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THE CHEMISTRY OF URANIUM(VI) ORTHOPHOSPHATE SOLUTIONS: PART III, THE SOLUBILITY BEHAVIOR OF $UO_2HPO_4 \cdot 4H_2O$ IN PERCHLORIC ACID SOLUTIONS

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

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THE CHEMISTRY OF URANIUM(VI) ORTHOPHOSPHATE SOLUTIONS: PART III, THE SOLUBILITY BEHAVIOR OF $UO_2HPO_4 \cdot 4H_2O$ IN PERCHLORIC ACID SOLUTIONS

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July 1, 1953

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ABSTRACT

The solubility behavior of $UO_2HPO_4 \cdot 4H_2O$ in perchloric acid solution has been determined as a function of the uranyl perchlorate, phosphoric acid, and hydrogen ion concentrations. These results, as well as those in pure phosphoric acid solution (ORNL-1578), have been interpreted in terms of the formation of four complexes in solution: $UO_2H_2PO_4^{+}$, $UO_2H_3PO_4^{++}$, $UO_2(H_2PO_4)_2$ and $UO_2(H_2PO_4)_2(H_3PO_4)$.

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THE CHEMISTRY OF URANIUM(VI) ORTHOPHOSPHATE SOLUTIONS: PART III, THE SOLUBILITY BEHAVIOR OF $UO_2HPO_4 \cdot 4H_2O$ IN PERCHLORIC ACID SOLUTIONS

INTRODUCTION

In the first report of this series,[1] spectrophotometric evidence was presented indicating the formation of complexes of the type $UO_2H_xPO_4^{+(x-1)}$ in uranyl phosphate, perchloric acid solution. A total formation quotient was determined in 1M perchloric acid ($K_1 = 38 \pm 12$). The second report[2] was concerned with the solubility behavior of three uranyl phosphates - $(UO_2)_3(PO_4)_2 \cdot 6H_2O$,* $UO_2HPO_4 \cdot 4H_2O$ and $UO_2(H_2PO_4)_2 \cdot 3H_2O$ - in pure phosphoric acid solution at 25°C. The concentration ranges in which these solids were found to be the stable phases are:

$(UO_2)_3(PO_4)_2 \cdot 6H_2O$	$<0.014\underline{M}$ $\sum PO_4^{-3}$
$UO_2HPO_4 \cdot 4H_2O$	$0.014 - 6.1\underline{M}$ $\sum PO_4^{-3}$
$UO_2(H_2PO_4)_2 \cdot 3H_2O$	$>6.1\underline{M}$ $\sum PO_4^{-3}$

In the present report, the solubility measurements are extended to perchloric acid solutions, the solubility behavior of $UO_2HPO_4 \cdot 4H_2O$ being determined as a function of the phosphoric acid concentration, the uranyl ion concentration and the hydrogen ion concentration. In addition, all the solubility results presented in this and the previous report are discussed in terms of complex ion formation.

A similar but less comprehensive series of solubility measurements in nitric acid solution has been reported by G. R. Leader;[3] however, the complication of nitrate

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*The state of hydration of the normal phosphate, which is the stable solid phase in dilute phosphoric acid solution, is in some doubt. The hexahydrate appears to result when the solid is separated from the mother liquor and dried in the air.

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complexing effects limits the usefulness of his results in any detailed examination of uranyl phosphate complex formation.

Due to limitations imposed by the solubility behavior of $UO_2HPO_4 \cdot 4H_2O$ and the stabilities of the complexes involved, the present solubility studies were confined to fairly concentrated perchloric or phosphoric acid solutions. Since the control of ionic strength is of doubtful value in such solutions, these studies were not limited to constant ionic strength. However, many of the equilibria involved appear to produce no change in the ionic charge type; e.g.,

$$UO_2^{++} + H_3PO_4 = UO_2H_3PO_4^{++}$$

$$\underline{UO_2HPO_4} + H_3PO_4 = UO_2(H_2PO_4)_2$$

therefore, the assumption of constancy of the concentration equilibrium quotients, which will be made in discussing the results, is probably justified in these cases.

It is desirable to point out here the system of notation which will be used in referring to equilibrium quotients for reactions involving uranyl phosphates, uranyl ion, and phosphoric acid. The K values appear usually in the form K_n or K_n^s, wherein the subscript n refers to the number of phosphate radicals per uranyl ion in the complex and the superscript s, when it appears, denotes that the equilibrium involves a solid phase ($\underline{UO_2HPO_4} = UO_2HPO_4 \cdot 4H_2O$, unless otherwise indicated). Thus for the two equilibria

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

and

$$\underline{UO_2HPO_4} + (n-1)H_3PO_4 = UO_2H_x(PO_4)_n^{+(2-3n+x)} + (3n-2-x)H^+$$

the concentration equilibrium quotients are denoted respectively by K_n and K_n^s. When it is desirable to distinguish between two complexes of the same n value, but with different x values (x referring to the number of H atoms), then x is included as a second subscript in the ex-

pression; i.e., $K_{n,x}$ or $K^{s}_{n,x}$. Finally, K_s and K_p, respectively, have been used to denote the concentration equilibrium quotients for the equilibria

$$\underline{UO_2HPO_4} + 2H^+ = UO_2^{++} + H_3PO_4$$

$$H_3PO_4 = H^+ + H_2PO_4^-$$

EXPERIMENTAL

The solubility of $UO_2HPO_4 \cdot 4H_2O$ was measured in two series of 1M perchloric acid solutions at 25°C; the first series contained 0 - 0.5M total uranium and the second, 0 - 3.1M total phosphate. The solubility measurements were carried out by shaking $UO_2HPO_4 \cdot 4H_2O$ with a solution of known initial composition (containing either $UO_2(ClO_4)_2$ or phosphoric acid). The preparation of this salt and the solubility apparatus employed have already been described.(2)

Rate of dissolution studies of $UO_2HPO_4 \cdot 4H_2O$ in 1M perchloric acid indicated that with sufficient agitation, saturation was reached in 15 minutes or less.* Various checks throughout the range of solution composition studied indicated that with the usual shaking procedure equilibrium was established in less than three days. To insure equilibrium in all the measurements, the samples were shaken from 11 to 21 days.

The saturated mother liquors were removed from the shaker flask by means of the pressure filter apparatus described previously,(2) and were sampled by means of calibrated pipettes or pycnometers depending on the viscosity of the solutions. After the determination of the density of the mother liquors, they were analyzed for uranium, phosphate and perchlorate according to the methods described in the previous reports.(1,2)

In most cases, filtration was not carried to completion, and the residual slurries were removed for analysis. These slurries were weighed, dissolved in a minimum amount of concentrated sulfuric acid (about 3 ml), made up to 100 ml volume with 7.5% sulfuric acid, and analyzed for uranium, phosphate and perchlorate. Due to limitations in analytical

---

*In these experiments vigorous stirring was employed.

accuracy and the low percentage of hydrate water in the solid, slurry analysis were mainly useful in confirming the 1:1 ratio of uranyl to phosphate in the compound.

In a few cases, solid samples were obtained by removing all the mother liquor, washing the solid with water and acetone, and drying in air for 12 hours. Microscopic examination of these samples proved very useful in detecting the tetragonal crystals characteristic of $UO_2HPO_4 \cdot 4H_2O$ and thus confirming that the initial solid phase had remained unchanged. A few solid samples were subjected to X-ray diffraction analysis with the same result.

Measurements to determine the acidity dependence of the solubility of $UO_2HPO_4 \cdot 4H_2O$ were carried out in the range 0.1M to 1M $HClO_4$ at an approximately uniform ionic strength of 1.15M, maintained by the addition of sodium perchlorate. Each sample was shaken for a period of one to two days before the mother liquor was analyzed. The solid phase resulting from the run at the lowest acidity was subjected to chemical analysis and found to be the unchanged $UO_2HPO_4 \cdot 4H_2O$.

RESULTS AND DISCUSSION

a. Solubility Behavior in 1M Perchloric Acid

The results of the solubility measurements in 1M perchloric acid are summarized in Table I. The subscript f denotes final equilibrium concentrations and the superscript o denotes concentrations corrected to an acidity of one molar. The calculated $[\sum PO_4^{-3}]_f$ and $[ClO_4^-]_f$ values which appear in the table along with the analytically determined values were obtained from the starting composition of the solutions used, the initial and final solution densities, and the analytical $[\sum UO_2^{++}]_f$ values. The details of this calculation are described in the appendix.

In performing the controlled acidity solubility measurements, it was necessary to estimate the acidity effect of the dissolution process. In addition, where the resulting final acidities differed appreciably from one molar, an attempt was made to correct the solubility results accordingly. Both these steps require a detailed knowledge of the complexing equilibria involved, and since the present investigation has thus far not resulted in a complete scheme of such equilibria, the calculation of

Table I

THE SOLUBILITY BEHAVIOR OF $UO_2HPO_4 \cdot 4H_2O$ IN 1M $HClO_4$

All concentrations expressed in moles/l.

Run No.	$[\sum UO_2^{++}]_f$ Found	$[\sum PO_4^{-3}]_f$ Calc'd.	$[\sum PO_4^{-3}]_f$ Found	$[\sum ClO_4^{-}]_f$ Calc'd.	$[\sum ClO_4^{-}]_f$ Found	$[H^+]_f$ Calc'd.	$[\sum UO_2^{++}]^o$	$[\sum PO_4^{-3}]^o$
1	0.498	0.0551	0.0635	1.948	2.011	0.95	0.498	0.0606
2	0.400	0.0558	0.0623	1.805	1.860	1.01	0.400	0.0552
3	0.247	0.0518	0.0545	1.445	1.478	0.95	0.247	0.0572
4	0.221	0.0522	0.0548	1.389	1.428	0.95	0.221	0.0581
5	0.1890		0.0544	1.348	1.367	0.97	0.1890	0.058
6	0.1564	0.0553	0.0574	1.254	1.297	0.94	0.1564	0.0624
7	0.1431		0.0630	1.263	1.287	0.98	0.1431	0.066
8	0.1262		0.0660	1.235	1.227	0.98	0.1262	0.068
9	0.0839	0.0839		1.128		0.96	0.0883	0.0883
10	0.0804	0.1101	0.1137	1.169	1.176	1.01	0.0791	0.1101
11	0.0718	0.1233	0.1252	1.145	1.156	1.00	0.0712	0.1233
12	0.0727	0.1420	0.1426	1.150	1.146	1.00	0.0721	0.1420
13	0.0708	0.1975	0.200	1.132	1.156	0.99	0.0722	0.1975
14	0.0785	0.296	0.294	1.147	1.196	1.07	0.0734	0.296
15	0.0992	0.484	0.486	1.094	1.156	1.02	0.0978	0.484
16	0.1358	0.677	0.675	1.132	1.247	1.05	0.1317	0.677
17	0.273	1.412	1.411	1.284	1.558	1.19	0.258	1.142
18	0.666	2.87	2.70	1.466	1.930	1.35	0.638	2.87
19	0.757	3.11		1.267		1.17	0.744	3.11

The notation is explained on page 4.

$[H^+]_f$, $[\sum PO_4^{-3}]^o$, and $[\sum UO_2^{++}]^o$ described in the appendix involves several approximations which, however, are probably adequate in view of the fairly small corrections involved.

The corrected solubility data are plotted in Figure 1 (curve I), along with similar data of G. R. Leader for 1M nitric acid, which have been corrected here for acidity effects in a fashion similar to that applied to the present data. The corrections in this case, however, involve more uncertainty mainly because the estimated final acidities for Leader's results are farther from one molar. The coordinates of the points on such a plot represent the total concentrations of uranyl and phosphate in the corresponding saturated solutions. In the region of excess uranyl perchlorate or in excess phosphoric acid, the solubilities of the salt are equal respectively to the total phosphate or total uranyl concentrations.

