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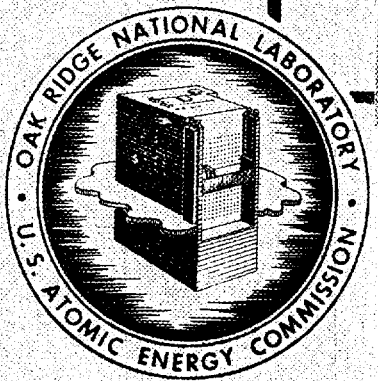
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ORNL 1577
Chemistry - General


THE CHEMISTRY OF URANIUM (VI)
ORTHOPHOSPHATE SOLUTIONS:
PART I, A SPECTROPHOTOMETRIC INVESTIGATION
OF URANYL PHOSPHATE COMPLEX
FORMATION IN PERCHLORIC ACID SOLUTION

C. F. Baes, Jr.
J. M. Schreyer
J. M. Lesser

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General

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OF URANYL PHOSPHATE COMPLEX FORMATION IN

PERCHLORIC ACID SOLUTION

C. F. Baes, Jr.
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June 22, 1953

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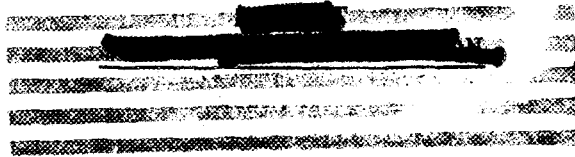





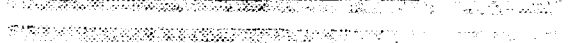


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ABSTRACT

Job's method of continuous variations has been applied to $UO_2(ClO_4)_2 - H_3PO_4$ mixtures in 1M and in 0.1M $HClO_4$. In both cases the data indicate the presence of complex species in which the ratio PO_4^{-3}/UO_2^{++} is unity. A formation constant, $K_1 = 38 \pm 12$, has been calculated from the data in 1M perchloric acid.

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THE CHEMISTRY OF URANIUM(VI) ORTHOPHOSPHATE SOLUTIONS:

PART I, A SPECTROPHOTOMETRIC INVESTIGATION

OF URANYL PHOSPHATE COMPLEX FORMATION IN

PERCHLORIC ACID SOLUTION

INTRODUCTION

This is the first in a series of reports describing an investigation of the chemistry of uranium(VI) orthophosphate solutions which is at present underway in this laboratory. Spectrophotometric, potentiometric and solubility studies have been carried out, and it is the first of these which is reported here.

Information available on other uranyl complex systems indicates that the equilibria involved are rapid and reversible and that polymerization complexes are not usually formed. The only previous investigation which supplies pertinent information regarding the solution compositions involved in the present measurements is that of G. R. Leader.⁽¹⁾ His solubility results in nitric acid solution indicate that a complex, $UO_2H_2PO_4^+$, is formed in solutions of moderate phosphoric acid concentration and that in excess phosphoric acid, higher complexes are formed.

When phosphoric acid is added to an acidified solution of uranyl perchlorate, a distinct color change occurs. Preliminary measurements revealed that these solutions obey Beer's law in the presence of a constant phosphoric acid concentration (indicating no polynuclear uranium complexes to be involved) and that a sufficient change in the absorption spectrum of uranyl ion is produced to permit Job's method of continuous variations⁽²⁾ to be reasonably applicable

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at several wavelengths. From the resulting continuous variation curves for 1M and 0.1M perchloric acid solutions, the presence of one-to-one uranyl phosphate complexes has been established and a total formation constant evaluated in 1M perchloric acid.

EXPERIMENTAL


All absorbancy measurements were performed with a Beckman D. U. spectrophotometer, using 1.00 cm corex and silica matched cells, for which no blank correction was required. All measurements were performed in a room thermostated at $25 \pm 2^\circ\text{C}$.

Uranium(VI) perchlorate stock solutions were prepared by dissolving purified UO_3 (free of nitrate) in an approximately equivalent amount of perchloric acid and diluting the filtered solution to the desired volume. The purification of UO_3 was accomplished by the peroxide method.(3)

Mallinckrodt's UO_3 was dissolved in a perchloric acid solution and diluted to a uranium concentration of 5%. Using a Beckman pH meter, the rapidly agitated solution was adjusted to pH 2 through the addition of a dilute ammonia solution. A 30% H_2O_2 solution was added dropwise, resulting in the precipitation of uranyl peroxide. The pH was kept at 2 by the simultaneous dropwise addition of ammonia. The hydrogen peroxide was added until further addition caused no change in pH. The slurry was then stirred for 1 hour and filtered through a 6-1/2" Buchner funnel containing coarse filter paper. The precipitate was washed with 1% H_2O_2 , which had been adjusted to a pH of 2 with perchloric acid. The precipitate was again washed with 1% H_2O_2 , filtered, and dried at 110°C . The cake was ground, placed in a large platinum dish, and heated at 350°C for 3 days.

