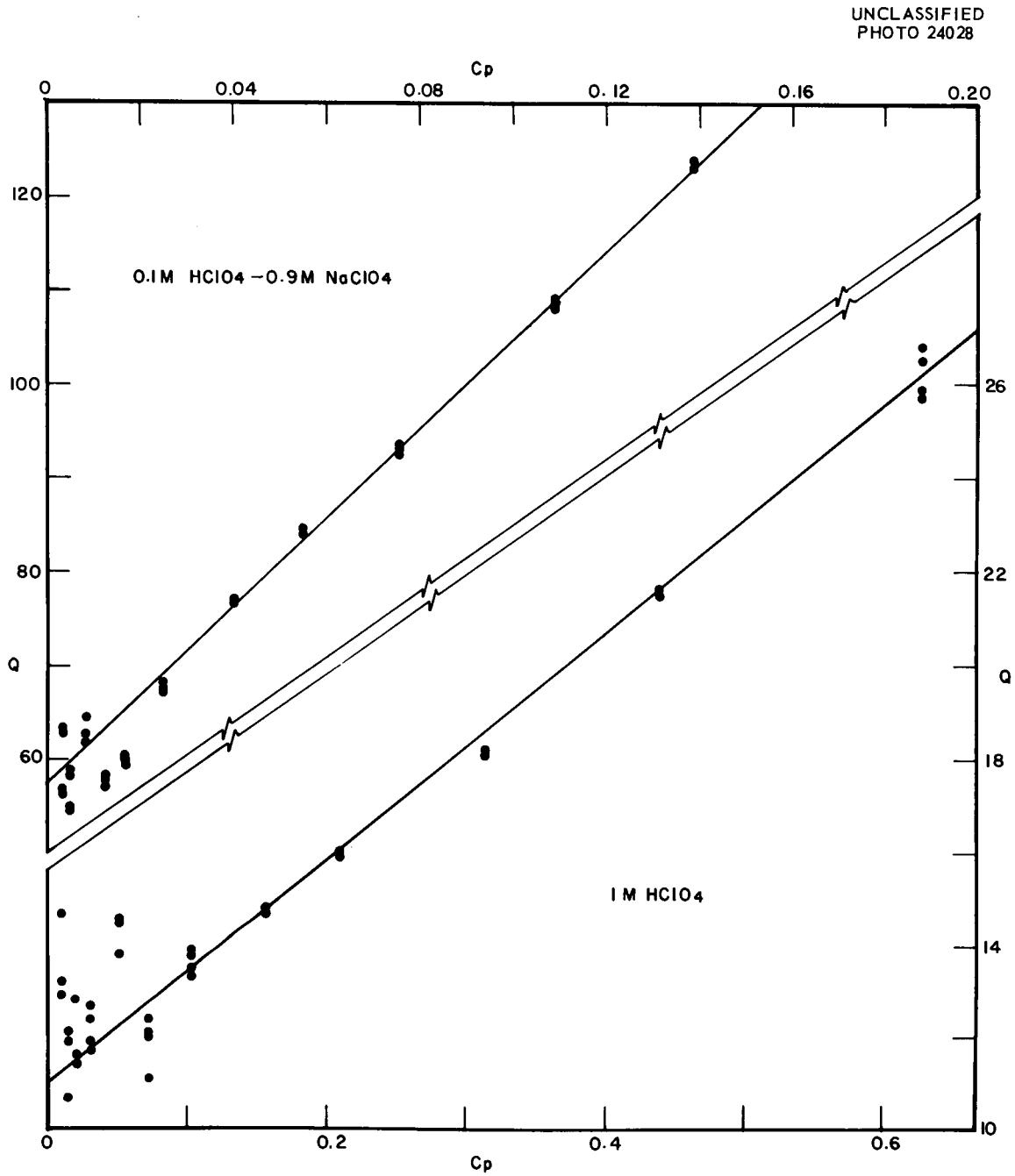

Fig. 3. The Evaluation of K_1 and K_2 According to Equation (11).