The dissolution reaction for $UO_2HPO_4 \cdot 4H_2O$ in acid solution to form uncomplexed uranyl ion may be written

$$\underline{UO_2HPO_4} + 2H^+ = UO_2^{++} + H_3PO_4 \qquad (1)$$

and, at equilibrium, the solubility product K_S may be defined as

$$K_S = \frac{[UO_2^{++}][H_3PO_4]}{[H^+]^2} \qquad (2)$$

The dissolution of the salt to form a 1:1 complex, may be written

$$\underline{UO_2HPO_4} + (x-1)H^+ = UO_2H_xPO_4^{+(x-1)} \qquad (3)$$

for which the concentration equilibrium quotient $K^S_{1,x}$ is given by

$$K^S_{1,x} = \frac{[UO_2H_xPO_4^{+(x-1)}]}{[H^+]^{(x-1)}}$$

or, summing over all 1:1 complexes,

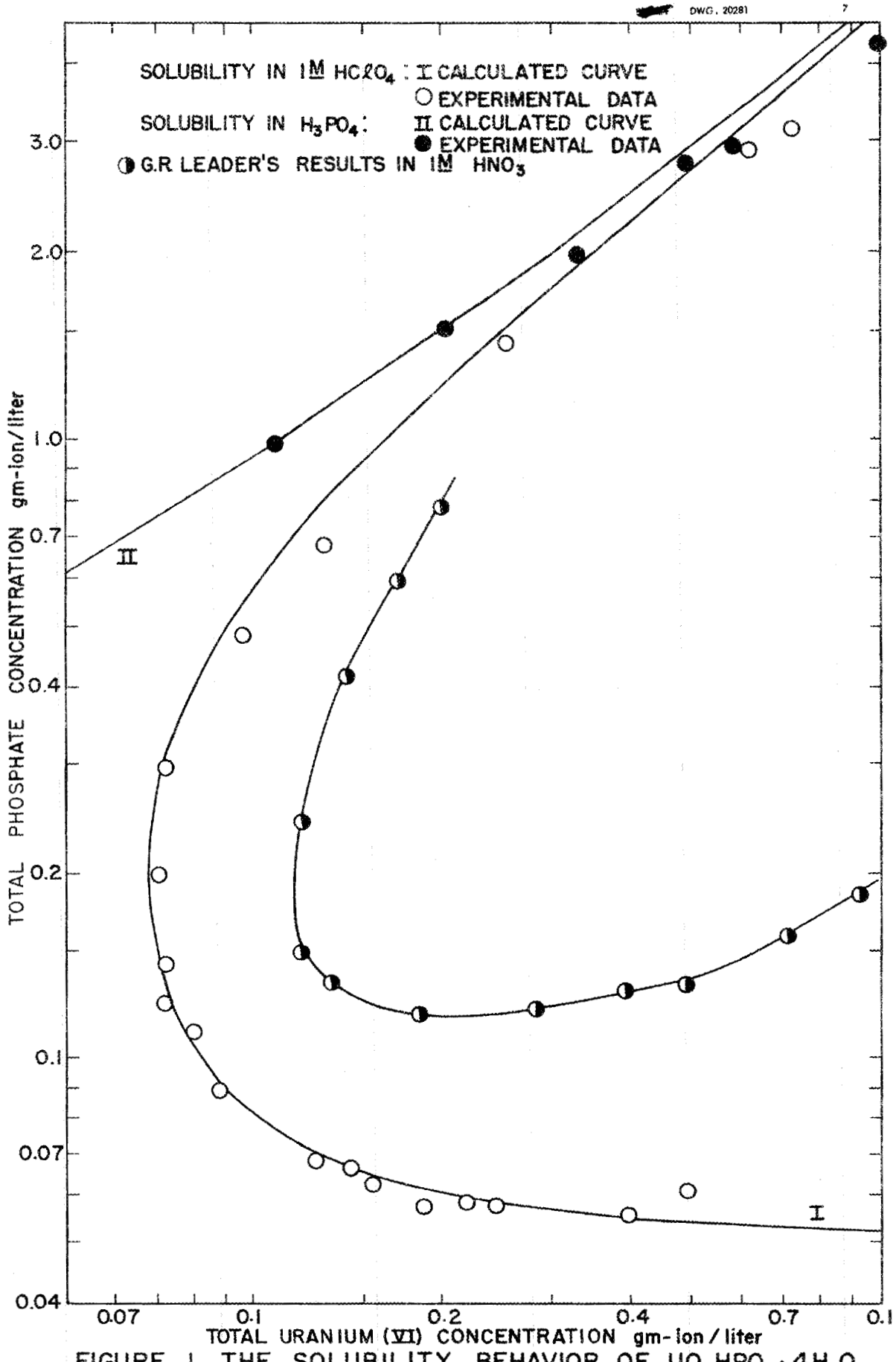

FIGURE 1. THE SOLUBILITY BEHAVIOR OF $UO_2HPO_4 \cdot 4H_2O$

$$K_1^s = \sum_{x=0}^{x} \frac{C_{1,x}}{[H^+]^{(x-1)}} \qquad (4)$$

Thus, at constant acidity, the total concentration of all 1:1 complexes, C_1, will be independent of $[UO_2^{++}]$ and $[H_3PO_4]$. If such complexes are the only ones which are relatively abundant in excess uranyl perchlorate, then (neglecting the small acid dissociation of H_3PO_4) the salt solubility S is given by

$$S = [H_3PO_4] + \sum C_{1,x}$$

and since, according to Eq. 1, $[H_3PO_4]$ must decrease as the uranyl concentration is increased, S evidently should decrease to a constant limiting value (equal to $\sum C_{1,x}$) as the uranyl perchlorate concentration is increased. It is evident from curve I in Figure 1 that this is at least approximately the case. The position deviation of the last point (0.5M $\sum UO_2^{++}$) is not serious in view of the rapidly increasing ionic strength.

It will be useful to point out in passing that

$$\frac{K_1^s}{K_s} = \sum_{x=0}^{x} \frac{C_{1,x}\,[H^+]^{(3-x)}}{[UO_2^{++}]\,[H_3PO_4]} = K_1 \qquad (5)$$

wherein K_1($= \sum K_{1,x}$) is the sum of the equilibrium quotients for all equilibria of the type

$$UO_2^{++} + H_3PO_4 = UO_2H_xPO_4^{+(x-1)} + (3-x)H^+$$

From Eq. 4, when $[H^+] = 1$,

$$C_1 = K_1^s \qquad (6)$$

wherein C_1 is the total concentration of the 1:1 complexes. If the 1;1 complexes are the only ones in appreciable abundance in the region of excess uranyl perchlorate, then from Eq. 2 one obtains

$$K_s = \left[\sum UO_2^{++} - K_1^s\right]\left[\sum PO_4^{-3} - K_1^s\right]$$

or

$$K_s = (\sum UO_2^{++})(\sum PO_4^{-3}) - K_1^s\left[\sum UO_2^{++} + \sum PO_4^{-3}\right] + (K_1^s)^2$$

Rearranging terms,

$$\sum UO_2^{++} + \sum PO_4^{-3} = \frac{1}{K_1^s}(\sum UO_2^{++})(\sum PO_4^{-3}) + K_1^s - \frac{1}{K_1} \quad (7)$$

wherein, K_1 has been substituted for K_1^s/K_s. According to this last equation, a plot of $(\sum UO_2^{++} + \sum PO_4^{-3})$ vs. $(\sum UO_2^{++})(\sum PO_4^{-3})$ should result in a straight line of slope $\frac{1}{K_1^s}$ and intercept $K_1^s - \frac{1}{K_1}$. This graphical method has been applied to the data in the range 0 - 0.344M excess uranyl in Table II and Figure 2. The resulting straight line plot has a slope of 1/0.051 and intercept 0.024, giving K_1^s = 0.051 (which corresponds to the limiting solubility), K_1 = 37, and K_s = 0.0014. Of these values, the most accurate is K_1^s since the slope of the plot is well defined by the points. The K_1 and K_s values are considerably more in doubt because of the uncertainty of the intercept at $(\sum PO_4^{-3})(\sum UO_2^{++}) = 0$. The value of K_1 = 37, however, is in complete agreement with the results of the continuous variation studies in 1M perchloric acid.[1]

The increasing solubility of $UO_2HPO_4 \cdot 4H_2O$ in 1M perchloric acid containing excess phosphoric acid indicates the formation in solution of complexes in which the phosphate to uranyl ratio is greater than unity. These data will not be used directly in the calculation of concentration equilibrium quotients for such complexes, however, since the contribution of these complexes to the salt solubility in one molar acid does not become appreciable compared to the 1:1 complexes until the total phosphate concentration is relatively large (>0.5M). The more dilute pure phosphoric acid solutions, in which the assumption of constant equilibrium quotients is probably more justified and for which concentration equilibrium quotients are calculated, will be discussed later.

Table II

THE DETERMINATION OF K_1^S AND K_1 FROM THE SOLUBILITY DATA IN 1M $HClO_4$

Run No.*	$\sum UO_2^{++}$	$\sum PO_4^{-3}$	$\sum UO_2^{++} + \sum PO_4^{-3}$	$[\sum UO_2^{++}][\sum PO_4^{-3}]$
2	0.400	0.0552	0.455	0.0221
3	0.247	0.0572	0.304	0.01412
4	0.221	0.0581	0.279	0.01283
6	0.1564	0.0624	0.219	0.00976
9	0.0883	0.0883	0.1766	0.00780

*Run Nos. 5, 7, and 8 have not been included in this table, since the uranium analyses were in some doubt, with the result that $[\sum PO_4^{-3}]_f$ could not be calculated with sufficient certainty (see Appendix).

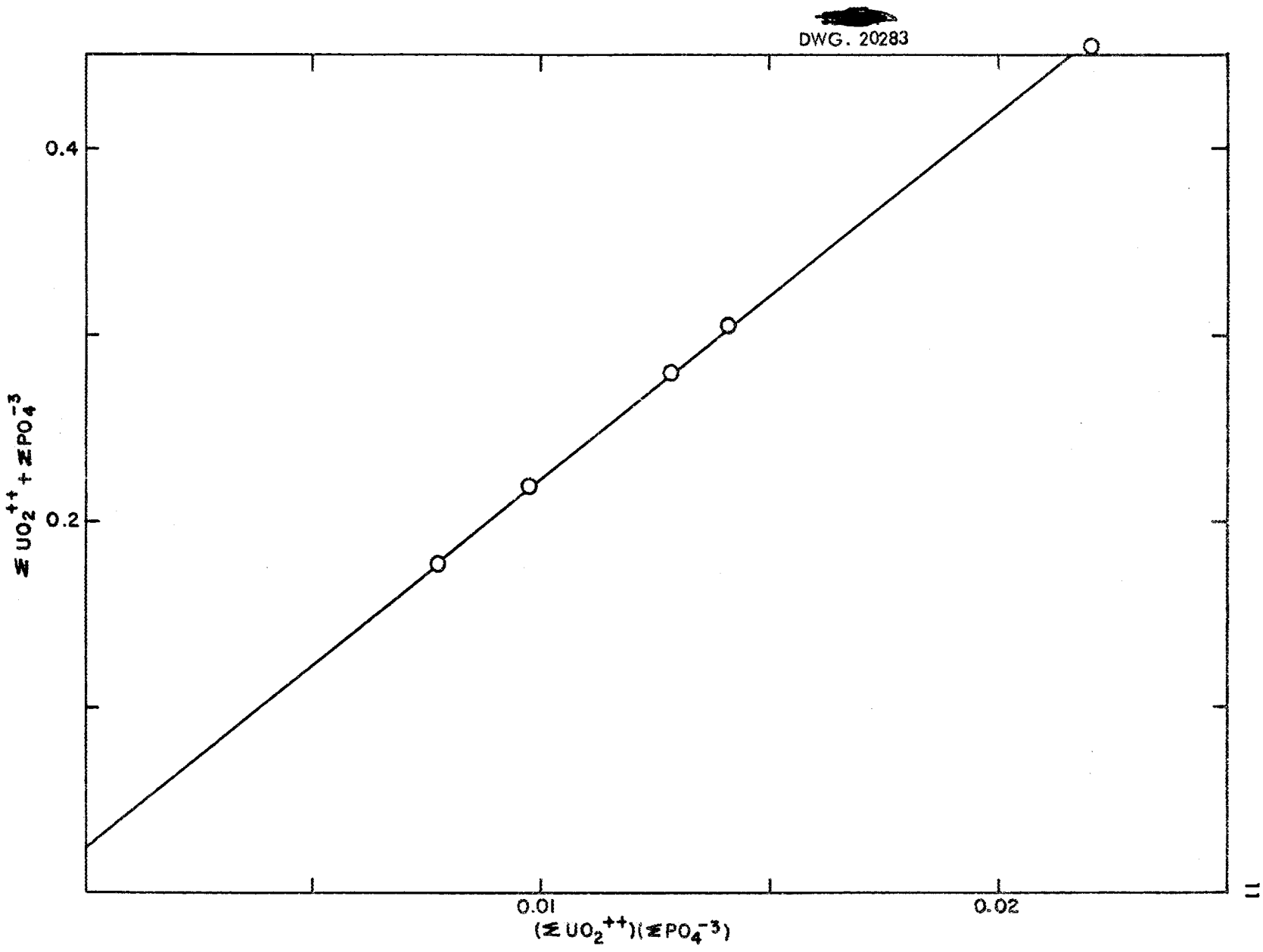

FIGURE 2. THE DETERMINATION OF K_1^S AND K_1

b. Acidity Dependence of $UO_2HPO_4 \cdot 4H_2O$ Solubility

G. R. Leader[3] has reported that the solubility of $UO_2HPO_4 \cdot 4H_2O$ in nitric acid solution is approximately proportional to the acidity. Neglecting acidity effects which accompany the dissolution of the salt and neglecting the effect of the changes in ionic strength which were involved, his results are consistent with the following equilibria,

$$\underline{UO_2HPO_4} + 2H^+ = UO_2^{++} + H_3PO_4 \qquad (1)$$

$$\underline{UO_2HPO_4} + H^+ = UO_2H_2PO_4^+;$$

$$K^S_{1,2} = \frac{[UO_2H_2PO_4^+]}{[H^+]} \qquad (8)$$

Thus, according to this scheme, the solubility $\underline{S}$ is given by,

$$S = \sum UO_2^{++} = [UO_2^{++}] + [UO_2H_2PO_4^+]$$

and noting that $[UO_2^{++}] \cong [H_3PO_4]$,

$$S = \sqrt{K_S}\,[H^+] + K^S_{1,2}\,[H^+]$$

or

$$S = [\sqrt{K_S} + K^S_{1,2}]\,[H^+]$$

wherein K_S and $K^S_{1,2}$ are defined in the usual way.