Solutions prepared from this purified UO_3 yielded a negative brown ring test for nitrate.

Analysis for uranium(VI) in the perchlorate stock solutions was performed by a volumetric dichromate method which has been described previously.(4) The perchlorate concentration was checked by analysis using the method of Loebich,(5) which involves the precipitation of nitron perchlorate. Stock solutions of phosphoric and perchloric acids



were prepared from reagent grade acids and their concentrations determined by titration against standardized sodium hydroxide.

The method of continuous variations was applied to two series of solutions. In one series, the acidity was adjusted to approximately one molar with perchloric acid and the sum of the analytical concentrations of uranium(VI) and phosphoric acid held at 0.137M. Twelve solutions were prepared such that the uranium(VI) concentration varied from 16.7% to 100% of the sum of the uranium(VI) and phosphoric acid concentration.

In a second series of measurements, the acidity was adjusted to approximately 0.1M with perchloric acid and the sum of the uranium(VI) and phosphoric acid concentrations was 0.014M. The ionic strength of these solutions was held approximately constant at 0.14M by the addition of C. P. sodium perchlorate. In these 0.1M acid solutions, it was necessary to reduce the uranium(VI)-phosphoric acid concentration level to 0.014M in order to avoid the precipitation of $\text{UO}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}$. As a result of this lower concentration, it was found convenient to make optical density measurements in the region of the ultraviolet (280-310 $\text{m}\mu$), where higher molar extinction coefficients are encountered, rather than in the range 350-500 $\text{m}\mu$ used for the more concentrated 1M acid solutions.

RESULTS AND DISCUSSION

During the course of the continuous variation measurements in one molar perchloric acid, complete spectral curves were run on several of the solutions. These data are listed in Table 1, and plotted in part in Figure 1. It is evident from these curves that the addition of phosphoric acid increases the maxima of the uranium(VI) absorption spectrum and shifts them to longer wavelengths.

The continuous variation results are plotted in Figures 2 and 3 from the data listed in Tables 2 and 3. In the last column of these tables are listed the calculated values of the hydrogen ion concentration which would result if no complexing occurred. These calculated final acidity values are greater than one molar because the $\text{UO}_2(\text{ClO}_4)_2$ stock solution used in these measurements contained an appreciable excess of free perchloric acid. The quantity X which appears in the tables and figures is the ratio of the total phosphate to the sum M of the total phosphate and the total uranyl concentration in solution, i.e.,

Table 1

ABSORBANCY DATA FOR $\text{UO}_2(\text{ClO}_4)_2 - \text{H}_3\text{PO}_4$
MIXTURES IN 1M HClO_4 , $\Sigma\text{UO}_2^{++} + \Sigma\text{PO}_4^{-3} = 0.1374\text{M}$

Optical Density Readings at Various
Mole Ratios, $\Sigma\text{PO}_4^{-3} / \Sigma\text{UO}_2^{++}$

λ m/μ	0	1/5	1/3	1/2	1/1	2/1	3/1	5/1
350	0.404	0.380	0.369	0.363	0.310	0.234	0.174	0.116
354	0.333	0.288	0.267	0.248	0.195	0.138	0.099	0.067
358	0.328	0.265	0.243	0.219	0.166	0.112	0.076	0.056
362	0.390	0.318	0.290	0.259	0.194	0.130	0.095	0.070
366	0.307	0.260	0.241	0.220	0.171	0.123	0.087	0.063
370	0.358	0.290	0.267	0.239	0.179	0.120	0.089	0.061
374	0.349	0.300	0.274	0.253	0.196	0.134	0.099	0.069
378	0.323	0.279	0.269	0.240	0.190	0.133	0.101	0.069
382	0.303	0.330	0.306	0.279	0.215	0.146	0.112	0.078
386	0.431	0.376	0.358	0.331	0.262	0.185	0.139	0.098
390	0.551	0.470	0.442	0.409	0.324	0.222	0.190	0.115
394	0.652	0.574	0.543	0.500	0.395	0.273	0.208	0.143
398	0.678	0.622	0.604	0.567	0.463	0.334	0.254	0.175
402	0.821	0.757	0.703	0.650	0.521	0.367	0.280	0.191
406	0.917	0.847	0.792	0.745	0.603	0.431	0.330	0.225
410	0.860	0.835	0.800	0.771	0.653	0.477	0.366	0.249
414	0.980	0.900	0.840	0.794	0.649	0.465	0.355	0.239
418	0.998	0.955	0.884	0.840	0.684	0.489	0.375	0.255
420	0.930	0.902	0.865	0.821	0.698	0.511	0.394	0.268
424	0.773	0.775	0.755	0.738	0.644	0.478	0.373	0.250
428	0.798	0.743	0.708	0.668	0.556	0.402	0.308	0.205
432	0.720	0.691	0.660	0.630	0.529	0.389	0.300	0.203
436	0.519	0.539	0.535	0.527	0.468	0.354	0.277	0.185
440	0.403	0.406	0.400	0.390	0.341	0.259	0.199	0.133
444	0.362	0.353	0.337	0.325	0.275	0.200	0.155	0.106
448	0.287	0.281	0.279	0.273	0.234	0.171	0.134	0.098
452	0.209	0.210	0.206	0.203	0.173	0.129	0.102	0.070
456	0.175	0.177	0.170	0.165	0.141	0.107	0.076	0.058
460	0.138	0.158	0.157	0.156	0.138	0.105	0.076	0.059
464	0.110	0.128	0.131	0.134	0.122	0.096	0.069	0.053
468	0.108	0.112	0.110	0.108	0.093	0.071	0.054	0.039
472	0.118	0.117	0.114	0.109	0.092	0.065	0.052	0.038
476	0.080	0.103	0.103	0.106	0.097	0.074	0.058	0.042
480	0.031	0.056	0.063	0.070	0.071	0.062	0.047	0.034
484	0.022	0.034	0.036	0.041	0.040	0.033	0.025	0.021
488	0.036	0.036	0.033	0.034	0.022	0.019	0.016	0.014
492	0.036	0.036		0.036	0.027	0.021	0.017	0.014
496	0.012	0.017			0.022	0.018	0.014	0.012
500	0.005	0.007	0.008	0.011	0.009	0.008	0.007	0.008