Table IV

FORMATION QUOTIENTS FOR URANIUM(VI)-

ORTHOPHOSPHATE COMPLEXES

	1 M $HClO_4$	0.1 M $HClO_4$ - 0.9 M $NaClO_4$
K_1 [a]	11 ± 2	58 ± 4 [b]
K_2 [a]	24 ± 5	470 ± 30 [b]

a) Cf. equation (3), p. 2.

b) If no corrections were made for the dissociation of phosphoric acid, the resulting K_n values would appear to be K_1 = 50; K_2 = 400.

Table V

SUMMARY OF A_1K_1 AND A_2K_2 VALUES, 0.000943 M $UO_2(ClO_4)_2$

	1 M $HClO_4$		0.1 M $HClO_4$ - 0.9 M $NaClO_4$	
λ(mμ)	A_1K_1	A_2K_2	A_1K_1	A_2K_2
290	0.794	3.00	6.85	90.3
300	.489	1.58	4.22	45.0
310	.491	1.01	3.67	26.8
318	.532	0.98	3.81	22.8

Table VI

SUMMARY OF A_1 AND A_2 VALUES, 0.0377 M $UO_2(ClO_4)_2$

λ(mμ)	A_1	A_2
410	0.358	0.171
420	0.371	0.152
424	0.422	0.282

vs. D will be linear with a slope equal to $-K_1$ and intercepts equal to A_1K_1.* The present data have been so plotted in Fig. 4. While the deviations from linearity at high D values and the dependence of slope on wavelength indicate the presence of higher complexes, it can be shown from equation (7) that in such a case, the intercept at D = 0 is still A_1K_1.** (2) The A_2K_2 values listed in Table V were derived from an analysis of the variation in the ratio R of D values for two wavelengths, compared at the same C_P values. If equation (10) is valid for the system, it can readily be shown that for two wavelengths designated by (') and (")

$$\frac{1-R_o/R}{C_P} = \frac{A_2'K_2}{A_1'K_1}(R_o/R) - \frac{A_2''K_2}{A_1''K_1} \qquad (12)$$

R_o is the limiting value of R as C_P approaches zero and is equal to $A_1'K_1/A_1''K_1$. In accordance with this equation, A_2K_2/A_1K_1 was determined for each wavelength from plots of $(1-R_o/R)/C_P$ vs. R_o/R (Fig. 5), and A_2K_2 was in turn evaluated using the known values of A_1K_1. While the uncertainties in the determination of individual slopes and intercepts in these plots are ca. ± 10% and ± 15%, respectively, the correspondence of

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*This is evident from equation (7) if only the first term in each summation is taken.

**Upon rearranging equation (7) to

$$\frac{D}{C_P} = \sum_{n=1}^{n} (A_n-D)K_nC_P^{\,n-1}$$

it is evident that as C_P and D approach zero, D/C_P approaches A_1K_1. Upon differentiating this equation with respect to D, then as D and C_P approach zero

$$\frac{d(D/C_P)}{dD} = -K_1 + A_2K_2\frac{dC_P}{dD}$$

and since the limiting value of dC_P/dD is $1/A_1K_1$, the limiting slope $d(D/C_P)/dD$ is $-K_1 + A_2K_2/A_1K_1$.