Since the acidity dependence of solubility could be crucial evidence in establishing the formulas of the 1:1 complexes which have been shown to exist in the acid solutions, these solubility measurements were repeated in perchloric acid at an approximately constant ionic strength of 1.15M. The results are summarized in Table III and plotted in Figure 3, along with the results of G. R. Leader for nitric acid. The correction for the acidity effect of

Table III

THE ACIDITY DEPENDENCE OF $UO_2HPO_4 \cdot 4H_2O$ SOLUBILITY IN $HClO_4$ SOLUTIONS; $\mu = 1.15$

Run No.	$[H^+]_{initial}$	$[\sum UO_2^{++}]_f$	$[H^+]_f$
20	0.1116	0.00414	0.1033
21	0.1674	0.00667	0.1541
22	0.2232	0.00955	0.2041
23	0.3340	0.01553	0.3029
24	0.5580	0.0315	0.4950
25	0.7812	0.0495	0.6823
9*	1.128	0.0839	0.9556

*This is the same run listed in Table I.

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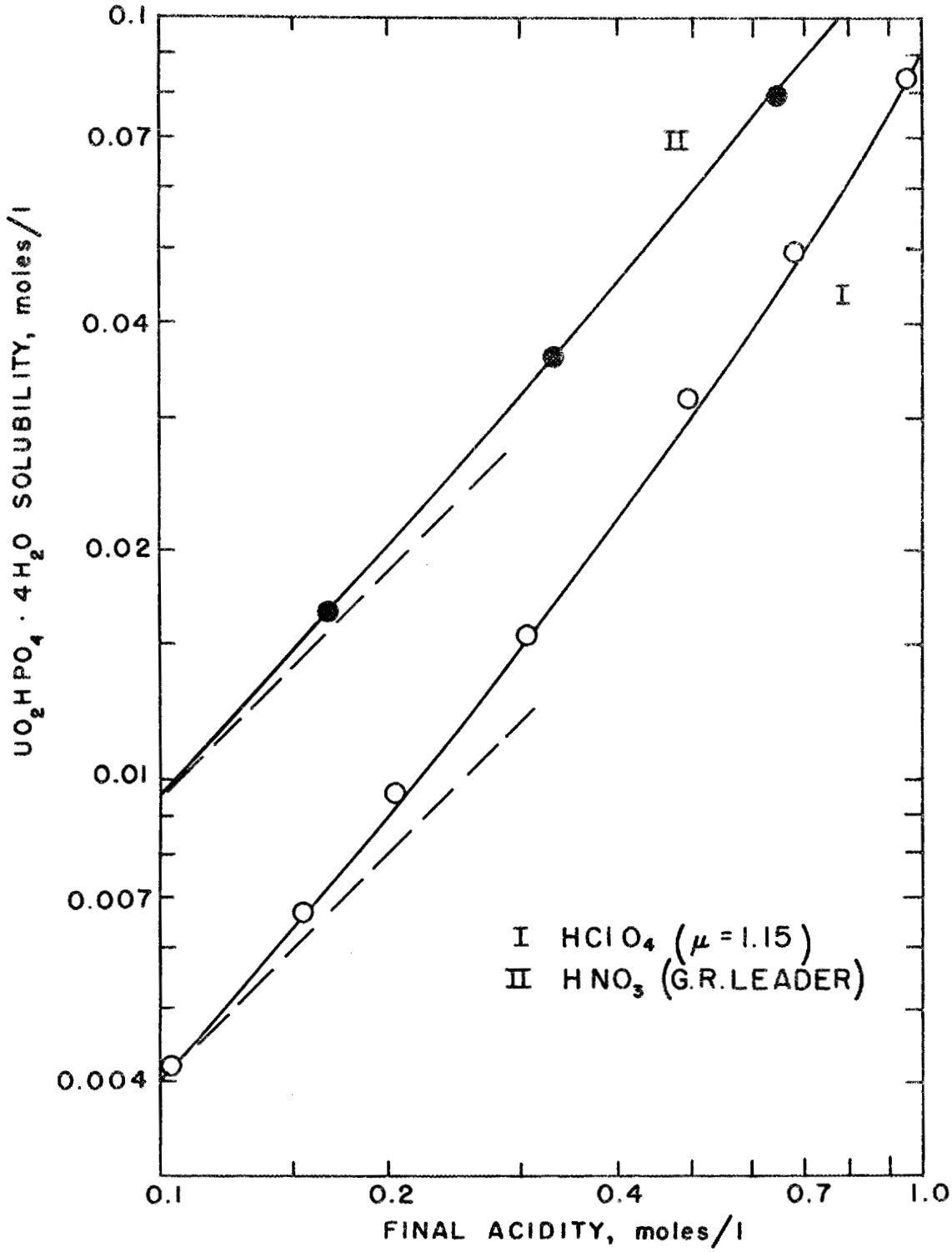

FIGURE 3. THE ACIDITY DEPENDENCE OF $UO_2HPO_4 \cdot 4H_2O$ SOLUBILITY IN $HClO_4$, μ = 1.15

the dissolution reaction was applied in the same fashion as in the 1M $HClO_4$ measurements;* i.e.,

$$[H^+]_{final} = [H^+]_{initial} - 2\sum UO_2^{++}$$

It is evident that in the solutions of constant ionic strength, the deviation of the perchloric acid data from a proportionality relationship (the deviation from the unit slope, which is indicated by the dashed line, in the log-log plot) is even larger than that exhibited by Leader's results. However, since, even at constant ionic strength, the activity coefficients of the various ionic species in solution will probably not remain constant over such a wide range of solution composition, the present results can be interpreted only in a qualitative fashion.

An acidity dependence higher than first power suggests that in addition to equilibria 1 and 8, one should also consider the equilibrium,

$$\underline{UO_2HPO_4} + 2H^+ = UO_2H_3PO_4^{++};$$

$$K^S_{1,3} = \frac{[UO_2H_3PO_4^{++}]}{[H^+]^2} \qquad (9)$$

Indeed, if equilibrium 8 is neglected, the acidity dependent data are adequately accounted for by $K_S = 0.0012$ and $K^S_{1,3} = 0.055$, a result in harmony with the K_1 and K_S values already obtained from the solubility data in 1M perchloric acid. More generally, the data are in agreement with

$$K^S_{1,2} + \sqrt{K_S} = 0.035; \quad K^S_{1,3} = 0.055$$

However, as yet unpublished potentiometric results suggest $K^S_{1,2} \sim 0.03$, which is not consistent with either of these schemes.**

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*This correction ignores the contribution of $UO_2HPO_4^+$ formation: the resulting error in acidity is probably less than 5% (cf. Appendix).

**In particular, the incorporation of both $K^S_{1,2}$ and K_S into this interpretation of the acidity dependent data requires that both values be changed considerably from those assigned ($K^S_{1,2} \sim 0.03$; $K_S = 0.0014$).

Until additional data are available, it can be said only that two forms of the one-to-one complex, $UO_2H_2PO_4^+$ and $UO_2H_3PO_4^{++}$, probably exist in acid solution and that the sum of the formation constants for all such complexes, K_1, is 38 ± 12 in 1M perchloric acid.

c. Solubility Behavior in Phosphoric Acid

The results of the $UO_2HPO_4.4H_2O$ solubility measurements in pure phosphoric acid[2] have also been plotted in Figure 1 (curve II) permitting a comparison with the 1M perchloric acid data. It is evident from the plot that the two solubility curves converge in excess phosphoric acid, suggesting that in such solutions the principle dissolution equilibrium is independent of acidity; i.e., that no hydrogen ions are liberated or consumed when $UO_2HPO_4.4H_2O$ reacts with H_3PO_4 molecules to produce complex species in solution. Thus one is led to conclude that the principle complex species in excess phosphoric acid are neutral:

$$\underline{UO_2HPO_4} + (n-1)H_3PO_4 = UO_2(H_2PO_4)_2(H_3PO_4)_{n-2} \qquad (10)$$

In order to confirm this conclusion, potential measurements were carried out on a series of saturated solutions from the phosphoric acid solubility runs, using a Beckman Model "G" pH meter. The results are plotted in Figure 4 along with the results of similar measurements on a series of pure phosphoric acid solutions. The agreement between the two sets of "measured pH" values is such that all the points may be fitted sufficiently well by a single curve.

From the measurements on pure phosphoric acid solutions, the following values for the first dissociation constant of phosphoric acid were calculated.*

$[H_3PO_4]$;	0.0179	0.0298	0.0596	0.0994	0.149	0.298	0.497	0.994
K_p';	0.009	0.009	0.010	0.011	0.012	0.015	0.019	0.032

These K_p' values are, of course, strictly empirical and certainly do not accurately represent the change of K_p with increasing phosphoric acid concentration. Thus, in yielding the "measured pH" values, the K_p' values must include the potential effect of the liquid junction,

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*The K_p' values were calculated from the equation

$$K_p = \frac{[H^+]^2}{\sum PO_4^{-3} - [H^+]}$$

$H_3PO_4(c)$ // KCl(Sat'd.),

as well as the medium effect resulting from the increasing phosphoric acid concentration. These values are useful, however, in that they permit the calculation of the two dashed curves in Figure 4, which represent the "measured pH" values which would result if a mole of hydrogen ion were consumed (curve I), or liberated (curve II) per mole of salt dissolved. By using these empirical Kp values, one corrects, at least approximately, the two calculated curves for the same effects which influence the "measured pH" values.

In general, one may conclude from the relatively small and random deviations of the saturated solution data that there is no appreciable acidity effect upon dissolution of $UO_2HPO_4 \cdot 4H_2O$ in phosphoric acid over the concentration range 0.001M to 1M H_3PO_4. Of course, below about 0.07M the salt solubility is so low that no appreciable acidity effects could reasonably be expected in any case, as indicated by the convergence of the curves in Figure 4; however, the lack of an acidity effect of dissolution above 0.07M provides additional evidence for the validity of Eq. 10 as the principle type of dissolution reaction in the upper concentration range.

