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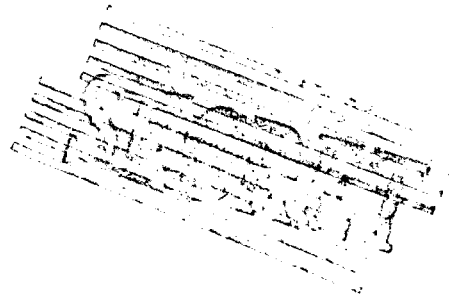
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SPECIES OF URANIUM(VI) WITH TTA IN BENZENE AND PERCHLORIC

ACID. THE CHARGE ON URANYL ION.

William C. Orr

September 1948

Berkeley, California

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Bureau of Ships	23
Carbide & Carbon Chemicals Corp. (K-25 Plant)	24-27
Carbide & Carbon Chemicals Corp. (Y-12 Plant)	28-31
Columbia University (Failla)	32
General Electric Company, Richland	33-38
Hanford Operations Office	39
Iowa State College	40
~~Kellex Corporation~~	~~41-42~~
Knolls Atomic Power Laboratory	43-46
Los Alamos	47-49
Massachusetts Institute of Technology (Kaufmann)	50
Massachusetts Institute of Technology (Gaudin)	51
Mound Laboratory	52-53
National Bureau of Standards	54-55
Naval Radiological Defense Laboratory	56
NEPA Project	57
New York Operations Office	58-59
North American Aviation, Inc.	60
Oak Ridge National Laboratory	61-72
Patent Branch, Washington	73
Sylvania Electric Products, Inc.	74
Technical Information Division, OROO	75-89
UCLA Medical Research Laboratory (Warren)	90
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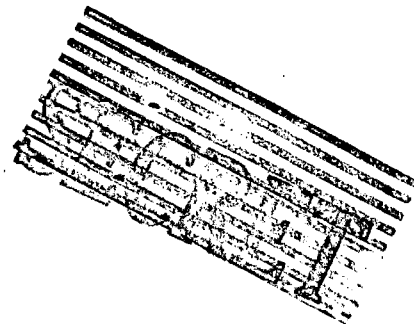
Abstract

Part I

A series of extraction experiments has been performed to determine the distribution coefficient of uranium(VI) between dilute perchloric acid and benzene solutions of TTA. The data are interpreted to show that the principal species in the acid phase is a doubly charged ion, UO_2^{++}. The discrepancies revealed in previous work[1] were not found.

Part II

The spectrophotometric method of analysis developed for use in Part I has shown the existence of previously unreported species of uranium(VI) in the presence of TTA: $UO_2K_2 \cdot HK$ in benzene, and UO_2K^+ in dilute acid.

The absorption spectra of all the principal species are reported.

Table of Contents

Table of Figures

Introduction

Experimental work by E. L. King[1] has demonstrated that in dilute acid solution the molecular species of uranium(VI) is a positive ion which is doubly charged. This species is commonly designated as uranyl ion, and is represented by the formula, UO_2^{++}. The technique used in King's work involved a study of the distribution of uranium(VI) between two immiscible liquid phases; an aqueous phase containing dilute perchloric acid, and a benzene phase containing TTA (thenoyltrifluoroacetone). The experimental results indicated the dipositive nature of the species in question, but contained, in addition, some unexpected features not entirely in accord with this conclusion. The present work was initiated with the aim of investigating these discrepancies, and was extended to include a study of the rather complicated system of molecular species found in aqueous and benzene solutions of uranium(VI) and TTA, a study which is of added interest in view of the wide usefulness of TTA as a complexing agent in extraction work.

The use of distribution experiments in demonstrating the charge on an ion is based in this case on the reaction:

$$UO_2^{++} + 2\ HK = UO_2K_2 + 2\ H^+ \tag{1}$$
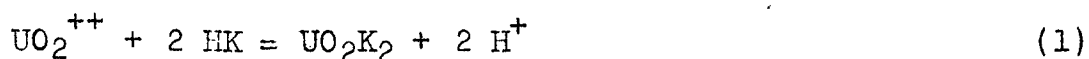
where HK represents a molecule of TTA; the symbol H^+ standing for the proton which is lost in forming a chelate compound, and the symbol K^- standing for the remainder of the molecule (the chelating group). The uranyl chelate is soluble in the organic phase and is found there, whereas the uranyl ion is found in the aqueous phase. Thus the extraction coefficient of uranium(VI) is the ratio, $(UO_2K_2)/(UO_2^{++})$, which enters directly into the expression for the equilibrium constant of the above reaction. By measuring the ex-

traction coefficient at different concentrations of H^+, it is pos-
sible to show that (H^+) enters the equilibrium constant expression
raised to the second power, as required by the coefficient two
which multiplies H^+ in the equation. Verification of the fact that
the coefficient of H^+ in this equation is two, constitutes verifi-
cation that the charge on the uranyl ion is also two.[*]