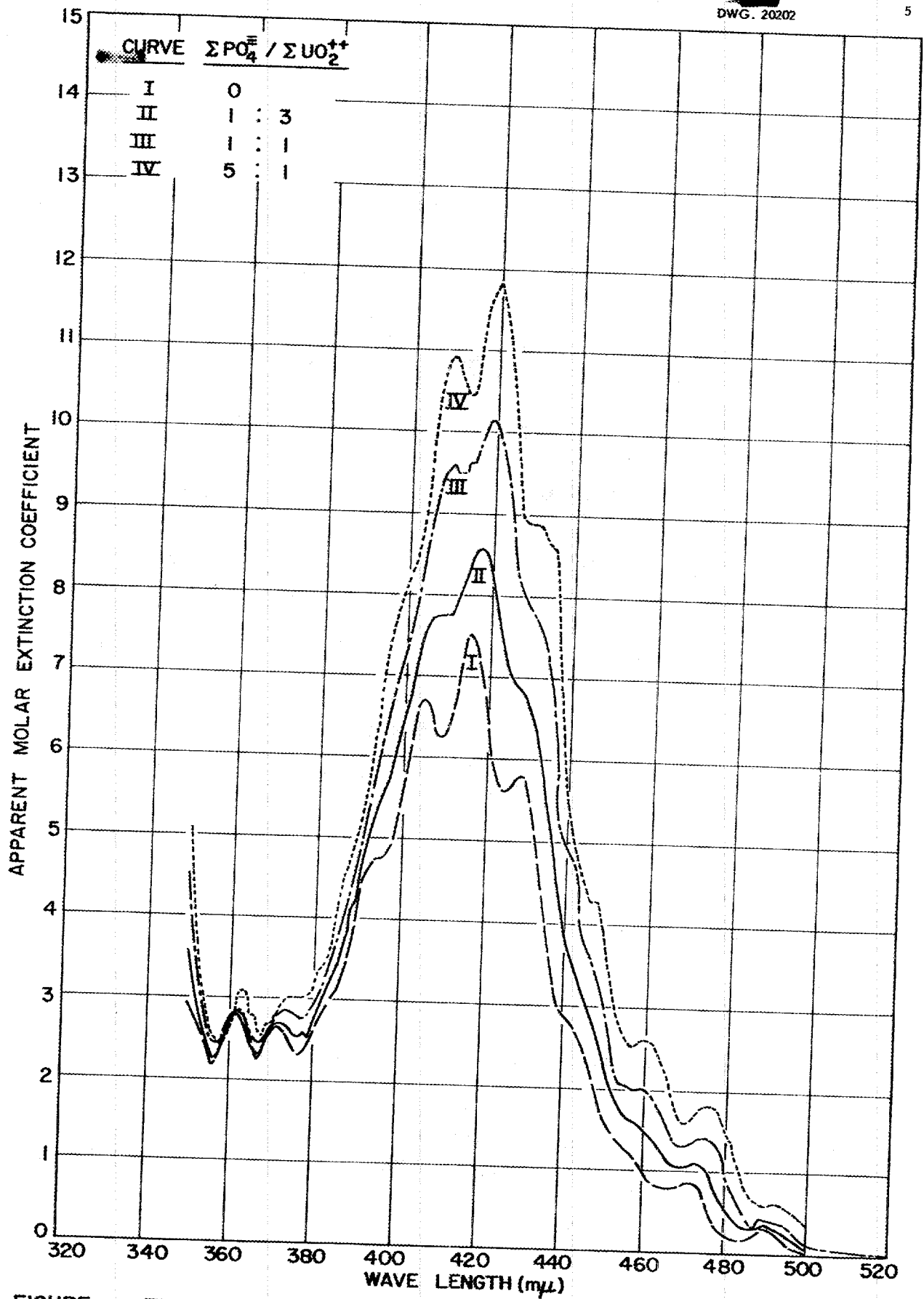


FIGURE 1. THE EFFECT OF H_3PO_4 ON THE ABSORPTION SPECTRA OF UO_2^{++} IN 1M HClO_4

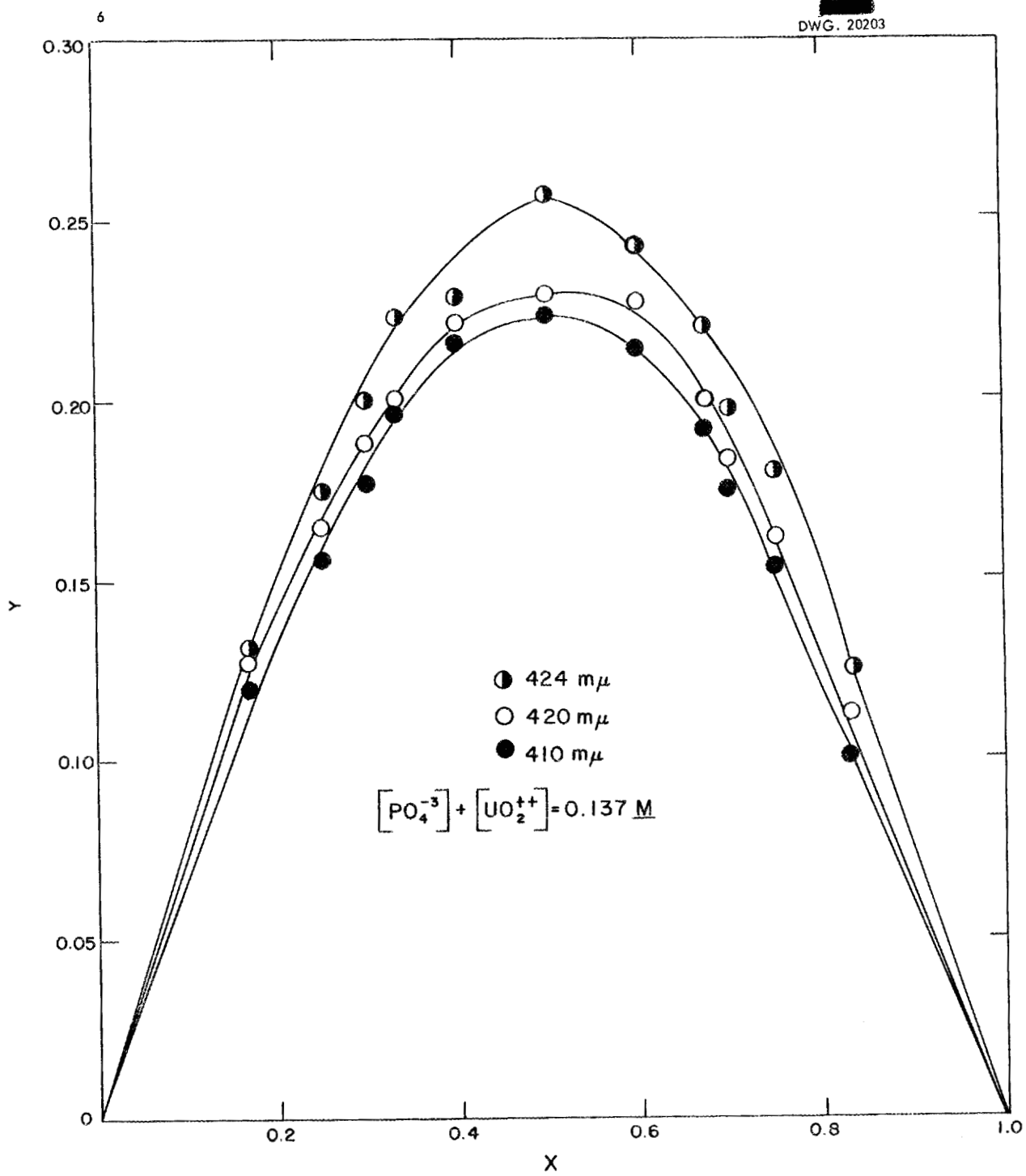


FIGURE 2. CONTINUOUS VARIATION METHOD APPLIED TO URANIUM VI PHOSPHATE SOLUTIONS, ONE MOLAR IN PERCHLORIC ACID

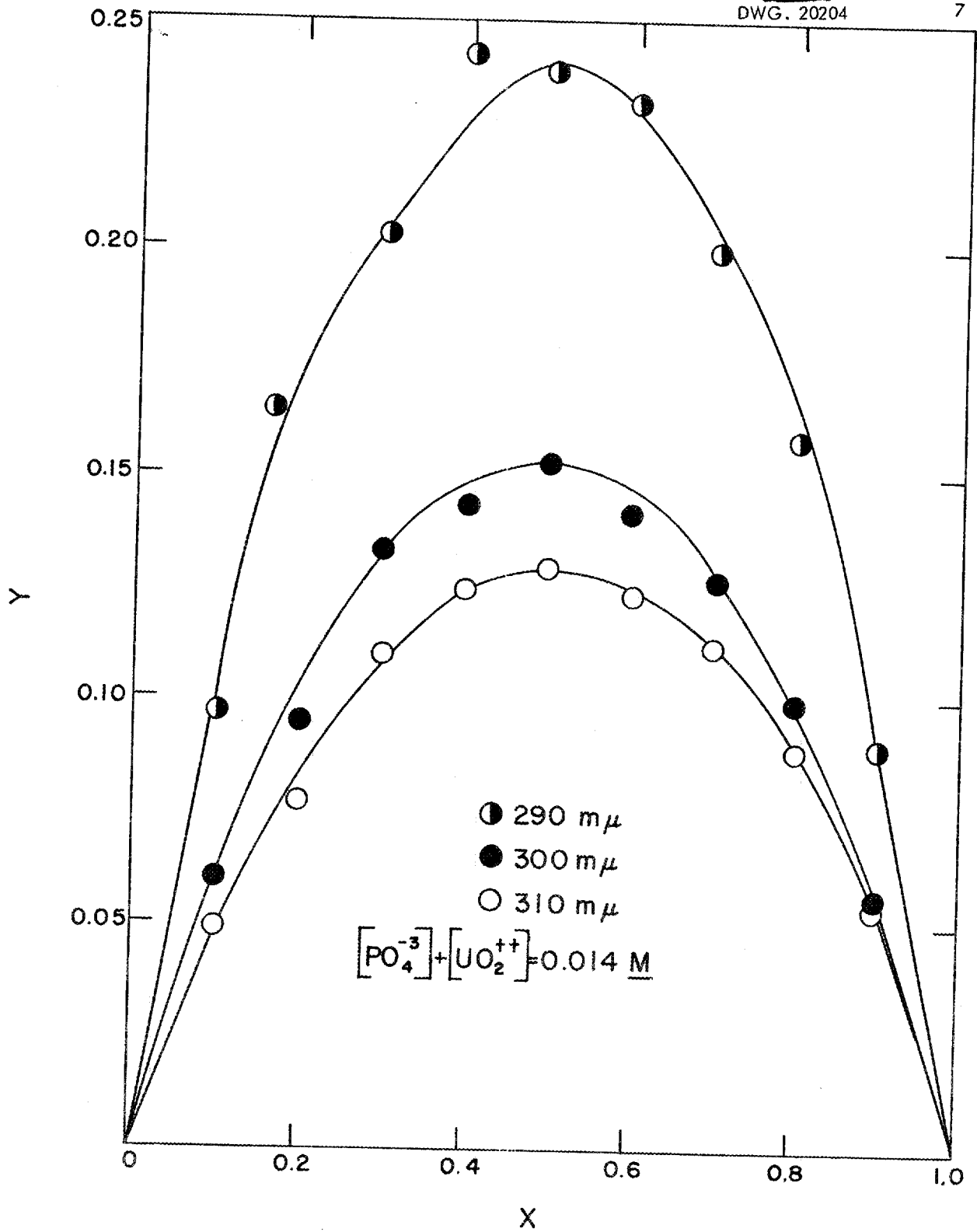
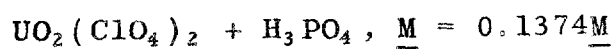


FIGURE 3. CONTINUOUS VARIATION METHOD APPLIED TO URANIUM VI PHOSPHATE SOLUTIONS; 0.1 MOLAR IN PERCHLORIC ACID

Table 2
CONTINUOUS VARIATION DATA IN 1M HClO₄ *

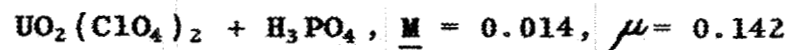


<u>X</u>	<u>Y₄₁₀</u>	<u>Y₄₂₀</u>	<u>Y₄₂₄</u>	<u>H⁺</u>
0.167	.120	.127	.131	1.19
0.250	.156	.165	.175	1.17
0.300	.177	.188	.200	1.16
0.333	.196	.201	.223	1.15
0.400	.216	.221	.229	1.14
0.500	.223	.229	.257	1.11
0.600	.214	.227	.243	1.09
0.667	.192	.201	.220	1.07
0.700	.175	.183	.198	1.07
0.750	.153	.161	.180	1.06
0.833	.109	.113	.125	1.04

*X and Y are defined on pages 3 and 10,
 respectively.