It is, of course, possible to conceive of a series of complexes

$$----UO_2(H_2PO_4)(H_3PO_4)^{+}_{n-1};\quad UO_2(H_2PO_4)_2(H_3PO_4)_{n-2};$$

$$UO_2(H_2PO_4)_2(H_3PO_4)^{-}_{n-3}----$$

in which the distribution is such that, on the average, the uranium is involved in a neutral species. Such a distribution would result in a zero change in acidity upon dissolution of a uranium phosphate salt; however, since the concentration of each species has a different hydrogen ion dependence this specific distribution would occur at only one acidity and the

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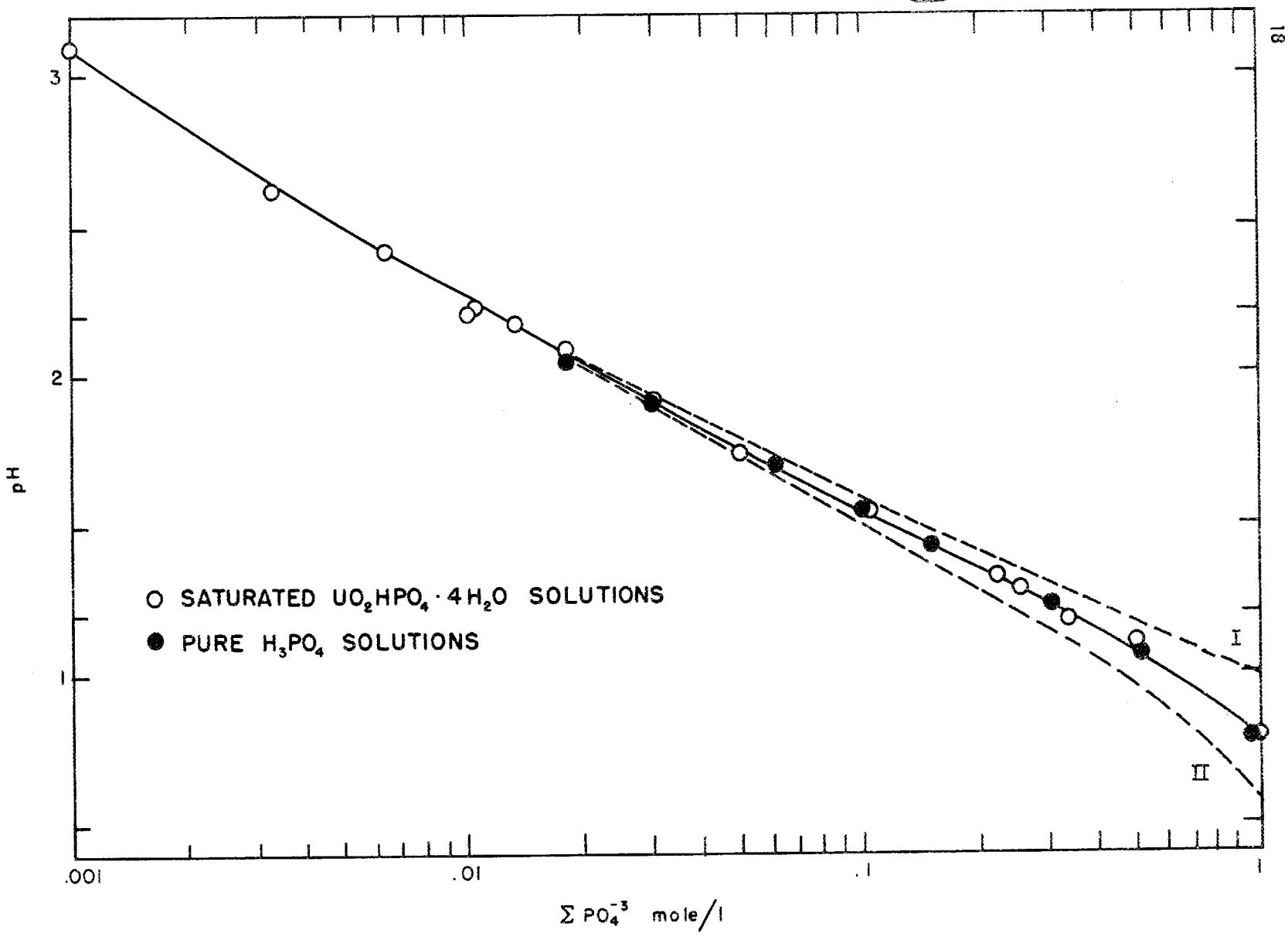

FIGURE 4. pH MEASUREMENTS IN PHOSPHORIC ACID SOLUTIONS

salt solubility, in general, would change with acidity in contrast to converging curves I and II in Figure 1.*

Assuming for the moment that the only important dissolution reaction of $UO_2HPO_4 \cdot 4H_2O$ in phosphoric acid is

$$\underline{UO_2HPO_4} + H_3PO_4 = UO_2(H_2PO_4)_2 \tag{11}$$

then

$$\sum UO_2^{++} = \left[UO_2(H_2PO_4)_2\right] \tag{12}$$

and, neglecting the dissociation of H_3PO_4,

$$\sum PO_4^{-3} = \left[H_3PO_4\right] + 2\left[UO_2(H_2PO_4)_2\right],$$

or

$$\sum PO_4^{-3} = \left[H_3PO_4\right] + 2\sum UO_2^{++} \tag{13}$$

---

*Another objection to such a scheme is that in the sequence of equilibria

$$UO_2(H_2PO_4)(H_3PO_4)_{n-1}^{+} = UO_2(H_2PO_4)_2(H_3PO_4)_{n-2} + H^+$$

$$K_a' = \frac{C_n^o\left[H^+\right]}{C_n^+}$$

$$UO_2(H_2PO_4)_2(H_3PO_4)_{n-2} = UO_2(H_2PO_4)_3(H_3PO_4)_{n-3}^{-} + H^+$$

$$K_a'' = \frac{C_n^-\left[H^+\right]}{C_n^o}$$

the acid constants, K_a' and K_a'', must be nearly equal in order that all three complexes, C_n^+, C_n^o and C_n^-, be appreciably abundant (i.e., that the ratios $\frac{C_n^o}{C_n^+}$ and $\frac{C_n^-}{C_n^o}$ be in the region of unity) for the same value of $\left[H^+\right]$. Such a similarity of consecutive acidity constants does not usually occur.

Substituting Eqs. 12 and 13 into the expression for the concentration equilibrium quotient for equilibrium 11, $K_2^S = \frac{[UO_2(H_2PO_4)_2]}{[H_3PO_4]}$, one obtains

$$K_2^S = \frac{\sum UO_2^{++}}{\sum PO_4^{-3} - 2\sum UO_2^{++}} .$$

Rearranging,

$$\sum UO_2^{++} = \left[\frac{K_2^S}{1+2K_2^S}\right] \sum PO_4^{-3} . \tag{14}$$

Thus, in the event that the solubility of UO_2HPO_4 in phosphoric acid were due entirely to the formation of a 2:1 complex, the solubility should be proportional to $\sum PO_4^{-3}$, or on a log-log plot, since

$$\text{Log} \sum UO_2^{++} = \log \sum PO_4^{-3} + \log \left[\frac{K_2^S}{1+2K_2^S}\right]$$

the slope of the curve should be +1.

Actually, the slope of the solubility curve (Figure 5) increases from a value of +1 at 0.014M $\sum PO_4^{-3}$ to +1.53 at 1M, indicating the presence of at least one higher complex - e.g., $UO_2(H_2PO_4)_2(H_3PO_4)$ - in the upper concentration range.

Considering the additional equilibrium,

$$\underline{UO_2HPO_4} + 2H_3PO_4 = UO_2(H_2PO_4)_2H_3PO_4 \tag{15}$$

one may write

$$\sum UO_2^{++} = C_2 + C_3 \tag{16}$$

wherein C_2 and C_3 denote the concentration of the 2:1 and 3:1 complexes, respectively. Since K_3^S is given by

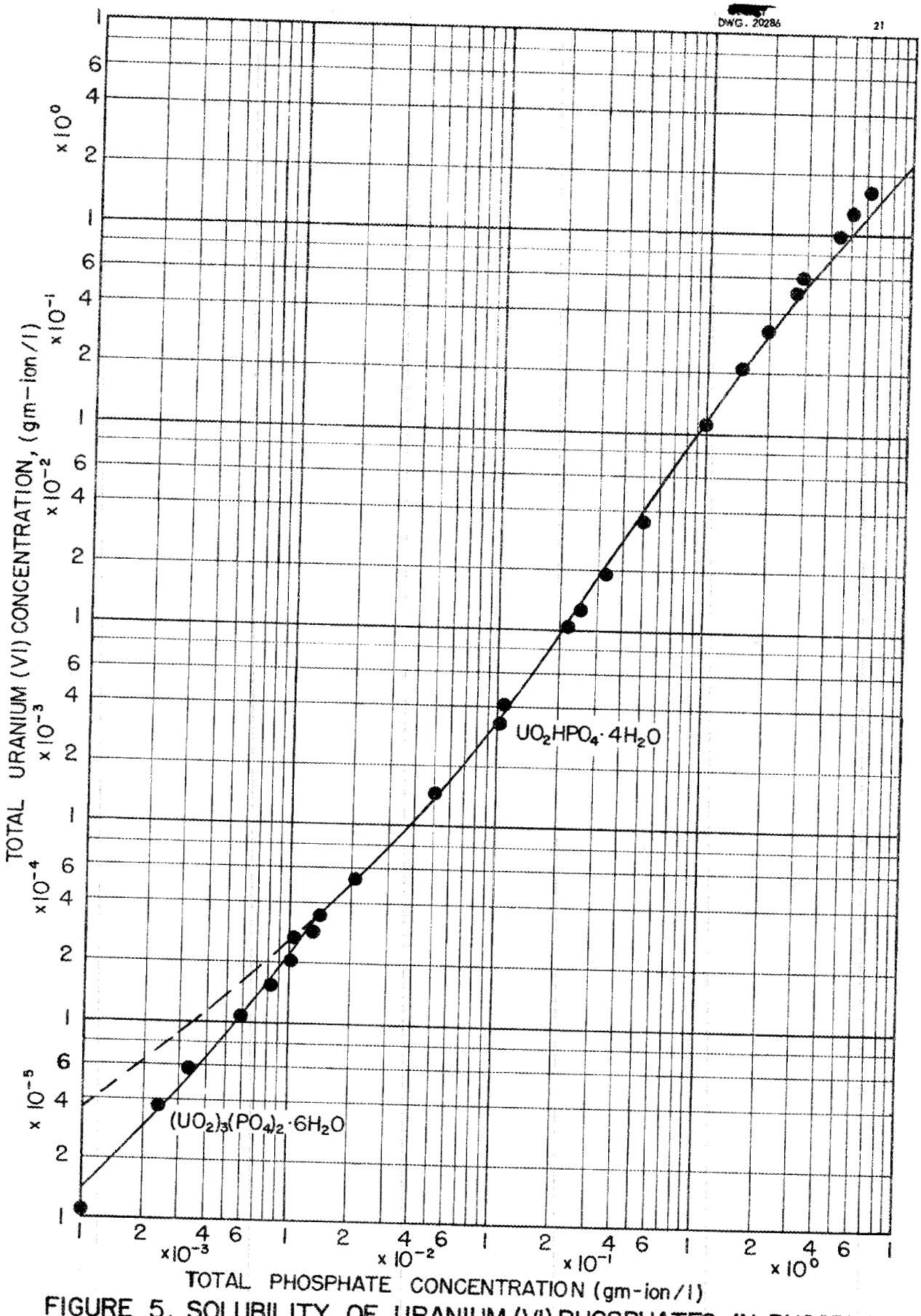

FIGURE 5. SOLUBILITY OF URANIUM (VI) PHOSPHATES IN PHOSPHORIC ACID SOLUTIONS

$$K_3^S = \frac{C_3}{[H_3PO_4]^2} , \tag{17}$$

and recalling that $K_2^S = C_2/[H_3PO_4]$, Eq. 17 may be written,

$$K_3^S = \frac{\sum UO_2^{++} - K_2^S[H_3PO_4]}{[H_3PO_4]^2} .$$

Rearranging terms,

$$\frac{\sum UO_2^{++}}{[H_3PO_4]} = K_3^S[H_3PO_4] + K_2^S \tag{18}$$

This equation indicates that a plot of $\frac{\sum UO_2^{++}}{[H_3PO_4]}$ vs. $[H_3PO_4]$ should result in a straight line of slope K_3^S and intercept K_2^S at $[H_3PO_4] = 0$.