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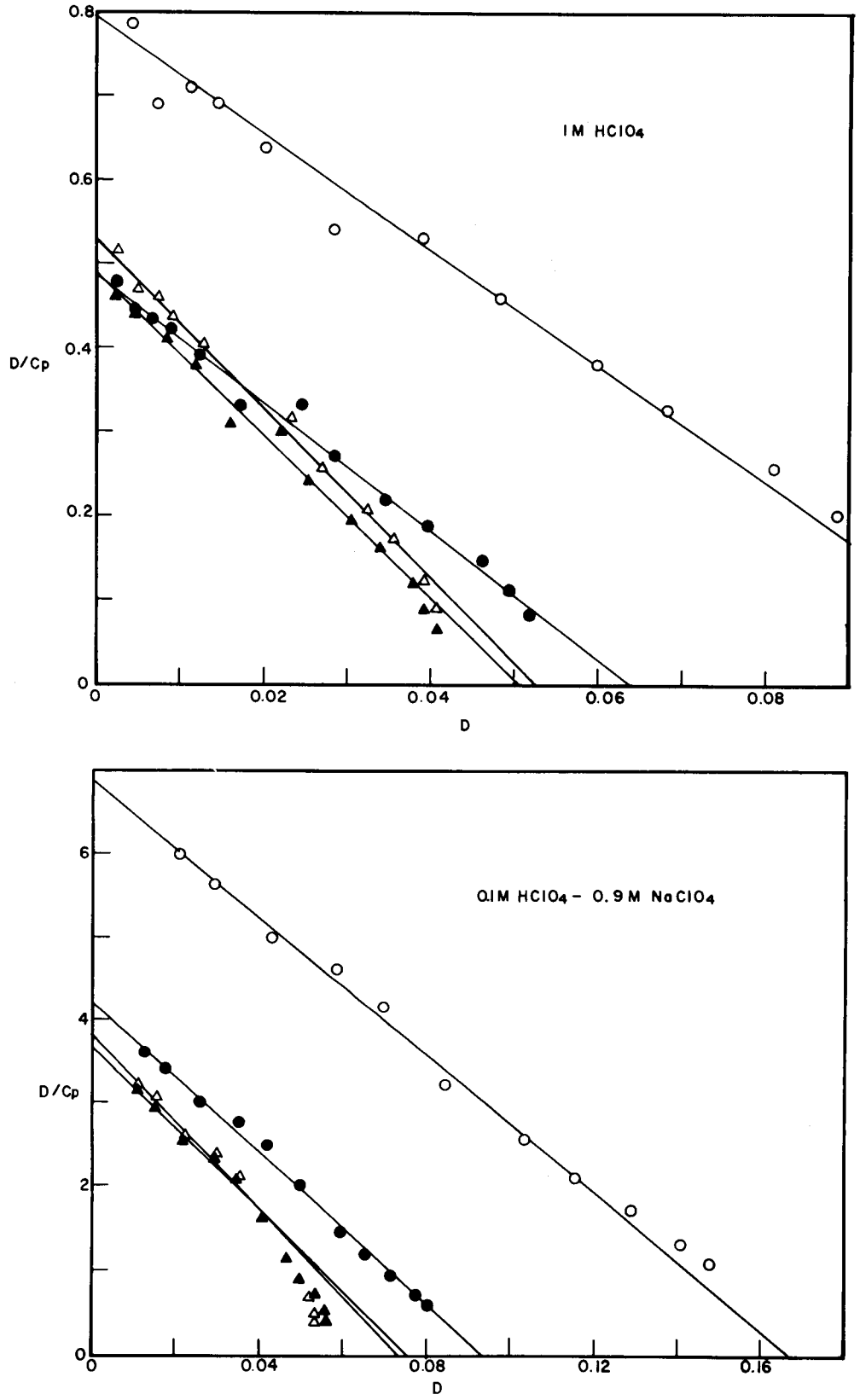

Fig. 4. The Determination of A_1K_1 Values, O, 290 mμ; ●, 300 mμ; ▲, 310 mμ; Δ, 318 mμ.