Table 3

CONTINUOUS VARIATION DATA IN 0.1M HClO₄ *



<u>X</u>	<u>Y₂₉₀</u>	<u>Y₃₀₀</u>	<u>Y₃₁₀</u>	<u>H⁺</u>
.1	.100	.061	.047	.0989
.2	.167	.097	.080	.0978
.3	.206	.135	.111	.0971
.4	.246	.146	.123	.0966
.5	.242	.155	.129	.0964
.6	.235	.146	.124	.0966
.7	.204	.132	.112	.0971
.8	.153	.102	.088	.0978
.9	.091	.062	.055	.0989

*X and Y are defined on pages 3 and 10, respectively.

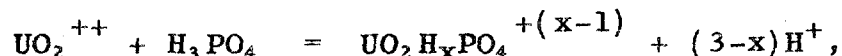
$$X = \frac{\sum \text{PO}_4^{-3}}{\sum \text{PO}_4^{-3} + \sum \text{UO}_2^{++}} = \frac{\sum \text{PO}_4^{-3}}{M}$$

The quantity Y is the difference between the observed optical density and that calculated for the case in which no complexing occurs. Thus, since the extinction coefficients for phosphoric acid at the wavelengths used may be neglected, and since uranyl ion in perchloric acid has been shown to obey Beer's law, (6) then

$$Y = d - \epsilon_{\text{U}} M (1-X) \quad (1)$$

wherein d is the observed optical density and ϵ_{U} is the corresponding molar extinction coefficient for uranyl ion.

The continuous variation curves in Figures 2 and 3 clearly indicate the presence of complex species in which the phosphate to uranyl ratio is one. Thus, a general equilibrium may be written,



for which the equilibrium quotient is

$$K_{1,x} = \frac{[\text{UO}_2\text{H}_x\text{PO}_4^{+(x-1)}] [\text{H}^+]^{(3-x)}}{[\text{H}_3\text{PO}_4] [\text{UO}_2^{++}]}$$

in which the bracketed quantities denote molar concentrations. Taking the acidity as one molar, a total formation constant K_1 may be defined as,

$$K_1 = \sum_{x=0}^x K_{1,x} = \frac{[\text{UO}_2\text{PO}_4^-] + [\text{UO}_2\text{HPO}_4] + \dots + [\text{UO}_2\text{H}_x\text{PO}_4^{+(x-1)}]}{[\text{H}_3\text{PO}_4] [\text{UO}_2^{++}]} \quad (2)$$

or

$$K_1 = \frac{C_1}{[H_3PO_4][UO_2^{++}]} \quad (3)$$

wherein C_1 represents the total concentration of all the 1:1 complex species.

Assuming these to be the only complexes present in appreciable concentration in these solutions, the formation constant K_1 may be evaluated from the continuous variation data as follows:

Since

$$[UO_2^{++}] = M(1-X) - C_1 \quad (4)$$

and

$$[H_3PO_4] = MX - C_1 \quad (5)$$

then,

$$\begin{aligned} [UO_2^{++}][H_3PO_4] &= [MX - C_1][M(1-X) - C_1] \\ &= M^2X(1-X) - C_1(M - C_1) \end{aligned} \quad (6)$$

substituting Eq. 6 into Eq. 3 and rearranging terms,

$$1/K_1 = \frac{M^2X(1-X)}{C_1} - M + C_1 \quad (7)$$

From Eq. 1, we have

$$Y = \epsilon_U[UO_2^{++}] + \epsilon_1 C_1 - \epsilon_U M(1-X)$$

wherein ϵ_1 is the average molar extinction coefficient of the one-to-one complexes. From Eq. 4,

$$Y = \epsilon_U [M(1-X) - C_1] + \epsilon_1 C_1 - \epsilon_U M(1-X)$$

or

$$Y = \epsilon_1 C_1 - \epsilon_U C_1 = C_1(\epsilon_1 - \epsilon_U)$$

Thus,

$$Y = AC_1$$

and

$$C_1 = \frac{Y}{A} \tag{8}$$

wherein A is a constant equal to $\epsilon_1 - \epsilon_U$. Substituting Eq. 8 into Eq. 7 gives

$$1/K_1 = \frac{M^2 X(1-X)A}{Y} - M + \frac{Y}{A}$$

which, upon rearrangement, gives

$$\frac{X(1-X)}{Y} = - \left[\frac{1}{M^2 A^2} \right] Y + \frac{1+K_1 M}{K_1 M^2 A} \tag{9}$$