It remains to evaluate $[H_3PO_4]$: If it is assumed that only the 2:1 and 3:1 complexes are present, then including the primary dissociation of phosphoric acid,

$$\sum PO_4^{-3} = [H_3PO_4] + 2C_2 + 3C_3 + (K_p[H_3PO_4])^{1/2} \tag{19}$$

wherein K_p is the first dissociation constant of phosphoric acid. The term $(K_p[H_3PO_4])^{1/2}$ is equal to $[H_2PO_4^-]$ since, in this scheme $[H^+]$ and $[H_2PO_4^-]$ would be essentially equal. Upon combining Eqs. 19 and 16,

$$\sum PO_4^{-3} - 3\sum UO_2^{++} = [H_3PO_4] - K_2^S[H_3PO_4] + (K_p[H_3PO_4])^{1/2} .$$

The solution of this equation for $[H_3PO_4]$ is

$$[H_3PO_4] = \frac{2AD + K_p}{2A^2} - \left[\left(\frac{2AD + K_p}{2A^2}\right)^2 - \frac{D^2}{A^2}\right]^{1/2} \tag{20}$$

wherein $A = 1 - K_2^S$; $D = \sum PO_4^{-3} - 3 \sum UO_2^{++}$. The calculated $[H_3PO_4]$ values (Table IV) were obtained from Eq. 20 using the values, $K_2^S = 0.03$ and $K_p = 0.0075$.* The plot of the data according to Eq. 33 is shown in Figure 6. The resulting value of K_3^S is 0.28 ± 0.04. The intercept gives a value for K_2^S of 0.02 ± 0.01, which is in good agreement with that used in calculating $[H_3PO_4]$. A more accurate evaluation of K_2^S cannot be obtained by extrapolation of the data to $[H_3PO_4] = 0$, because the lower points are undoubtedly increased by the contribution of the 1:1 complexes to the salt solubility. In drawing the line as shown, a satisfactory fit is obtained over the maximum range (ca. 0.1M - 1.5M $\sum PO_4^{-3}$). The experimental data above $\sum PO_4^{-3}$ = 1.5M would show large positive deviations on such a plot, caused perhaps by higher complex formation or by medium effects resulting from the increasingly non-aqueous character of the solvent.

d. Calculated Solubility Curves

A complete solubility curve was calculated for $UO_2HPO_4 \cdot 4H_2O$ in the range 0.014M - 6M H_3PO_4 as follows: From Eqs. 2, 8, 9, 14, and 17, the concentrations of the following species in solution are given as functions of $[H_3PO_4]$ and $[H^+]$ by:

$$[UO_2^{++}] = \frac{K_S [H^+]^2}{H_3PO_4} \tag{21}$$

$$[UO_2H_3PO_4^{++}] = C_{1,3} = K_{1,3}^S [H^+]^2 \tag{22}$$

$$[UO_2H_2PO_4^{+}] = C_{1,2} = K_{1,2}^S [H^+] \tag{23}$$

$$UO_2(H_2PO_4)_2 = C_2 = K_2^S [H_3PO_4] \tag{24}$$

$$UO_2(H_2PO_4)_2(H_3PO_4) = C_3 = K_2^S [H_3PO_4]^2 \tag{25}$$

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*This value of K_2^S has been estimated from as yet unpublished data. A recalculation of $[H_3PO_4]$ values using the K_2^S value obtained from Figure 6 (0.02) resulted in essentially no change. In fact it can be shown that if K_2^S is varied from 0 to 0.05, only about ± 2% change in the $[H_3PO_4]$ values result. The K_p value is that for infinite dilution and was used here as an adequate approximation.

Table IV

THE DETERMINATION OF K_3^s FROM THE $UO_2HPO_4 \cdot 4H_2O$ SOLUBILITY DATA IN H_3PO_4 SOLUTIONS

All concentrations expressed in moles/l.

$K_2^s = 0.03$, $K_p = 0.0075$*

Run No.	$\sum UO_2^{++}$	$\sum PO_4^{-3}$	$\sum PO_4^{-3} - 3\sum UO_2^{++}$	$[H_3PO_4]$	$\frac{\sum UO_2^{++}}{[H_3PO_4]}$
A-13	0.000528	0.0205	0.0189	0.0104	0.0509
A-12	0.001443	0.0497	0.0459	0.0310	0.0466
A-10	0.00330	0.103	0.0931	0.0716	0.0460
A-25	0.00407	0.108	0.0958	0.0742	0.0550
A-9	0.01035	0.220	0.1890	0.1586	0.0653
A-8	0.01237	0.249	0.212	0.1799	0.0688
A-6	0.01860	0.328	0.272	0.2361	0.0786
A-5	0.0352	0.495	0.389	0.347	0.1015
A-1	0.1099	0.987	0.657	0.605	0.1815
A-4	.207	1.477	0.856	0.800	0.2588
A-2	.339	1.970	0.953	0.895	0.379

*See footnote on page 23.

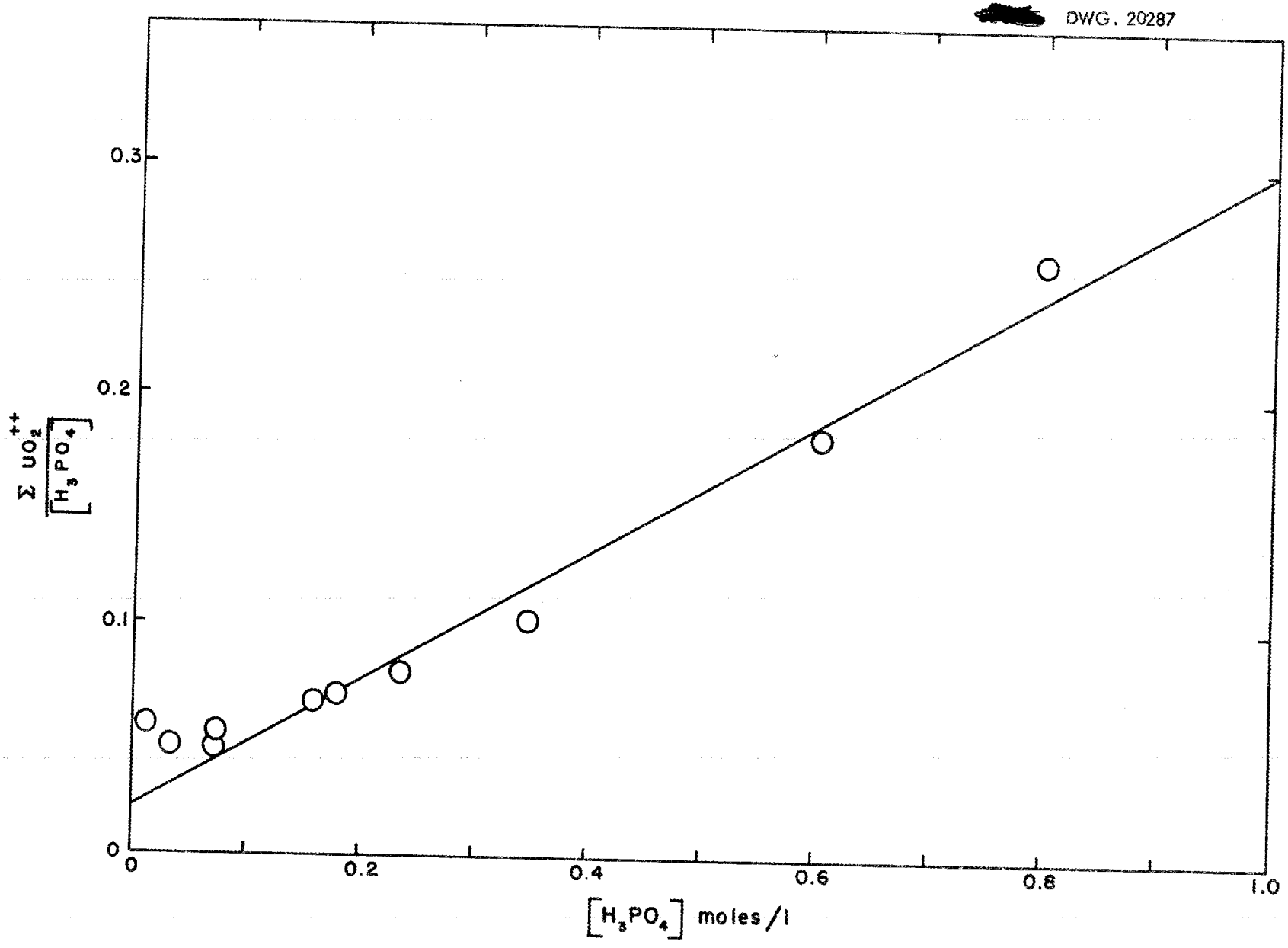

FIGURE 6. THE DETERMINATION OF K_3^s

In the calculations, all K values were assumed to be constant. In view of the formal independence of ionic strength of the corresponding equilibria, this is probably not a bad assumption for $K^S_{1,2}$, K^S_2, and K^S_3.

Since the contribution of the 1:1 complexes to the salt solubility is appreciable only in the more dilute phosphate solutions (Figure 7) wherein the acidity is also low (e.g., at $\sum PO_4^{-3} = 0.02M$, $[H^+] = 0.01M$), the contribution of $UO_2H_3PO_4^{++}$ in turn is negligible since

$$\frac{[UO_2H_2PO_4^{++}]}{[UO_2H_2PO_4^{+}]} = \frac{K^S_{1,3}}{K^S_{1,2}}[H^+]$$

and $K^S_{1,3}/K^S_{1,2}$ is probably in the region of unity.* The concentration in solution of the neutral 1:1 complex, UO_2HPO_4, in the region of stability of $UO_2HPO_4.4H_2O$ is constant since

$$\underline{UO_2HPO_4} = UO_2HPO_4$$

$$K^S_{1,1} = [UO_2HPO_4]$$

Even at the lower limit of stability of this salt (the transition point at $0.014M \sum PO_4^{-3}$ in Figure 5), there is no evidence of a levelling off of the solubility to a constant value, which suggests that $K^S_{1,1}$ is considerably less than $3 \times 10^{-4}M$. Accordingly, it has been assumed in constructing the present solubility curve for $UO_2HPO_4.4H_2O$ that the contribution of the neutral 1:1 complex also is negligible, leaving only $UO_2H_2PO_4^+$ to be considered in the calculation. The question of the neutral complex will be considered further in the calculation of the curve for the normal phosphate (below $0.014M \sum PO_4^{-3}$) to be discussed presently.

J. Sutton[4] suggests the primary hydrolysis equilibrium for uranyl ion to be

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*As already mentioned on page 15, $K^S_{1,2}$ appears to be ca. 0.03, which value is used in the present calculation of solubilities with satisfactory results. Since $K_1 = 0.05$, then $K^S_{1,3} \sim 0.02$ and the ratio $K^S_{1,3}/K^S_{1,2} \sim 0.7$.

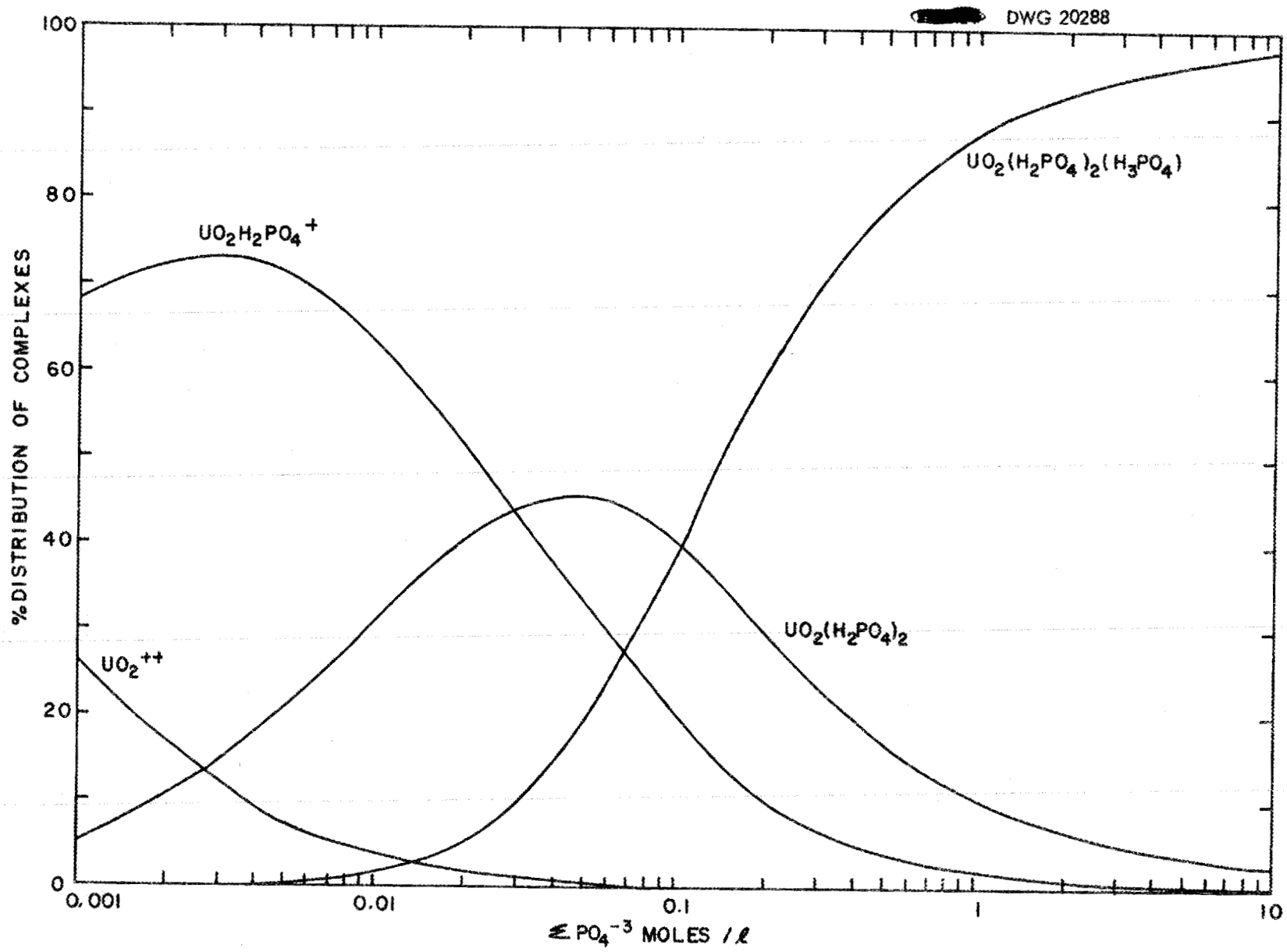

FIGURE 7. THE DISTRIBUTION OF URANYL PHOSPHATE COMPLEXES IN H_3PO_4 SOLUTIONS AS A FUNCTION OF ΣPO_4^{-3}

$$2UO_2^{++} + H_2O = UO_3UO_2^{++} + 2H^+ ,$$

$$K = \frac{[UO_3UO_2^{++}][H^+]^2}{[UO_2^{++}]^2} = 1.24 \times 10^{-6}$$

In the most dilute region of the present solubility data, wherein $[H^+] \sim 10^{-3}$M and $\sum UO_2^{++} \sim 1 \times 10^{-5}$M, it may be calculated accordingly that the hydrolysis of free uranyl ion is ca. 0.001%. Thus the solubility effect of hydrolysis would be utterly negligible.