In practice, a further complication is introduced by the neces-
sity of using not concentrations but activities. The expression
for the equilibrium constant is the following, where parentheses
refer to concentrations in moles per liter in the aqueous phase
for UO_2^{++} and H^+, and in the benzene phase for UO_2K_2 and HK. The
Υ's represent the appropriate activity coefficients,

$$K = \frac{(UO_2K_2)(H^+)^2 \; \Upsilon_{UO_2K_2} \; \Upsilon^2_{H^+}}{(UO_2^{++})(HK)^2 \; \Upsilon_{UO_2^{++}} \; \Upsilon^2_{HK}} \tag{3}$$

The acid used was perchloric acid, and whereas its concentration
was altered throughout the series of solutions used, the total
ionic strength was made the same in all aqueous phases by the addi-
tion to each of a calculated quantity of lithium perchlorate. The
activity coefficients of the ions may thus be regarded as practical-
ly constant throughout the series of extraction experiments, since
the ionic strength was constant, and they may be transferred to the

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[*]The generality of this statement may be made more evident by
rewriting equation (1) in the following more general form where the
correct value two is not assumed, but is represented by n:

$$U(OH)_{6-n}^{+n} + 2\,HK = UO_2K_2 + (4-n)\,H_2O + n\,H^+ \tag{2}$$
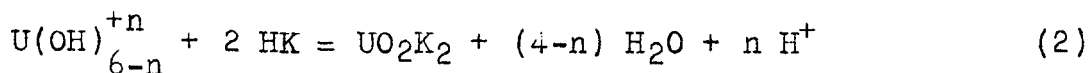
left side of the equation and incorporated in the value of K to give $K' = K(\gamma_{UO_2^{++}})/(\gamma^2_{H^+})$. The activity coefficient of TTA, γ_{HK}, has been independently determined by E. L. King and W. H. Reas[2], who measured the distribution of TTA between dilute acid and benzene phases. The remaining activity coefficient, $\gamma_{UO_2K_2}$, was determined by King[1], who measured the solubility of solid uranyl chelate in benzene solutions of various concentrations of TTA. An acid phase was present with the saturated solutions so that the conditions were comparable with those of the present experiments. The values of γ_{HK} and $\gamma_{UO_2K_2}$ at low TTA concentration were taken as unity.

The experiments consist of shaking or stirring together an aqueous phase containing a known concentration of acid, and a benzene phase containing a known concentration of TTA. In addition, the total amount of uranium(VI) is known, and by analysis of its concentration in either of the phases after the attainment of equilibrium, the extraction coefficient, $E = (UO_2K_2)/(UO_2^{++})$ may be determined. This quantity multiplied by $\gamma_{UO_2K_2}$ is denoted by E' ($E' = E\gamma_{UO_2K_2}$), and with it the expression for the equilibrium constant, equation (3), becomes,

$$K' = E' \frac{(H^+)^2}{(HK)^2 \gamma^2_{HK}} , \qquad (4)$$

from which may be obtained,

$$\log E' = -2 \log (H^+) + \log (K' \cdot (HK)^2 \gamma^2_{HK}). \qquad (5)$$

For any series of experiments in which (HK), the concentration of TTA in benzene, is kept unchanged, the last term on the right is constant. Plotting $\log E'$ against $\log (H^+)$ for such a series should give a straight line with a slope of minus two.

The data from King's experiments were treated in this fashion and yielded the straight lines reproduced in Fig. 1. The slope of the middle line is exactly minus two, whereas the slopes of the other two deviate somewhat from this value. The magnitude of the discrepancy is at most 13 percent, but it has the appearance of being a real deviation in slope, rather than a mere error in the position of one or two experimental points. This contention is supported by the fact that the slopes decrease in order, suggesting a definite trend.

In order to investigate the nature of the deviations from a slope of minus two obtained by King, his extraction experiments have been repeated and extended. Furthermore, a different analytical method has been employed, eliminating the chief source of uncertainty in the original work.