It is evident from Eq. 9 that a plot of $\frac{X(1-X)}{Y}$ vs. Y should result in a straight line of slope \underline{S} equal to $-1/M^2 A^2$ and intercept \underline{I} equal to $\frac{1+K_1 M}{K_1 M^2 A}$. These quantities permit the calculation of K_1 ; thus,

$$A = \frac{1}{M \sqrt{-S}}$$

Table 4
THE DETERMINATION OF K_1 FROM THE
CONTINUOUS VARIATION DATA IN 1M HClO_4 *

<u>X(1-X)</u>	$\lambda = 410 \text{ m}\mu$		$\lambda = 420 \text{ m}\mu$		$\lambda = 424 \text{ m}\mu$	
	<u>Y</u>	<u>$\frac{X(1-X)}{Y}$</u>	<u>Y</u>	<u>$\frac{X(1-X)}{Y}$</u>	<u>Y</u>	<u>$\frac{X(1-X)}{Y}$</u>
.139	.120	1.16	.127	1.09	.131	1.06
.188	.156	1.21	.165	1.14	.175	1.07
.210	.177	1.19	.188	1.12	.200	1.05
.222	.196	1.13	.201	1.10	.223	1.00
.240	.216	1.11	.221	1.09	.229	1.05
.250	.223	1.12	.229	1.09	.257	.97
.240	.214	1.12	.227	1.06	.243	.99
.222	.192	1.16	.201	1.10	.220	1.01
.210	.175	1.20	.183	1.15	.198	1.06
.188	.153	1.23	.161	1.17	.180	1.04
.139	.109	1.28	.113	1.23	.125	1.11