In view of these considerations,

$$\sum UO_2^{++} = [UO_2^{++}] + C_{1,2} + C_2 + C_3 ,$$

or, substituting Eqs. 21 - 25,

$$\sum UO_2^{++} = \frac{K_S [H^+]^2}{[H_3PO_4]} + K^S_{1,2}[H^+] + K^S_2[H_3PO_4] + K^S_3[H_3PO_4]^2 . \tag{26}$$

Similarly,

$$\sum PO_4^{-3} = [H_3PO_4] + [H_2PO_4^-] + C_{1,2} + 2C_2 + 3C_3 ,$$

or

$$\sum PO_4^{-3} = [H_3PO_4] + \frac{K_p[H_3PO_4]}{[H^+]} + K^S_{1,2}[H^+]$$

$$+ 2K^S_2[H_3PO_4] + 3K^S_3[H_3PO_4]^2 , \tag{27}$$

wherein only the primary dissociation of phosphoric acid is considered. It remains to relate $[H^+]$ to $[H_3PO_4]$: Upon equating the cation and anion concentrations in these solutions

$$[H_2PO_4^-] = [H^+] + C_{1,2} + 2[UO_2^{++}] ,$$

or

$$[H_2PO_4^-] = [H^+]\ (1 + K^s_{1,2}) + \frac{2K_s[H^+]^2}{[H_3PO_4]}.$$

Replacing $[H_2PO_4^-]$ by $\frac{K_p[H_3PO_4]}{[H^+]}$, and rearranging terms,

$$2K_s[H^+]^3 + (1+K^s_{1,2})[H_3PO_4][H^+]^2 - K_p[H_3PO_4]^2 = 0. \quad (28)$$

In general, the calculated solubilities were obtained by first solving Eq. 28 by successive approximation for $[H^+]$ or $[H_3PO_4]$; i.e., one or the other being chosen arbitrarily and the remaining quantity adjusted to satisfy the equation. The resulting $[H^+]$ and $[H_3PO_4]$ values (Table V) were then substituted in Eqs. 26 and 27 to yield $\sum UO_2^{++}$ and $\sum PO_4^{-3}$.

The solid line in Figure 5 (and curve II, Figure 1) is the calculated solubility curve which results when:

$K_s = 0.014$ $\qquad$ $K^s_3 = 0.28$

$K^s_{1,2} = 0.03$ $\qquad$ $K_p = 0.0075$

$K^s_2 = 0.02$

The indicated value of $K^s_{1,2}$ was found to give the best fitting curve. The calculations are summarized in Table V and the resulting distribution of complexes as a function of the total phosphate concentration is shown in Figure 7.

Below the solid phase transition point at 0.014M $\sum PO_4^{-3}$, where $(UO_2)_3(PO_4)_2 \cdot 6H_2O$ becomes the stable solid phase, the theoretical solubility curve in Figure 5 was calculated by means of the following equilibria:

$$\underline{(UO_2)_3(PO_4)_2} + 6H^+ = 3UO_2^{++} + 2H_3PO_4:$$

$$K_s' = \frac{[UO_2^{++}]^3[H_3PO_4]^2}{[H^+]^6} = 7.2\times10^{-7}$$

Table V

THE CALCULATION OF $UO_2HPO_4 . 4H_2O$ SOLUBILITY IN H_3PO_4 SOLUTIONS

All concentrations expressed in moles/l.

$K^s_{1,2} = 0.03$, $K^s_2 = 0.02$, $K^s_3 = 0.28$, $K_s = 0.0014$, $K_p = 0.0075$

$[H_3PO_4]$	$[H^+]$	$[UO_2^{++}]$ x10^4	C_1 x10^4	C_2 x10^4	C_3	$[H_2PO_4^-]$ x10^2	$\sum UO_2^{++}$	$\sum PO_4^{-3}$
3	0.1485	0.103	44.5	600	2.52	15.30	2.584	10.84
2	0.1212	0.103	36.4	400	1.12	12.48	1.164	5.57
1.5	0.1050	0.103	31.5	300	0.63	10.82	0.663	3.56
1	0.08573	0.103	25.7	200	0.28	8.83	0.3026	1.971
0.8	0.07668	0.103	23.0	160	0.179	7.90	0.1973	1.450
0.6	0.06641	0.103	19.9	120	0.1008	6.84	0.1148	0.997
0.4	0.05422	0.103	16.3	80.0	0.0448	5.59	0.0544	0.608
0.3	0.04695	0.103	14.08	60.0	0.0252	4.84	0.0326	0.437
0.2	0.03834	0.103	11.50	40.0	0.0112	3.95	0.01636	0.282
0.15	0.0332	0.103	9.96	30.0	0.00630	3.42	0.01031	0.210
0.1	0.02711	0.103	8.13	20.0	0.00280	2.80	0.00563	0.1412
0.08	0.02425	0.103	7.28	16.0	0.00179	2.50	0.00413	0.1143
0.06	0.02100	0.103	6.30	12.0	0.001008	2.17	0.00285	0.0877
0.04	0.01715	0.103	5.15	8.00	4.48×10^{-4}	1.77	0.001774	0.0612
0.03061	0.015	0.103	4.50	6.12	2.62×10^{-4}	1.55	0.001335	0.0485
0.02127	0.0125	0.103	3.75	4.24	1.27×10^{-4}	1.290	9.37×10^{-4}	0.0358
0.01361	0.01	0.103	3.00	2.72	5.19×10^{-5}	1.033	6.34×10^{-4}	0.0249
0.01102	0.009	0.103	2.70	2.20	3.40×10^{-5}	0.930	5.35×10^{-4}	0.02113
0.00871	0.008	0.103	2.40	1.74	2.12×10^{-5}	0.827	4.46×10^{-4}	0.01763
0.00667	0.007	0.103	2.10	1.33	1.25×10^{-5}	0.724	3.66×10^{-4}	0.01442
0.00490	0.006	0.103	1.80	0.98	6.7×10^{-6}	0.621	2.95×10^{-4}	0.01150
0.00340	0.005	0.103	1.50	0.68	3.2×10^{-6}	0.518	2.32×10^{-4}	0.00887
0.00218	0.004	0.103	1.20	0.436	1.3×10^{-6}	0.415	1.75×10^{-4}	0.00654
0.00167	0.0035	0.103	1.05	0.334	8×10^{-7}	0.363	1.50×10^{-4}	0.00547
0.00123	0.003	0.103	0.90	0.246	4×10^{-7}	0.312	1.25×10^{-4}	0.00449
0.000551	0.002	0.102	0.60	0.110	1×10^{-7}	0.209	8.2×10^{-5}	0.00272
0.000139	0.001	0.100	0.30	0.028		0.105	4.3×10^{-5}	0.00123

$$\underline{(UO_2)_3(PO_4)_2} + 3H^+ + H_3PO_4 = 3UO_2H_2PO_4^+;$$

$$K_{1,2}^{s\prime} = \frac{(C_{1,2})^3}{[H_3PO_4][H^+]^3} = 0.0042$$

$$\underline{(UO_2)_3(PO_4)_2} + 4H_3PO_4 = 3UO_2(H_2PO_4)_2;$$

$$K_2^{s\prime} = \frac{(C_2)^3}{[H_3PO_4]^4} = 0.00125$$

$$\underline{(UO_2)_3(PO_4)_2} + 7H_3PO_4 = 3UO_2(H_2PO_4)_2(H_3PO_4);$$

$$K_3^{s\prime} = \frac{(C_3)^3}{[H_3PO_4]^7} = 3.42$$

These equilibria represent the dissolution of $(UO_2)_3(PO_4)_2 \cdot 6H_2O$ to form the same complex ions as in the case of $UO_2HPO_4 \cdot 4H_2O$. In general, it may be shown that

$$K_n^{s\prime} = \frac{(K_n^s)^3}{[H_3PO_4]_T} \tag{29}$$

wherein $[H_3PO_4]_T$ is the concentration of free phosphoric acid at the transition point. The value of this quantity (obtained by interpolation of the data in Table V) is 0.00642M (taking $\sum PO_4^{-3} = 0.014$M as the transition point).

The calculation of the theoretical solubility curve is summarized in Table VI. This calculation has involved no new assumptions and only one additional parameter; i.e., the total phosphate concentration at the transition point, which has been evaluated experimentally.

It seems evident from the satisfactory fit of the curve to the data that the neutral complex UO_2HPO_4 does not contribute appreciably to the solubility of the normal

Table VI

THE CALCULATION OF $(UO_2)_3(PO_4)_2 \cdot 6H_2O$ SOLUBILITY IN H_3PO_4 SOLUTIONS

All concentrations expressed in moles/l.

$K^{s'}_{1,2} = 0.0042$, $K^{s'}_{2} = 0.00125$, $K^{s'}_{3} = 3.42$, $K_{s'} = 7.2 \times 10^{-7}$, $K_p = 0.0075$.

$[H_3PO_4]$	$[H^+]$	$[UO_2^{++}]$ $\times 10^5$	C_1 $\times 10^5$	C_2 $\times 10^5$	C_3 $\times 10^5$	$[H_2PO_4^-]$ $\times 10^3$	$\sum UO_2^{++}$ $\times 10^4$	$\sum PO_4^{-3}$ $\times 10^3$
0.006415	0.00680	1.16	20.4	12.97	1.16	7.03	3.57	13.94
0.004913	0.00596	1.06	16.38	8.99	0.62	6.15	2.71	11.42
0.003375	0.00498	0.94	12.09	5.40	0.26	5.12	1.87	8.73
0.0025	0.00424	0.84	9.31	3.63	0.12	4.35	1.39	7.02
0.001	0.00272	0.63	4.39	1.08	0.02	2.777	0.612	3.84
0.0002	0.001215	0.37	1.15	0.125	0.00035	1.235	0.164	1.15

phosphate. In order to place an upper limit on the values of $K^{s\prime}_{1,1}$ and $K^{s}_{1,1}$, let it be assumed that the true salt solubility in 0.001M phosphoric acid is 2×10^{-5}M instead of the calculated 1.4×10^{-5}M.* Then $[UO_2HPO_4] = (2.0 - 1.4)\times10^{-5} = 0.6\times10^{-5}$M, and substituting this value into $K^{s\prime}_{1,1}$ wherein

$$(UO_2)_3(PO_4)_2 + H_3PO_4 = 3UO_2HPO_4$$

$$K^{s\prime}_{1,1} = \frac{[UO_2HPO_4]^3}{[H_3PO_4]}$$

then $K^{s\prime}_{1,1} \sim 2\times10^{-13}$. Substituting this value into Eq. 29, $K^{s}_{1,1} \sim 1\times10^{-5}$. This latter value represents the upper limit of the constant molarity of UO_2HPO_4 in equilibrium with the solid $UO_2HPO_4.4H_2O$ above the transition point.

The fit of the calculated solubility curve to the data, in general, is satisfactory up to 2M $\sum PO_4^{-3}$. As mentioned earlier, the higher observed solubilities in more concentrated solution may indicate the appearance of higher complexes, however, because of the increasingly non-aqueous character of the solvent, such a conclusion is quite tentative.

A similar calculated solubility curve has been prepared for the 1M perchloric acid data and is represented by the solid curve (I) in Figure 1. Since the equilibria involving the formation of the 2:1 and the 3:1 complexes,

$$\underline{UO_2HPO_4} + H_3PO_4 = UO_2(H_2PO_4)_2$$

$$\underline{UO_2HPO_4} + 2H_3PO_4 = UO_2(H_2PO_4)_2(H_3PO_4),$$

should be relatively independent of ionic strengths effects, essentially the same K^{s}_{n} values have been used in this as in the preceding calculation.** Considering the formation of 1:1, 2:1, and 3:1 complexes in the saturated 1M perchloric acid solutions, then

*This is the estimated maximum uncertainty involved in the polarographically determined value (1.1×10^{-5}M) in this, the lowest concentration measured.