To determine the concentration of uranium extracted into the benzene phase the optical density of this phase was measured by means of a Beckman Model DU quartz spectrophotometer. A study of the absorption spectra of the species present in this phase and the determination of their molar extinction coefficients enabled the calculation of concentration to be made. The analyses for uranium in the case of King's experiments were performed by first extracting the uranium from an aliquot of the benzene phase into normal sulfuric acid solution, then extracting again with pure benzene to reduce the concentration of TTA, and finally, after reduction by zinc amalgam in a Jones reductor, titrating the uranium(IV) with standardized ceric sulfate in the presence of ferric ion[3]. In the series of cases where the aqueous phase too was analyzed by the same
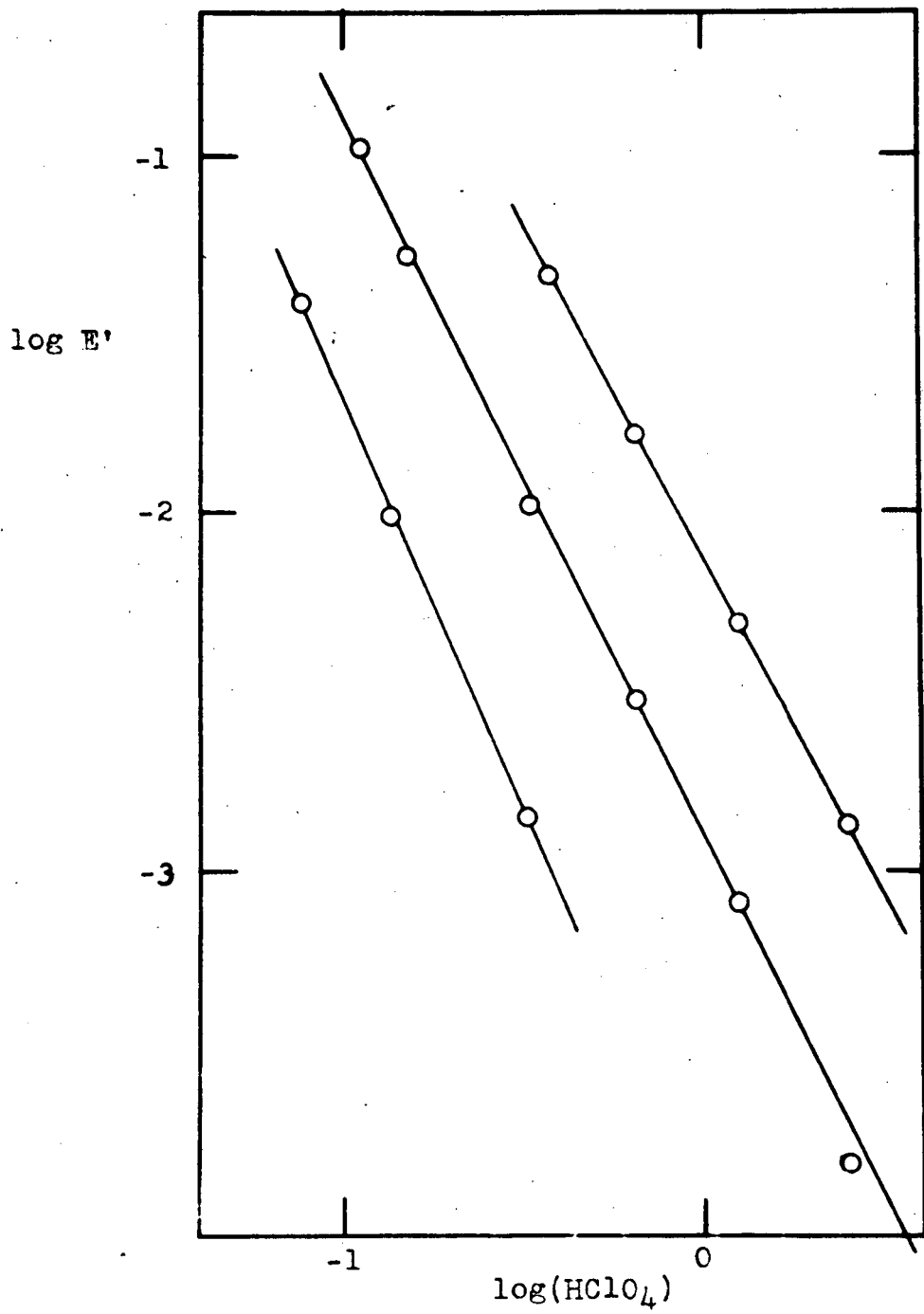
Figure 1

procedure, the total uranium found could be compared with the total taken initially. At best the material balance deviated from 100 percent by approximately two percent, which indicates the order of magnitude of the errors encountered in the procedure.

The uranyl perchlorate used by King was prepared by fuming with perchloric acid the uranyl salt of a more volatile acid, and was kept as a stock solution in the presence of acid. There is some question as to the accuracy with which it is possible to determine by titration the exact concentration of acid in such a solution containing uranium(VI). Any error in this determination would appear in the value taken for the acid concentrations in the extraction experiments.

To avoid this source of uncertainty in the present work, a supply of pure solid uranyl perchlorate was prepared. Thus all acid used in the experiments could be added separately from a carefully standardized solution of perchloric acid.

Part I.   Extraction Experiments

A.   Experimental Procedure

A series of experiments was performed to determine the distri-
bution coefficient of uranium(VI) between dilute perchloric acid
solutions and solutions of TTA in benzene. The data obtained for a
variety of concentrations were then interpreted as outlined in the
introduction.

The experimental procedure consisted of vigorously stirring
together a benzene and an aqueous phase, allowing rapid extraction
of the dissolved uranium(VI) from one into the other. After equili-
bration. the stirring was stopped, the phases were allowed to sepa-
rate into two layers, and the optical absorption spectrum of each
phase was measured to determine its uranium content.

The vessel used for the equilibrations was made by sealing a
rounded bottom end onto a 15 cm length of 3 cm diameter pyrex tubing.
The open top end was then closed by a cap which fitted tightly by
means of a standard-taper ground glass joint. Ten milliliters each
of the aqueous and benzene solutions were pipetted into the vessel
and were kept intimately mixed by means of a motor-driven glass
stirring propeller whose shaft passed down through a hole in the
center of the cap, supported by a cylindrical gasket made of Teflon
and fitted to the hole. After thirty minutes of stirring the motor
was stopped and time was allowed for the phases to separate. A
pipette was then lowered into the vessel through a side arm made for
the purpose, set into the wall at an angle to the vertical, and
normally closed by a ground glass stopper. Enough of the benzene

phase was withdrawn to fill a Beckman cell of two centimeters length (about 6 ml.). Its absorption was measured at once in a Model DU quartz spectrophotometer. A like sample of the aqueous layer was then withdrawn and its absorption measured in the same fashion.