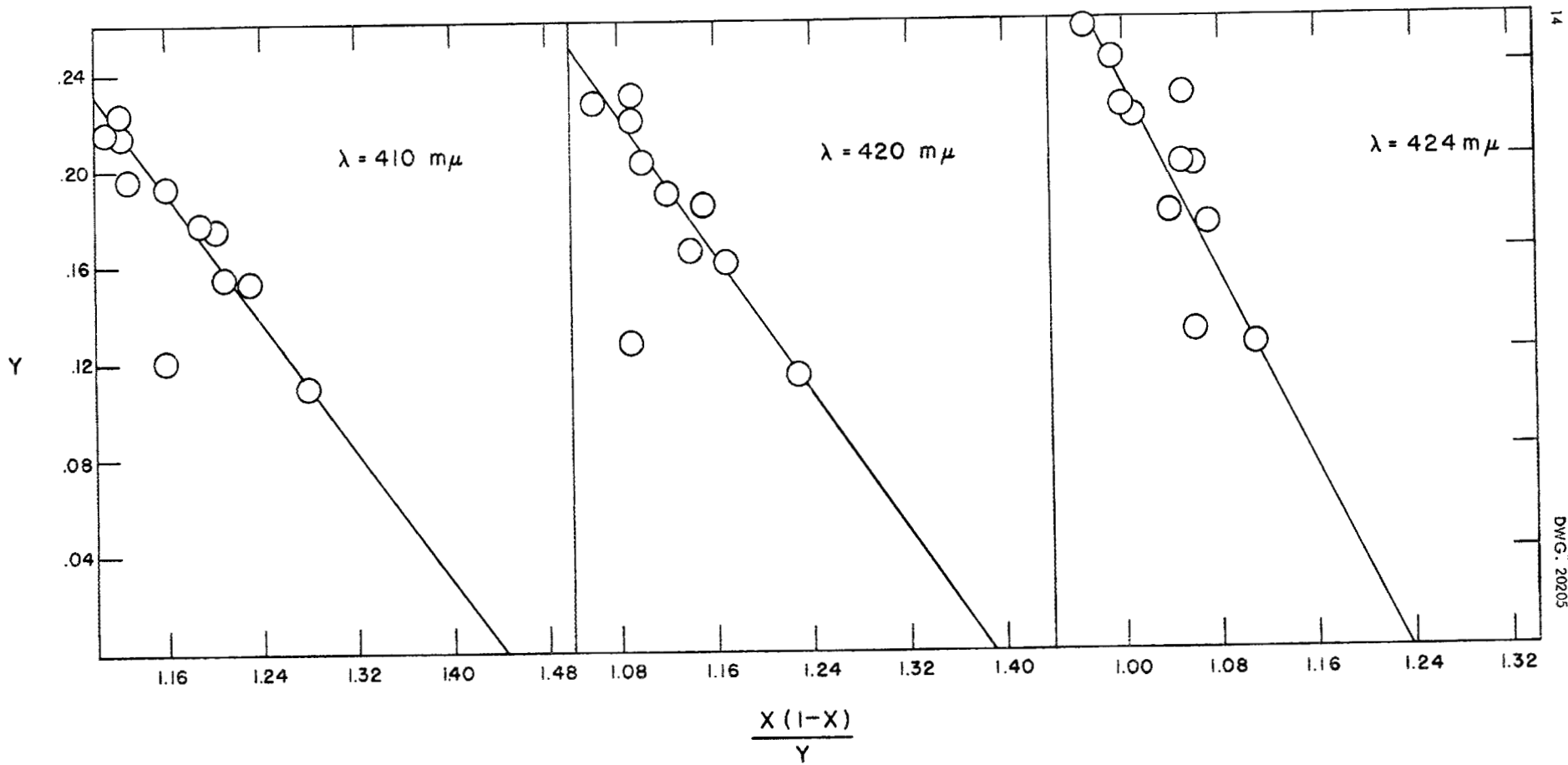


FIGURE 4. THE DETERMINATION OF K_1

and

$$K_1 = \frac{1}{IM^2A - M}$$

or

$$K_1 = \frac{\sqrt{-S}}{M [I - \sqrt{-S}]}$$

The application of this graphical method for the determination of K_1 to the data in IM acid is shown in Table 4 and Figure 4. The results are summarized below:

	<u>410 mμ</u>	<u>420 mμ</u>	<u>424 mμ</u>
S:	-1.48	-1.40	-1.04
I:	1.44	1.39	1.24
K_1 :	38	41	34

The A values which correspond to these values of K_1 are:

	<u>410 mμ</u>	<u>420 mμ</u>	<u>424 mμ</u>
A:	5.96	6.17	7.14

The uncertainty of the individual Y values is larger for the low X values since here the quantity results from the difference between two relatively large numbers. Accordingly, in plotting the three lines in Figure 4, the points corresponding to $X = 0.5$ to 0.833 were favored. The resulting slopes have an estimated uncertainty of $\pm 20\%$, giving A to $\pm 10\%$ and K_1 to perhaps $\pm 30\%$. Thus the agreement between the above three determinations is better than could be expected from the accuracy of the data. In this calculation, no attempt has been made to correct for the relatively small variation in the acidity of the solutions used (Table 3), since it can be shown that the resulting changes in K_1 are within the uncertainty of the present determination. From the above values,

$$K_1 = 38 \pm 12.$$

A similar graphical treatment of the 0.1M acid data results in positive S values, which is a physically meaningless result indicating distortion of the continuous variation curve from that to be expected for only one-to-one complex formation. Whereas it is possible to deduce on the basis of additional K values to be presented in a later report that the higher complexes are not appreciably abundant in the 1M perchloric acid solutions involved in the present measurements, no such simplifying condition can be deduced for the 0.1M acid solutions. The possible interference of higher complexes here, along with the generally less accurate ultraviolet spectral data*, evidently limits the resulting continuous variation curve to only a qualitative interpretation.

The present results give no information concerning the average number of hydrogen ions involved in the one-to-one complexes. The solubility results of G. R. Leader⁽¹⁾ suggest

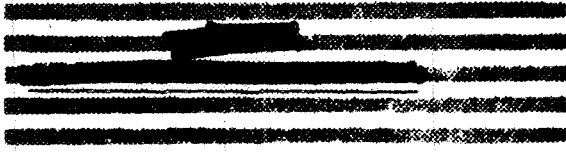


On the basis of solubility results to be presented in a subsequent report, one may suggest



also to be a contributing equilibrium in acid solution. At any rate, whatever number of different one-to-one species exist in solution, K_1 is the sum of their formation quotients in 1M perchloric acid (Eq. 2). This matter will be discussed further in later reports.

*In the wavelength range (290-310 m μ) used here, the absorbancy increases rapidly with decreasing wavelength for all the solutions, resulting in a high dependence of the measured optical densities on the precision of wavelength selection.



REFERENCES

1. G. R. Leader, "Solubility of Uranyl Phosphate in UNH Solutions, Progress Report, August 15, 1944 to October 1, 1944," Chemistry Division, Clinton Laboratories, CN-2195,
2. Job, Ann. Chim., (10), 9, 113(1928).
3. a. D. W. Mogg and C. E. Larson, "Factors Affecting the Precipitation of Uranium Peroxide," Clinton Engineer Works, Tennessee Eastman Corporation, C-0.375.5, 1946.
b. K. B. Brown and C. E. Larson, "Precipitation of Uranium Peroxide from Highly Contaminated Solutions," Clinton Engineer Works, Tennessee Eastman Corporation, C-0.375.7, 1946.
4. J. M. Schreyer and C. F. Baes, Jr., "The Volumetric Determination of Uranium(VI) in Phosphate Solutions," Oak Ridge National Laboratory, Y-12, ORNL-1292, May 7, 1952; Anal. Chem. 25, 644(1953).
5. Frank J. Welcher, Organic Analytical Reagents, D. Van Nostrand Company, Inc., New York, N. Y., Volume III, 1947, p. 144.
6. J. Sutton, J. Chem. Soc., S-275(1949).