**K^{s}_{2} is here taken as 0.03, a value based on as yet unpublished potentiometric results (at $\mu \sim 1$M). This value is within the range of uncertainty of the value obtained from the phosphoric acid solubility data and is probably more reliable. K_p is taken as 0.021 on the basis of the same results. It is evident from the term $(1+2K^{s}_{2}+K_p)$ in Table VII that the calculated solubility is not sensitive to the choice of these K values.

$$\sum UO_2^{++} = [UO_2^{++}] + C_1 + C_2 + C_3$$

and

$$\sum PO_4^{-3} = [H_3PO_4] + [H_2PO_4^-] + C_1 + 2C_2 + 3C_3.$$

Substituting Eqs. 6, 21, 24, and 25 into the above, and noting that $[H^+] = 1$, one obtains:

$$\sum UO_2^{++} = \frac{K_S}{[H_3PO_4]} + K_1^S + K_2^S[H_3PO_4] + K_3^S[H_3PO_4]^2$$

$$= \frac{0.0014}{H_3PO_4} + 0.051 + 0.03\,[H_3PO_4]$$

$$+ 0.28[H_3PO_4]^2 , \qquad (30)$$

$$\sum PO_4^{-3} = K_1^S + (1+2K_2^S + K_p)[H_3PO_4] + 3K_3^S[H_3PO_4]^2$$

$$= 0.051 + 1.08\,[H_3PO_4] + 0.84\,[H_3PO_4]^2 \qquad (31)$$

The calculated curve was constructed using Eqs. 30 and 31. The calculations are summarized to Table VII, and the distribution of the various complexes is indicated as a function of the total phosphate concentration in Figure 8.

In general, the fit of the data to the calculated curve is satisfactory. The positive deviation shown by the data in excess phosphoric acid are similar to that shown by the pure phosphoric acid data and, as already pointed out, may arise either from additional complex formation or simply medium effects.

The generally higher results reported by G. R. Leader[3] for 1M nitric acid, which have also been plotted in Figure 1, are not unexpected, since nitrate ion is known to form complexes with uranyl ion,[5] though the difference is larger than the available formation constant would indicate.

Table VII

THE CALCULATION OF $UO_2HPO_4 \cdot 4H_2O$ SOLUBILITY IN 1M $HClO_4$ SOLUTIONS

All concentrations expressed in moles/l.

$K_1^S = 0.051$, $K_2^S = 0.03$*, $K_3^S = 0.28$, $K_S = 0.0014$, $K_p = 0.021$*

$[H_3PO_4]$	$(1+2K_2^S+K_p)[H_3PO_4]$	$3K_3^S[H_3PO_4]^2$	$\sum PO_4^{-3}$	$\frac{K_S}{[H_3PO_4]}$	$K_2^S[H_3PO_4]$	$K_3^S[H_3PO_4]^2$	$\sum UO_2^{++}$
0.002	0.00215	3×10^{-6}	0.0529	0.685	3×10^{-5}	1×10^{-6}	0.736
0.0035	0.00376	1×10^{-5}	0.0545	0.391	0.00010	3×10^{-6}	0.442
0.005	0.00538	2×10^{-5}	0.0561	0.274	0.00014	7×10^{-6}	0.325
0.007	0.00752	4×10^{-5}	0.0583	0.196	0.00019	1×10^{-5}	0.247
0.01	0.01075	8×10^{-5}	0.0615	0.1370	0.00027	3×10^{-5}	0.188
0.015	0.01613	0.00019	0.0670	0.0913	0.00041	6×10^{-5}	0.1425
0.02	0.0215	0.00034	0.0725	0.0685	0.00054	0.00011	0.1199
0.03	0.0323	0.00076	0.0838	0.0457	0.00081	0.00025	0.0975
0.037	0.0398	0.00115	0.0917	0.0370	0.00100	0.00038	0.0891
0.04	0.0430	0.00134	0.0950	0.0343	0.00108	0.00045	0.0865
0.055	0.0591	0.00254	0.1123	0.0249	0.00149	0.00085	0.0779
0.075	0.0805	0.00473	0.1359	0.0183	0.00203	0.00158	0.0726
0.1	0.1075	0.00840	0.1666	0.0137	0.00270	0.00280	0.0699
0.15	0.1613	0.0189	0.2309	0.00913	0.00405	0.00630	0.0702
0.2	0.215	0.0336	0.2993	0.00685	0.00540	0.01120	0.0742
0.3	0.323	0.0756	0.449	0.00457	0.00810	0.0252	0.0886
0.4	0.430	0.134	0.615	0.00343	0.0108	0.0448	0.1097
0.6	0.645	0.302	0.998	0.00228	0.0162	0.1008	0.1670
0.8	0.859	0.538	1.448	0.00171	0.0216	0.1792	0.2532
1	1.075	0.840	1.966	0.00137	0.0270	0.280	0.359
1.5	1.613	1.89	3.55	0.00091	0.0405	0.630	0.722
2	2.15	3.36	5.56	0.00069	0.0540	1.120	1.225

*See footnote on page 33.

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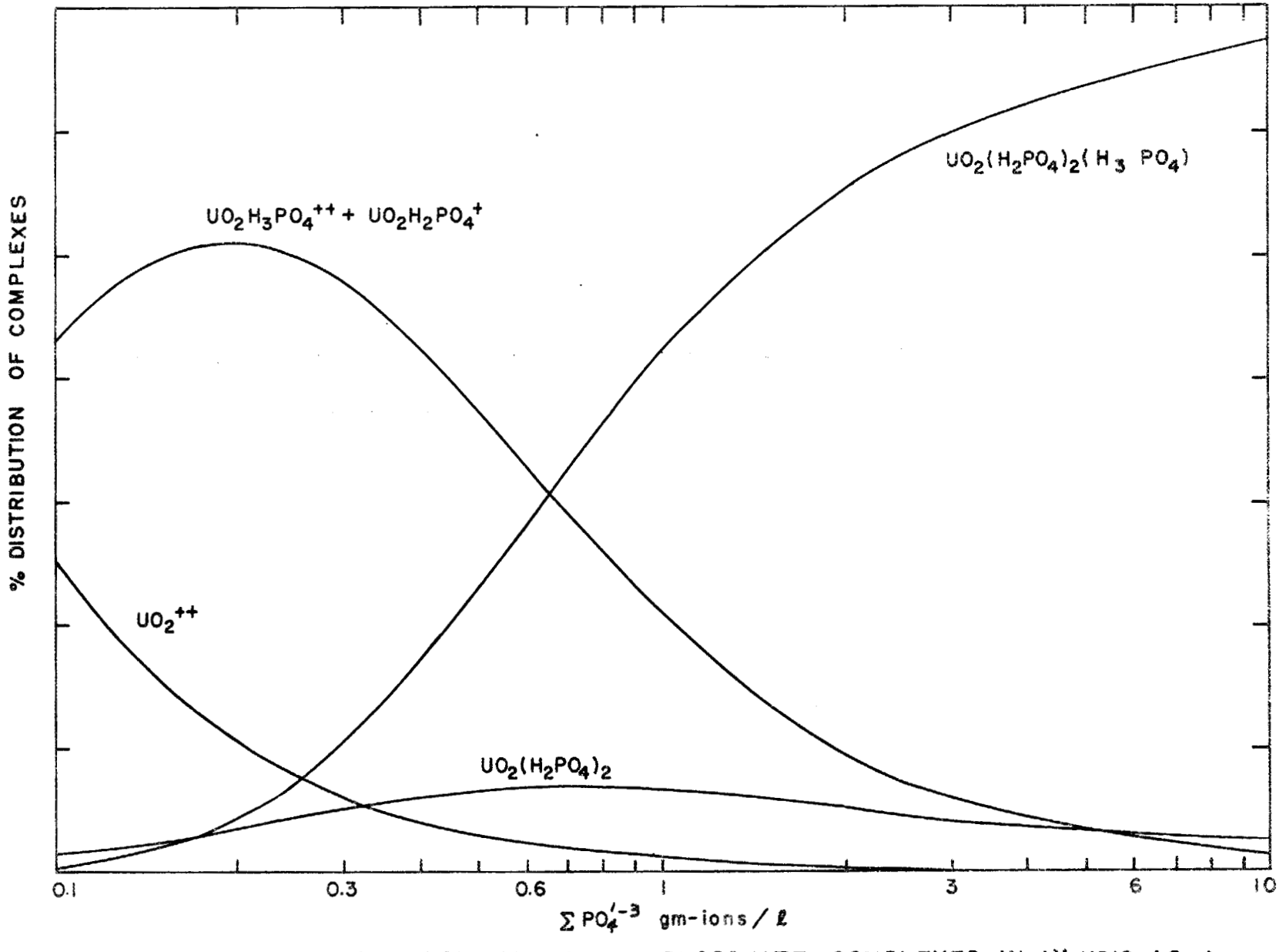

FIGURE 8. THE DISTRIBUTION OF URANYL PHOSPHATE COMPLEXES IN 1M $HClO_4$ AS A FUNCTION OF ΣPO_4^{-3}

CONCLUSIONS

The solubility data presented in this and the preceding report (ORNL-1578) may be interpreted in terms of the formation of four complex species in solution:

$UO_2H_2PO_4^+$, $UO_2H_3PO_4^{++}$

$UO_2(H_2PO_4)_2$

$UO_2(H_2PO_4)_2(H_3PO_4)$

The corresponding equilibria, involving $UO_2HPO_4 \cdot 4H_2O$ and $(UO_2)_3(PO_4)_2 \cdot 6H_2O$ as the solid phases, are listed in Table VIII along with their concentration equilibrium quotients of formation. Using these K values, solubility curves have been calculated for 1M perchloric acid and for phosphoric acid solutions. In the latter case, adequate agreement between the calculated solubilities and the measured values in obtained over a two-thousandfold change in total phosphate (0.001M - 2M) and a twenty-thousandfold change in total uranium concentration (1.5×10^{-5}M - 0.3M).

From these K values, the following additional equilibrium quotients may be evaluated in 1M perchloric acid:

$$UO_2^{++} + H_3PO_4 = UO_2H_2PO_4^+ + H^+$$

$$K_{1,2} = \frac{[UO_2H_2PO_4^+][H^+]}{[UO_2^{++}][H_3PO_4]}$$

$$UO_2^{++} + H_3PO_4 = UO_2H_3PO_4^{++}$$

$$K_{1,3} = \frac{[UO_2H_3PO_4^{++}]}{[UO_2^{++}][H_3PO_4]}$$

$$K_{1,2} + K_{1,3} = K_1 = 37 \pm 13$$

Table VIII

SUMMARY OF COMPLEX-FORMING EQUILIBRIA

INVOLVING $UO_2HPO_4 \cdot 4H_2O$ AND $(UO_2)_3(PO_4)_2 \cdot 6H_2O$

Equilibrium	K 25°C	Medium
$\underline{UO_2HPO_4} + 2H^+ = UO_2^{++} + H_3PO_4$	$K_S = 0.0014 \pm 0.0005$	1M $HClO_4$, 0-.05M $UO_2(ClO_4)_2$
$\underline{UO_2HPO_4} + H^+ = UO_2H_2PO_4^+$	$K_1^S = 0.051 \pm .005$	"
$\underline{UO_2HPO_4} + 2H^+ = UO_2H_3PO_4^{++}$ $K_{1,2}^S + K_{1,3}^S =$		
$\underline{UO_2HPO_4} + H_3PO_4 = UO_2(H_2PO_4)_2$	$K_2^S = 0.02 \pm 0.01$	0.014 - 2M H_3PO_4
$\underline{UO_2HPO_4} + 2H_3PO_4 = UO_2(H_2PO_4)_2(H_3PO_4)$	$K_3^S = 0.28 \pm 0.03$	"
$\underline{(UO_2)_3(PO_4)_2} + 6H^+ = 3UO_2^{++} + 2H_3PO_4$	$K_{S'} = 7 \times 10^{-7}$	0-0.014M H_3PO_4
$\underline{(UO_2)_3(PO_4)_2} + H_3PO_4 + 3H^+ = 3UO_2H_2PO_4^+$	$K_{1,2}^{S'} = 0.004$	"
$\underline{(UO_2)_3(PO_4)_2} + 4H_3PO_4 = 3UO_2(H_2PO_4)_2$	$K_2^{S'} = 0.0013 \pm 0.0007$	"
$\underline{(UO_2)_3(PO_4)_2} + 7H_3PO_4 = 3UO_2(H_2PO_4)_2(H_3PO_4)$	$K_3^{S'} = 3.4 \pm 0.3$	"

$$UO_2^{++} + 2H_3PO_4 = UO_2(H_2PO_4)_2 + 2H^+$$

$$K_2 = \frac{[UO_2(H_2PO_4)_2][H^+]^2}{[UO_2^{++}][H_3PO_4]^2} = \frac{K_2^S}{K_S} = 15 \pm 8$$

$$UO_2^{++} + 3H_3PO_4 = UO_2(H_2PO_4)_2(H_3PO_4) + 2H^+$$

$$K_3 = \frac{[UO_2(H_2PO_4)_2(H_3PO_4)][H^+]^2}{[UO_2^{++}][H_3PO_4]^3} = \frac{K_3^S}{K_S} = 200 \pm 50$$

Of the four complexes which have been proposed to exist in the solutions thus far studied, the least well established is $UO_2(H_2PO_4)_2$. While it seems reasonable to suppose that 2:1 complexes are formed, their stability is such that the number of hydrogen ions cannot be assigned with certainty. Similarly, for the 1:1 complexes, while it seems evident from the solubility behavior of $UO_2HPO_4.4H_2O$ in 0.1 to 1M perchloric acid that at least $UO_2H_3PO_4^{++}$ and $UO_2H_2PO_4^+$ are both formed in 1M perchloric acid, their separate formation quotients cannot be determined with any accuracy.