It has been shown[2] that TTA is affected by light. A photo-decomposition occurs which is, however, not sufficiently rapid to change appreciably the concentration of TTA in experiments such as those under consideration, provided that exposure to brilliant illumination is avoided. The effect which is of importance to the present work is the change in the absorption spectrum of TTA in benzene which is presumably due to the formation of small amounts of decomposition products.

To minimize the exposure of TTA solutions to light, the vessel in which the solutions were stirred was coated with an opaque layer of black paint. Similarly coated were the flasks used for keeping the TTA solutions before equilibration.

The temperature of all solutions at the time of extraction equilibrium was $25.0^\circ C$. This temperature was maintained by partially immersing the mixing vessel in a large water bath whose temperature deviated from the desired value by less than $0.1^\circ C$.

The solutions used in each group of extraction determinations were prepared in advance and kept in glass-stoppered flasks. In most cases the initial aqueous solutions contained all the uranium as uranyl perchlorate, and the benzene solutions contained only TTA. In a few cases the uranium was all contained in the initial benzene solution, as the chelate, UO_2K_2, and the aqueous solution contained only perchloric acid and the lithium perchlorate added to maintain the same ionic strength in the aqueous phase of all extractions. The

results were independent of which phase was chosen to contain the uranium initially.

The aqueous solutions were prepared first in every case, so that the extraction experiments might be performed with the least delay after the preparation of the light-sensitive TTA benzene solutions.

Solid uranyl perchlorate was prepared as the source of uranium for the aqueous solutions. Since this compound is deliquescent, it is difficult to weigh it with accuracy. Hence, stock solutions with a known concentration of added perchloric acid were prepared, and standardized by a gravimetric determination of their uranium content. The preparation of uranyl perchlorate and the standardization of its solutions is discussed in Appendix B.

Solutions of perchloric acid of several convenient concentrations made by diluting Baker's vacuum distilled 72 percent $HClO_4$, were standardized by titration. A stock solution of lithium perchlorate was prepared by dissolving a weighed amount of reagent grade salt to make a known volume of solution. The concentration was calculated on the assumption that the crystalline form was the trihydrate.

The required volumes of these stock solutions were delivered from 10 ml and 50 ml burets, mixed, and diluted in volumetric flasks to a final volume in each case of 50 ml. All volumetric glassware was calibrated, and the errors in concentrations of the initial solutions so prepared are in general small compared to the uncertainties in the final concentrations as determined spectrophotometrically.

The benzene used was of the quality designated "thiophene free". It contained no impurities detectable in its absorption spectrum, and no special steps were taken to increase its purity.

The TTA used was obtained through the courtesy of Dr. J. C. Reid. It was freshly prepared and of high purity, melting in a capillary between 43.6 - 44.0°C. The odor associated with TTA, which belongs chiefly to its decomposition products, was remarkably slight when the supply was first received. The crystalline material was pulverized in a mortar and kept in a dry condition by storage in a dessicator over anhydrous calcium sulfate. It could be weighed without difficulty, and solutions were prepared by dissolving a weighed amount to make a known final volume. As the absorption spectrum was known, the concentrations of TTA solutions could be checked by measuring their optical density.

The uranyl TTA chelate used in the benzene solutions containing the uranium was prepared by slowly adding ammonium hydroxide to an acid solution of uranyl nitrate and TTA. It appeared under these conditions as a bright orange, flocculent precipitate. It was dissolved and recrystallized from benzene. The solution used in experiment 4c was prepared by dissolving a weighed amount of the chelate in the TTA - benzene solution prepared for experiments 4a and 4b. The solution used for experiments 5b and 5c was prepared by dissolving in a single volumetric flask weighed amounts of TTA and uranyl chelate by adding benzene to make a known final volume.

B. Experimental Results

The data obtained from five series of extraction experiments are summarized in Table 1 of this section, and the corrected extraction coefficients calculated are plotted in Figs. 2 and 3. A detailed discussion of the procedure used in determining all the quantities that appear in Table 1 is given following the table.

Each of the five series of experiments consists of three or more extractions performed with the same, or approximately the same, concentration of TTA. The data for each series are therefore expected to yield a straight line, as shown by Equation (5), page 8, when log E' is plotted against log (H^+). The straight lines corresponding to the first four series are shown in Fig. 2. All have been drawn with slopes of minus two, as required by Equation (5). The scale of the plot is reduced in Fig. 3, so that two points from series 5 may be included. The numbering of the series gives the order in which the experiments were performed.

Series 1 consists of three extractions at a TTA concentration of 1.56$\underline{M}$ (moles per liter), slightly higher than the highest concentration used by King. The points fall well on the line, and fail to confirm any deviation from the expected slope.