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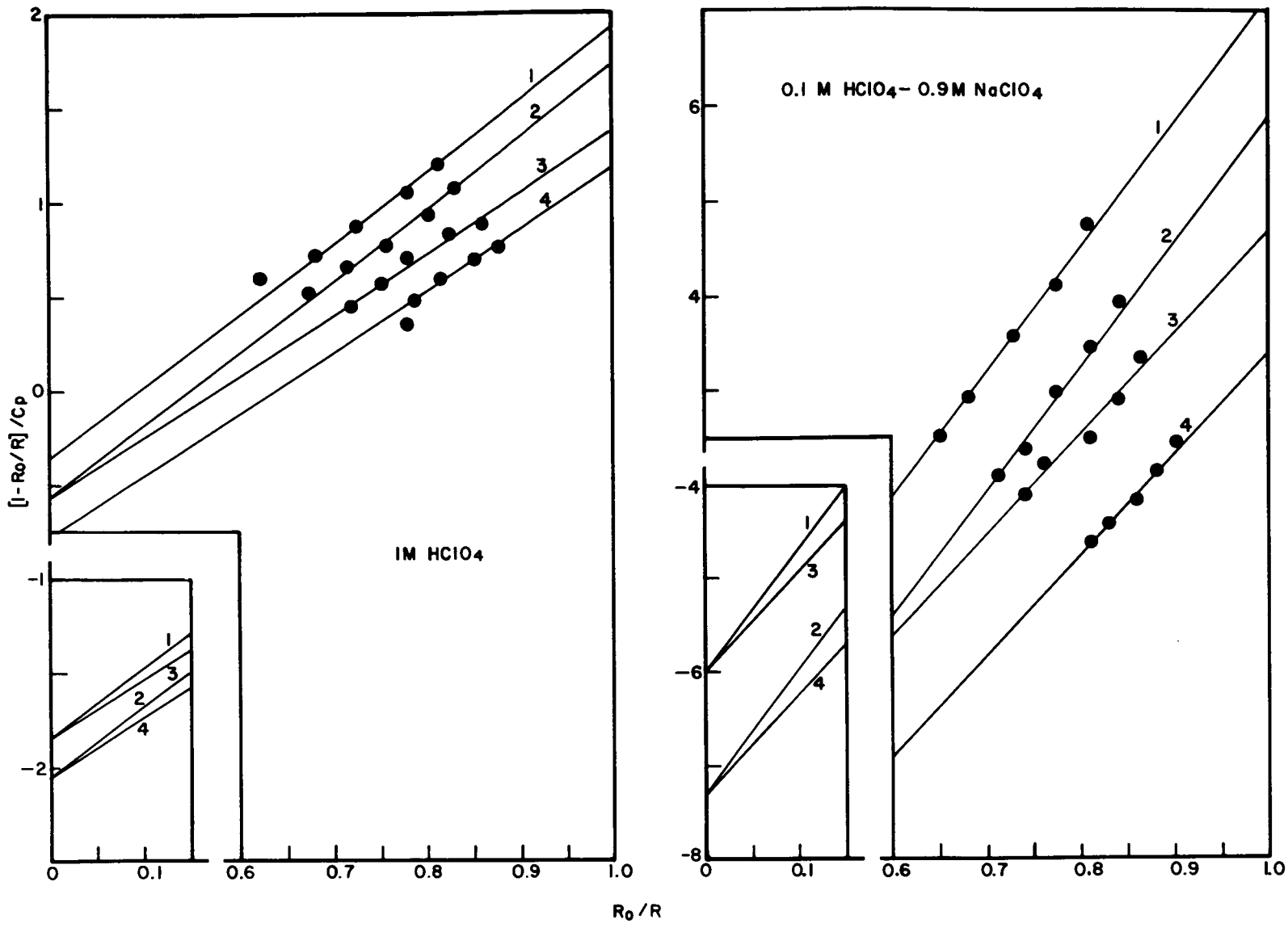

Fig. 5. The Determination of A_2K_2/A_1K_1 Values. In drawing the straight lines for the pairs of wavelengths, (1) 290/310, (2) 290/318, (3) 300/310, (4) 300/318, the following conditions, required by equation (12), were satisfied: Slopes of lines (1) and (2) are equal; slopes of lines (3) and (4) are equal, intercepts of lines (1) and (3) are the same, intercepts of lines (2) and (4) are the same.

slopes and of intercepts in the sets of lines reduces these uncertainties somewhat. A check against non-systematic errors in the resulting A_2K_2 values is provided by the agreement among calculated values of Q (cf. equation (11)) for the different wavelengths at each value of C_P (Table III); however, a systematic uncertainty in A_2K_2 values of ± 10% is estimated, which in turn introduces a similar uncertainty into K_2.