Further discussion of these considerations will be postponed until the presentation of potentiometric measurements in a subsequent report.

ACKNOWLEDGEMENTS

The authors with to express their sincere thanks to Dr. Kurt A. Kraus, Dr. Charles F. Coleman and Mr. Keith B. Brown, all of this laboratory, for their participation in many valuable discussions concerned with the present investigation.

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REFERENCES

1) C. F. Baes, Jr., J. M. Schreyer, J. M. Lesser, "The Chemistry of Uranium(VI) Orthophosphate Solutions: Part I, A Spectrophotometric Investigation of Uranyl Phosphate Complex Formation in Perchloric Acid Solutions," ORNL - Y-12, ORNL-1577, June 22, 1953.

2) J. M. Schreyer and C. F. Baes, Jr., "The Chemistry of Uranium(VI) Orthophosphate Solutions: Part II, The Solubilities of Uranium(VI) Orthophosphates in Phosphoric Acid Solutions," ORNL - Y-12, ORNL-1578, June 30, 1953.

3) G. R. Leader, "Solubility of Uranyl Phosphate in UNH Solutions," Progress Report, August 15 to October 1, 1944, Chemistry Division, Clinton Laboratories, CN-2195, 1944.

4) J. Sutton, J. Chem. Soc., S-275 (1949).

5) S. Ahrland, Acta Chem. Scand., 5, 1271 (1951).

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APPENDIX

CALCULATION OF THE SOLUBILITY DATA IN 1M $HClO_4$

The following discussion summarizes the calculation of the various data in Table I.

a. Calculation of $[ClO_4^-]_f$ and $[\sum PO_4^{-3}]_f$

While in all but two runs, perchlorate analyses were available for each saturated mother liquor, more accurate values for $[ClO_4^-]_f$ were obtained by calculation. Thus, if w and d refer, respectively, to the total weight and the density of the liquid phase, then from the material balance

$$\frac{[ClO_4^-]_s \; w_s}{d_s} = \frac{[ClO_4^-]_f \; w_f}{d_f}$$

and

$$\frac{[ClO_4^-]_f}{[ClO_4^-]_s} = \frac{w_s \; d_f}{w_f \; d_s} = A \qquad (1)$$

the subscripts s and f referring to initial and final values. The bracketed quantities refer to concentration in moles/l. Also, from the material balance

$$w_s = w_f - w_p$$

Wherein w_p is the total weight of salt that has dissolved during the run. If M_p is the equivalent weight of salt per uranium atom, then,

$$w_s = w_f - \left\{ \frac{[\sum UO_2^{++}]_f \; w_f}{d_f} - \frac{[\sum UO_2^{++}]_s \; w_s}{d_s} \right\} M_p$$

or

$$\frac{w_s\ d_f}{w_f\ d_s} = \frac{d_f - M_p\ [UO_2^{++}]_f}{d_s - M_p\ [UO_2^{++}]_s} \qquad (2)$$

Substituting into Eq. 1,

$$[ClO_4^-]_f = \frac{d_f - M_p\ [\sum UO_2^{++}]_f}{d_s - M_p\ [\sum UO_2^{++}]_s}\ [ClO_4^-]_s = A\,[ClO_4^-]_s \qquad (3)$$

The agreement between the calculated and measured $[ClO_4^-]$ values is in general satisfactory (Table I). In the calculation of the final acidity, to be described presently, the calculated $[ClO_4^-]_f$ values were used throughout since the term A (Eq. 3) was known more accurately than the perchlorate analyses.

The final phosphate concentration was also calculated and compared with the analyzed values. Since the uranyl to phosphate ratio in the salt is 1, then

$$\frac{[\sum PO_4^{-3}]_f\ w_f}{d_f} - \frac{[\sum PO_4^{-3}]_s\ w_s}{d_s} = \frac{[\sum UO_2^{++}]_f\ w_f}{d_f} - \frac{[\sum UO_2^{++}]_s\ w_s}{d_s}$$

and

$$\frac{w_s\ d_f}{w_f\ d_s}\ \frac{[\sum PO_4^{-3}]_f - [\sum UO_2^{++}]_f}{[\sum PO_4^{-3}]_s - [\sum UO_2^{++}]_s} \qquad (4)$$

From Eq. 1,

$$\frac{[\sum PO_4^{-3}]_f - [\sum UO_2^{++}]_f}{[\sum PO_4^{-3}]_s - [\sum UO_2^{++}]_s} = A$$

or

$$[\sum PO_4^{-3}]_f = A\,[\sum PO_4^{-3}]_s - A\,[\sum UO_2^{++}]_s + [\sum UO_2^{++}]_f \qquad (5)$$

The agreement between the calculated and observed values is satisfactory except in the runs involving excess uranyl perchlorate. Although the calculated $[\sum PO_4^{-3}]_f$ values for these runs involve differences between two relatively large numbers, they were still preferred to the analytical $[\sum PO_4^{-3}]_f$ results because of relatively better accuracy of the uranyl analyses.* Exceptions to this procedure are runs 5, 7, and 8, in which the uranyl analyses were in some doubt.

b. Calculation of $[H^+]_f$

In the calculation of the final acidity values listed in column seven of Table I, two cases were considered.

(Case 1.) In the absence of a large excess of phosphoric acid ($\sum PO_4^{-3} < 0.2M$, run Nos. 1-12), it was assumed that the final acidity was approximately the same as that corresponding to no complex formation. The basis for this assumption is the evidence, presented in this report, that the only complexes present in this solubility region in appreciable amounts are $UO_2H_2PO_4^+$ and $UO_2H_3PO_4^{++}$. Of these, only the former will produce a change in acidity from that corresponding to no complex formation,

$$UO_2^{++} + H_3PO_4 = UO_2H_2PO_4^+ + H^+$$

and, in general, this effect (amounting to a maximum of 5% change in acidity) may be neglected without causing serious error. Defined in this way, the final acidity is given by

$$[H^+]_f = [ClO_4^-]_f - 2\,[\sum UO_2^{++}]_f \qquad (6)$$

since, in the absence of complexing, and neglecting the small acidity effect of H_3PO_4, the only ions which would be present in solution are H^+, ClO_4^- and UO_2^{++}.

(Case 2.) In the region of high H_3PO_4 (run Nos. 13-19), the final acidity was given by

*In the presence of excess uranyl perchlorate, the accuracy of the phosphate analysis appeared to be considerably below that normally expected of the method used here (cf. ORNL-1578).

$$[H^+]_f = [ClO_4^-]_f - 2[UO_2H_3PO_4^{++}] - [UO_2H_2PO_4^+] \qquad (7)$$

in which the concentration of free uranyl ion is assumed to be negligibly low, and the higher phosphate complexes of uranyl are assumed to be neutral (on the basis of pH measurements). Introducing the stability constants $K^S_{1,3}$ and $K^S_{1,2}$ in the usual way,

$$[H^+]_f = [ClO_4^-]_f - 2K^S_{1,3}[H^+]^2_f - K^S_{1,2}[H^+]_f$$

or, rearranging

$$2K^S_{1,3}[H^+]^2_f + (1+K^S_{1,2})[H^+]_f - [ClO_4^-]_f = 0.$$

This equation was solved for $[H^+]$, using the K values,

$$K^S_{1,2} = 0.027, \quad K^S_{1,3} = 0.023$$

These values are derived from as yet unpublished results and are subject to considerable uncertainty; however, the resulting errors which may be involved in $[H^+]_f$ are not serious in view of the low acidity dependence of salt solubility in the region of excess phosphoric acid (Figure 1).

c. Calculation of $[\sum UO_2^{++}]^o$ and $[\sum PO_4^{-3}]^o$

The corrected uranyl and phosphate concentrations listed in the last two columns of Table I correspond to a final acidity of one molar. The values were obtained as follows:

(Case 1.) In run 9 ($\sum PO_4^{-3} = \sum UO_2^{++}$), assuming the only complexes present in appreciable concentration in the solutions to be $UO_2H_2PO_4^+$ and $UO_2H_3PO_4^{++}$, then

$$[\sum PO_4^{-3}]_f = [\sum UO_2^{++}]_f = [UO_2^{++}] + [UO_2H_2PO_4^+] + [UO_2H_3PO_4^{++}]$$

Introducing K's and noting that $[UO_2^{++}] \cong [H_3PO_4]$,

$$[\sum UO_2^{++}]_f = \sqrt{K_S}[H^+]_f + K^S_{1,2}[H^+]_f + K^S_{1,3}[H^+]^2_f$$

$$\frac{[\sum UO_2^{++}]_f}{[H^+]_f} = \sqrt{K_s} + K^s_{1,2} + K^s_{1,3}[H^+]_f \qquad (9)$$

In the case where $[H^+]_f = 1$,

$$[\sum PO_4^{-3}]^o = [\sum UO_2^{++}]^o = \sqrt{K_s} + K^s_{1,2} + K^s_{1,3} \qquad (10)$$

combining 9 and 10

$$[\sum UO_2^{++}]^o = \frac{[\sum UO_2^{++}]_f}{[H^+]_f} + K^s_{1,3}(1-[H^+]_f)$$

In calculating the correction, $K^s_{1,3}$ was again taken as 0.023.

(Case 2.) In excess $UO_2(ClO_4)_2$, $\sum PO_4^{-3}$ only was corrected for the acidity effect. Similarly, in excess H_3PO_4, $\sum UO_2^{++}$ only was corrected. In the first eight runs,

$$[\sum PO_4^{-3}]^o = \frac{[\sum PO_4^{-3}]_f}{[H^+]^2_f} \qquad (11)$$

and in runs 10-13, i.e., up to moderate excess of H_3PO_4,

$$[\sum UO_2^{++}]^o = \frac{[\sum UO_2^{++}]_f}{[H^+]^2_f} \qquad (12)$$

were the corrections used. This may be shown as follows: In the case of excess uranyl

$$[\sum PO_4^{-3}]_f = [H_3PO_4] + [UO_2H_2PO_4^+] + [UO_2H_3PO_4^{++}]$$

$$= \frac{K_s[H]^2}{[UO_2^{++}]} + K^s_{1,2}[H^+]_f + K^s_{1,3}[H^+]^2_f$$

[redacted]

or,

$$\frac{[\sum PO_4^{-3}]_f}{[H^+]_f^2} = \frac{K_s}{[UO_2^{++}]} + \frac{K_{1,2}^s}{[H^+]_f} + K_{1,3}^s \qquad (13)$$

In the case that $[H^+]_f = 1$,

$$[\sum PO_4^{-3}]^o = \frac{K_s}{[UO_2^{++}]^o} + K_{1,2}^s + K_{1,3}^s \qquad (14)$$

and, as an approximation, the right hand numbers of Eqs. 13 and 14 may be taken as equal. In a similar fashion Eq. 12 was derived. A more rigorous correction of the data is not justified since the various equilibrium constants and their variation with solution composition are not sufficiently well known.

(Case 3.) The last case to be considered is that in high excess H_3PO_4 (the last six runs). Since, as shown by pH measurements, the only acid dependent equilibria which contribute appreciably to the solubility here are those involving $UO_2H_2PO_4^+$ and $UO_2H_3PO_4^{++}$, then one may write directly,

$$[\sum UO_2^{++}]^o - [\sum UO_2^{++}]_f = K_{1,2}^s(1-[H^+]_f) + K_{1,3}^s(1-[H^+]_f^2) \qquad (15)$$

[redacted]