Series 2 consists of five extractions at a TTA concentration of 0.165$\underline{M}$. Points 2a, 2b and 2c lie below the line defined by 2d and 2e, and approach it progressively. An explanation of this behavior was found on examination of the concentrations used. It has been pointed out that an approximately uniform ionic strength ($\mu = 1.90$) was maintained in the aqueous phase of all extractions for the purpose of making effectively constant the activity coefficients of all ionic species present. The major contribution to the ionic strength
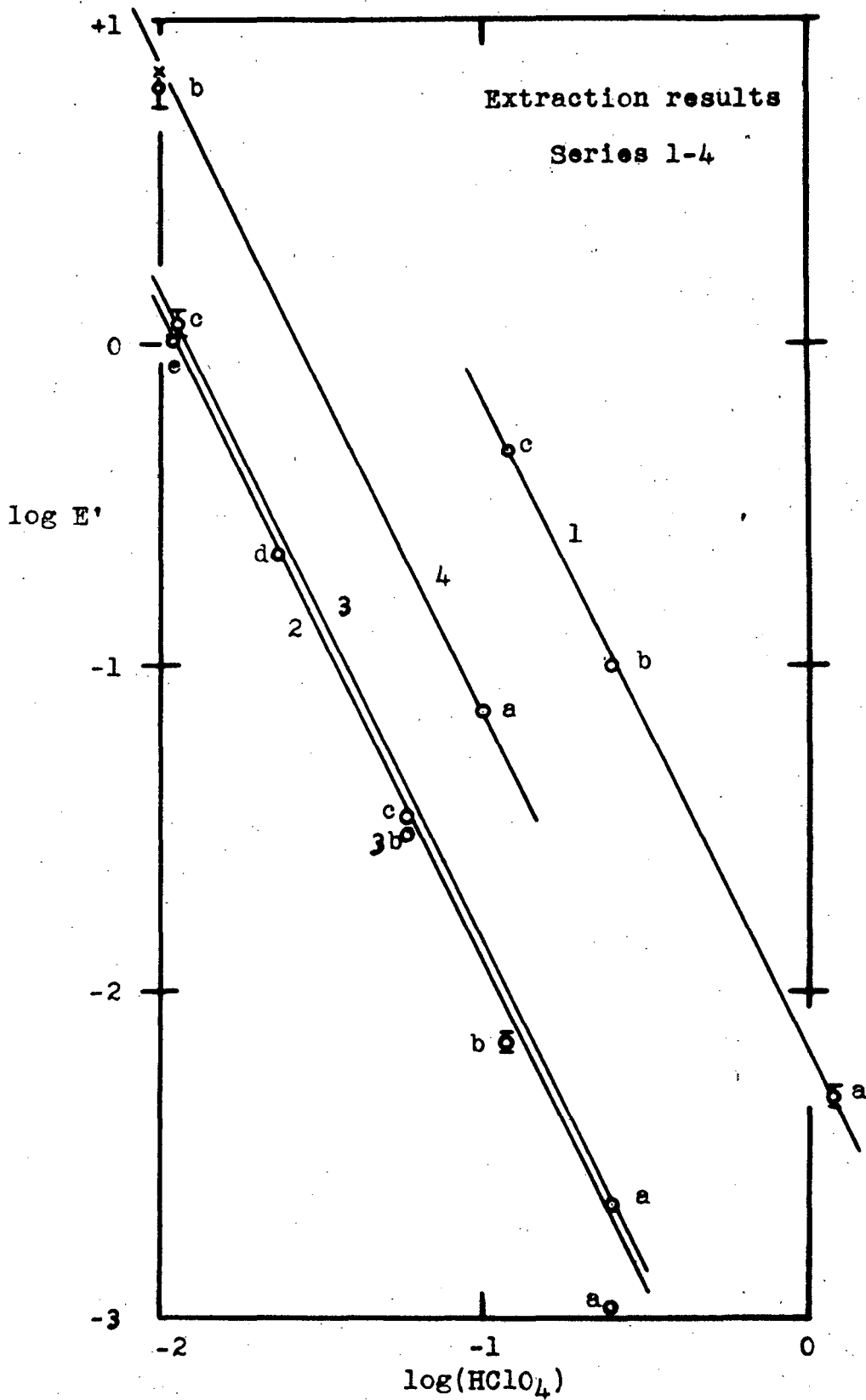
Figure 2
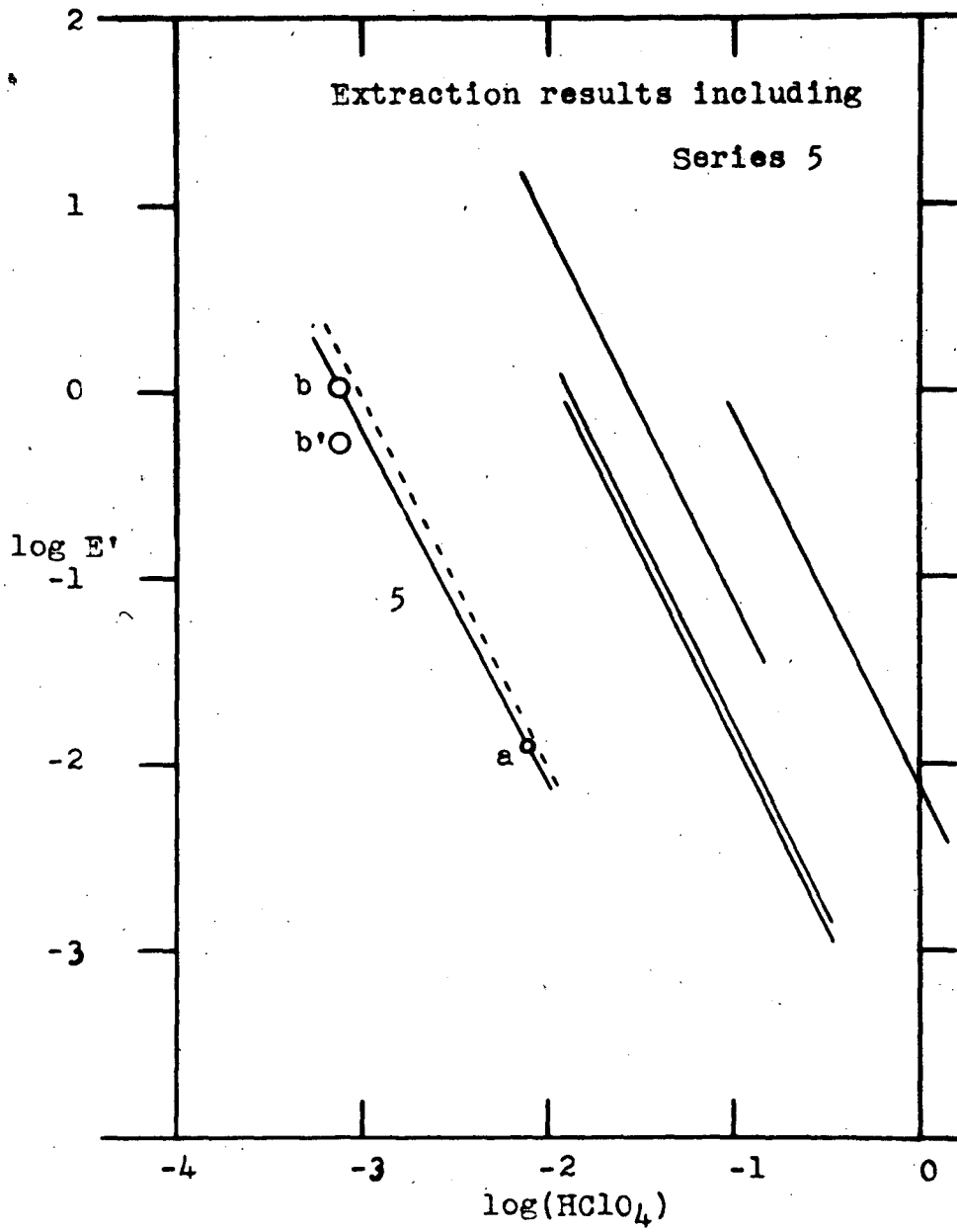
Figure 3