The curves shown in Fig. 1 were calculated by substituting appropriate values of K_1, K_2, A_1K_1 and A_2K_2 into equation (10).

It may be shown from equation (7) that in general the limiting slope of a D/C_P vs. D plot should be $-K_1+A_2K_2/A_1K_1$ (cf. footnote on p. 18). Using the appropriate quantities from Table VI, the calculated limiting slope was found to agree with the observed values within an average deviation of about 5%. It is of particular interest to point out that, at a given wavelength, if equation (10) is valid and if

$$K_2 = \frac{A_2K_2}{A_1K_1}\left[K_1 - \frac{A_2K_2}{A_1K_1}\right] \qquad (13)$$

the resulting D/C_P vs. D plot will be linear throughout. Equation (13) is approximated by the present results, which account for the wide range of linearity of the plots in Fig. 4, in spite of the appreciable contribution of 2:1 complexes.

Similar determinations of K_1 and K_2 could not be made from the data in Fig. 4 since, at the higher uranium(VI) concentration involved, an appreciable part of the phosphoric

acid is consumed in complex formation. However, the conformity of these results to $K_1 = 11$ and $K_2 = 24$ was established as follows: The concentration of uncomplexed phosphoric acid C_P was first calculated for each $\sum C_P$ value from the equation

$$C_P = \sum C_P - \sum C_U \left[\frac{K_1 C_P + 2K_2 C_P^2}{1+K_1 C_P + K_2 C_P^2}\right]^* \qquad (14)$$

Using these same K_n values, A_1 and A_2 were then evaluated from a graphical solution of the equation

$$\frac{D}{C_P}(1+K_1 C_P + K_2 C_P^2) = A_2 K_2 C_P + A_1 K_1 \qquad (15)$$

(a rearranged form of equation (10)) for each wavelength. The resulting A_n values (Table VI) along with these K_n values lead to the calculated D vs. $\sum C_P$ curves drawn in Fig. 2.

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*This equation is obtained by combination of the two material balance relations,

$$\sum C_P = C_P + C_1 + 2C_2$$
$$\sum C_U = C_U + C_1 + C_2$$

with equation (3), p. 2.

DISCUSSION

The present values of K_1 and K_2 in 1 M perchloric acid are compared to those previously estimated from solubility and continuous variation measurements[1,3] in Table VII. An analysis of these earlier results suggests that the discrepancy in K_1 values is, at least to some extent, real.* If such is the case, it would seem that polymerization-complex forming reactions such as

$$2UO_2H_xPO_4 = (UO_2H_xPO_4)_2 \qquad (16)$$

may occur to an appreciable extent in the more concentrated uranium solutions. However, the conformity of the present results for 0.0377 M uranium(VI) solutions to the K_1 and K_2

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*The observed continuous variation curves for 1 M perchloric acid solutions at λ = 410, 420 and 424 mμ (Ref. 1, p. 6) are approximately 20% higher than curves calculated from the present K_1, K_2, A_1 and A_2 values. Even so, it is of interest to note that the calculated curves are of the same shape as those observed, showing no break at $\Sigma C_P/(\Sigma C_P + \Sigma C_U) = 0.667$.

A calculated solubility curve, incorporating the present K_1 and K_2 values, is found to fit the 1 M perchloric acid solubility results (Ref. 3, p.) adequately in the region of excess phosphoric acid; however, it falls below the observed results in excess uranyl perchlorate.