in most cases is that of the added lithium perchlorate. However, in those experiments where this is not true, of which the most conspicuous example is 2a, the data fall below the line. Although the ionic strength is indeed the same, the ionic environment has in fact been altered by exchanging UO_2^{++} for Li^+ as the principal positive species. That such a change results in the lowering of the ratio $(\gamma_{UO_2^{++}}/\gamma_H^{+2})$ is indicated by the behavior of the points. It is valid to assume the constancy of activity coefficients in solutions of constant ionic strength only when the concentrations being altered are low.

Series 3 consists of three extractions performed at TTA concentrations only slightly higher than that of series 2. It was designed to verify the explanation proposed above. The concentration of uranium was greatly reduced in this series with the result that points 3a and 3c fall on a line of slope minus two. Point 3b is below its expected position because of an error in the performance of the experiment. That an error occurred was shown by measurements of the absorption of a sample of the benzene phase diluted to the point where the only absorbing species of consequence was TTA. These measurements gave a value of only 0.163$\underline{M}$ for the TTA concentration before dilution, a value that should have been 0.170$\underline{M}$. Similar dilution measurements on benzene phases 3a and 3c showed no such discrepancy. Accepting the lower value for the concentration of TTA one expects to find point 3b about on the line of series 2. That it is still slightly low is probably due to errors in the concentrations of species other than TTA, errors which occurred in the same unknown operation which led to the one discovered. Since there was no reason to suspect either 3a or 3c of inaccuracy, it was regarded as unnecessary to repeat the series.

Series 4 consists of three extractions, only two of which are shown in Fig. 2. It was to be expected that this series, made at a concentration of TTA intermediate between those of series 1 and series 3, should show no new behavior in the same region, and the chief aim of these extractions was to extend the data to the region of lower acidities and consequently higher extraction coefficients than previously investigated. In this region the accuracy of the present experimental method becomes less and less, as will be discussed shortly, and in the case of 4c, it has passed its useful limit. The position of this point is so ill-defined within the experimental error that it has not been plotted. The x which appears above the point 4b in Fig. 2 is discussed in the final section of Part II of this report.

Series 5 consists of three extractions at greatly reduced concentrations of TTA, of which 0.0192$\underline{M}$ in the case of 5a is the lowest. Again only the first two points are plotted (Fig. 3) and the accuracy of even these is in serious question. Adjusting the position of point 5b to correspond to the case where its TTA concentration is the same as that for point 5a lowers it far below the position required for a slope of minus two. This adjustment is made by subtracting from log E' the quantity, $\log(0.0269)^2 - \log(0.0192)^2$, which is the correction required according to Equation (5). The corrected point is marked 5b' in Fig. 3.

In order properly to investigate extraction coefficients in the concentration region of series 5, it would be desirable to have a more complete understanding of the species present in the aqueous phases of this region. The work discussed in Part II shows clearly that complexing of uranium by TTA becomes important here, and this

is a factor which would serve to lower the values of log E' as plot-
ted, but quantitatively the lowering observed is not fully accounted
for by calculations based on the data available. It should be fur-
ther observed that hydrolysis of uranyl ion is not expected to con-
tribute greatly to the lowering of the extraction coefficient in
this region, according to calculations based on the value of the
constant given by Best, Taub and Longsworth[4],

$$1.38 \times 10^{-6} = \frac{(U_2O_5^{++})(H^+)^2}{(UO_2^{++})^2} . \tag{6}$$

At concentrations of hydrogen ion of the order of 0.001$\underline{M}$, the ratio
$(U_2O_5^{++})/(UO_2^{++})^2$ is of the order of unity. For total uranium con-
centrations which are small compared to one, the squared denominator
means a very small value indeed for the ratio $(U_2O_5^{++})/(UO_2^{++})$.

The difficulties to be met in any study by spectrophotometric
measurements of molecular species present in solutions of low acidi-
ty such as these are discussed in Part II.

To further test the agreement of the experimental data with the
behavior predicted by Equation (5), page 8, a second type of plot
may be made which shows the dependence of the extraction coefficient
on the activity of TTA. Rewriting Equation (5) gives

$$\log E' = 2 \log (HK) \, \Upsilon_{HK} + \log \frac{K'}{(H^+)^2} \tag{7}$$

from which it may be seen that at constant acid concentration the
plot of log E' as a function of log (HK) Υ_{HK} should give a straight
line of slope two.

The value of log E' for each curve in Fig. 2 has been read at
the point corresponding to an acid concentration of 0.1$\underline{M}$, log (H$^+$) =
-1. These values have been plotted in Fig. 4 against log(HK) Υ_{HK},
where Υ_{HK} has been obtained from the data of King and Reas[2] which
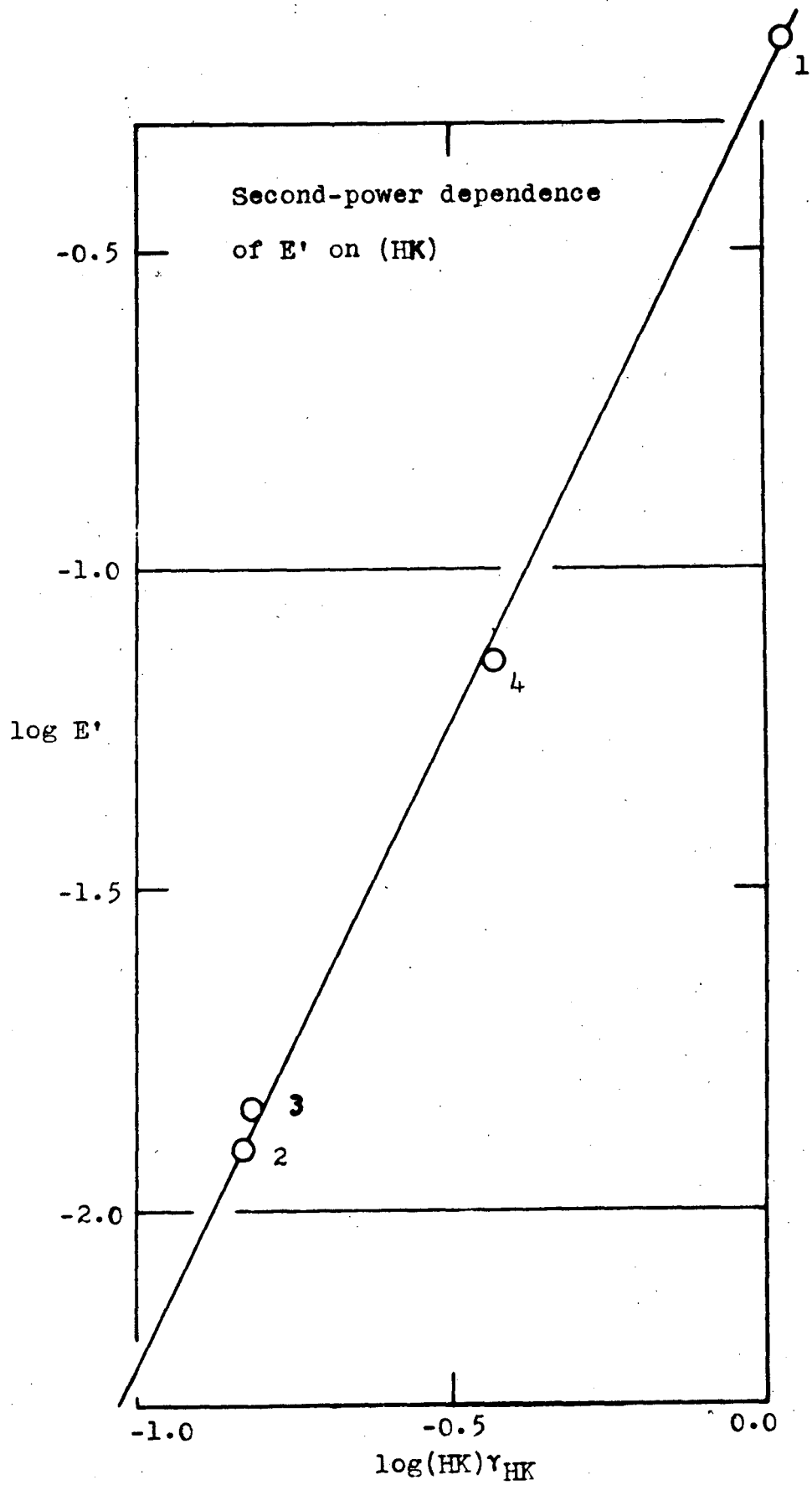
Figure 4