Table VII

COMPARISON OF K_1 AND K_2 VALUES IN

1 M $HClO_4$ ESTIMATED BY VARIOUS METHODS

Method	Total Uranium(VI) Molarity	K_1	K_2	Ref.
Spectrophotometric	0.001	11 ± 2	24 ± 5	
Spectrophotometric (Continuous variations)	0 - 0.14	38 ± 12		(1)
Solubility	0.09 - 0.5	37 ± 13	15 ± 8	(3)

values derived from the 0.000943 M uranium(VI) data (Table IV) provides strong evidence that the neglect of polynuclear complex formation in the present treatment is justified. If such complexes were formed to an appreciable extent in the dilute uranium(VI) solutions, their contribution would be much higher in the more concentrated solutions and would be expected to produce inconsistencies in the latter case.

If 3:1 complexes are formed to an appreciable extent in the present 1 M and 0.1 M acid solutions,* the corresponding A_3 term in equation (7) must be such that the resulting effect on D is not apparent. Accordingly, the values of K_2 should be regarded as less certain than those of K_1, which would be relatively unaffected by such a complication.

From the values listed in Table IV, it appears that the acidity dependence of K_1 is less than first power, while that of K_2 lies between first and second power. Considering the general relationship between K_n and the individual formation quotients $K_{n,x}$, given by equation (5), these acid dependencies may be accounted for most simply by

$$K_1 = K_{1,2}/C_H + K_{1,3} \; ; \quad K_2 = K_{2,4}/C_H^2 + K_{2,5}/C_H \qquad (17)$$

which corresponds to the formation of the following complex species

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*The value $K_{3,7}$ = 200, previously estimated (Ref. 3, p. 39) would suggest appreciable 3:1 complex formation at the higher phosphoric acid concentrations in the present measurements.

$UO_2H_2PO_4^+$	$UO_2(H_2PO_4)_2$
$UO_2H_3PO_4^{++}$	$UO_2(H_2PO_4)(H_3PO_4)^+$

If it is further assumed that the individual $K_{n,x}$ values are the same for both 1 M $HClO_4$ and 0.1 M $HClO_4$ - 0.9 M $NaClO_4$, the resulting values of $K_{1,2}$, $K_{1,3}$, $K_{2,4}$ and $K_{2,5}$ would appear to be, respectively, 5.2, 5.8, 2.5 and 22. Since this is a gross assumption, however, the best then can be said at this time is that these four complex species are probably formed in 1 M to 0.1 M acid solutions.

More reliable estimates of individual $K_{n,x}$ values as well as evidence concerning possible polynuclear complex formation should result from potentiometric measurements now underway.

SUMMARY

The formation quotients

$$K_1 = \frac{C_1}{C_U C_P} \quad \text{and} \quad K_2 = \frac{C_2}{C_U C_P^2}$$

(in which C_1 and C_2 are the total concentration of 1:1 and 2:1 phosphate-uranium complexes) were evaluated from spectrophotometric measurements using the relationship

$$D = \frac{\sum_{n=1}^{n} A_n K_n C_P^{\,n}}{1 + \sum_{n=1}^{n} K_n C_P^{\,n}}$$

where D is the observed absorbency difference between acidic uranium(VI) solutions with and without phosphate present and

$$A_n = (\epsilon_n - \epsilon_U) \Sigma C_U$$

The values obtained from perchlorate solutions containing uranium at ca. 0.001 M and phosphate in the range 0.002 to 0.6 M were

	1 M $HClO_4$	0.1 M $HClO_4$ - 0.9 M $NaClO_4$
K_1	11 ± 2	58 ± 4
K_2	24 ± 5	470 ± 30

The absorbencies of similar 1 M $HClO_4$ solutions containing

uranium at ca. 0.04 M were shown to be consistent with these values, indicating that polynuclear complexes were not formed to any important extent at these uranium levels. However, these values are different from those previously obtained (at still higher uranium levels) from spectrophotometric data in connection with analysis by the method of continuous variations and from solubility data.

The observed acid dependencies of the formation quotients may be accounted for most simply by assumption that the principal complex species formed are

$UO_2H_2PO_4^+$ $\qquad$ $UO_2(H_2PO_4)_2$

$UO_2H_3PO_4^{++}$ $\qquad$ $UO_2(H_2PO_4)(H_3PO_4)^+$

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