are reproduced in Appendix A. The quantities plotted are tabulated in Table 2.

The points fall well on the line which has been drawn to have the required slope of two. This serves to confirm the second power dependence on TTA which was expected.

It is now possible to express the results of the extraction experiments in a single mathematical statement, namely, by evaluating the equilibrium constant of Equation (4), page 8. From this equation it is seen that where (HK) γ_{HK} is equal to (H^+), there K' is equal to E'. Fig. 4 is plotted for the case that $\log (H^+)$ equals minus one, so where $\log (HK)$ γ_{HK} in that figure is also minus one the value of E' is equal to K'. This value is $K' = 0.0055$. The extraction coefficient for any concentration of acid and TTA (within the limits shown to be valid) may be calculated from the following equation:

$$E' = 0.0055 \frac{(HK)^2 \ \gamma_{HK}^2}{(H^+)^2} \tag{8}$$

This equation is strictly correct only for solutions of uranyl perchlorate at low concentration, and at an ionic strength of 1.9 contributed by perchloric acid and lithium perchlorate.

Table 1

Extraction Experiments. Summary of Data.

(Concentrations expressed in moles per liter)

Series 1

Experiment number	1a	1b	1c
Concentrations of solutions prepared			
Benzene - TTA	1.59	1.59	1.59
UO_2K_2	0	0	0
Aqueous - $UO_2(ClO_4)_2$	0.0586	0.00477	0.00279
$HClO_4$	1.184	0.245	0.1161
$LiClO_4$	0.546	1.645	1.780
Concentrations after equilibration			
Benzene - TTA	1.56	1.56	1.56
Total U	0.0016 ±0.0001	0.00176 ±0.00006	0.00204 ±0.00001
Aqueous - Total U	0.0570	0.00301	0.00075
$HClO_4$	1.187 ±0.000	0.248 ±0.000	0.1202 ±0.0000
Calculated extraction coefficient			
γ_U	0.17	0.17	0.17
E'	0.00477 ±0.00032	0.0995 ±0.0010	0.463 ±0.008

Table 1 (continued)

Series 2

Expt. No.	2a	2b	2c	2d	2e
Concentrations of solutions prepared					
Benzene - TTA	0.171	0.171	0.171	0.171	0.171
UO_2K_2	0	0	0	0	0
Aqueous - $UO_2(ClO_4)_2$	0.533	0.1025	0.0231	0.00479	0.00252
$HClO_4$	0.246	0.1160	0.0565	0.02105	0.00800
$LiClO_4$	0.060	1.48	1.77	1.865	1.886
Concentrations after equilibration					
Benzene - TTA	0.165	0.165	0.165	0.165	0.164
Total U	0.00083 $\pm$0.00003	0.00102 $\pm$0.00005	0.00108 $\pm$0.00003	0.00116 $\pm$0.00004	0.00150 $\pm$0.00004
Aqueous - Total U	0.532	0.1015	0.0220	0.00362	0.00102
$HClO_4$	0.248 $\pm$0.000	0.118 $\pm$0.000	0.0587 $\pm$0.0001	0.0234 $\pm$0.0001	0.0110 $\pm$0.0001
Calculated extraction coefficient					
γ_U	0.694	0.694	0.694	0.694	0.695
E'	0.00108 $\pm$0.00004	0.00697 $\pm$0.00036	0.0341 $\pm$0.0011	0.222 $\pm$0.010	1.02 $\pm$0.07

Table 1 (continued)

Series 3

Experiment number	3a	3b	3c
Concentrations of solutions prepared			
Benzene - TTA	0.180	0.180	0.180
UO_2K_2	0	0	0
Aqueous - $UO_2(ClO_4)_2$	0.0633	0.0664	0.00519
$HClO_4$	0.247	0.0527	0.00485
$LiClO_4$	1.46	1.65	1.88
Concentrations after equilibration			
Benzene - TTA	0.176	0.170	0.170
Total U	0.000205 ±0.000010	0.00278 ±0.00006	0.00324 ±0.00012
Aqueous - Total U	0.0631	0.0636	0.00195
$HClO_4$	0.251 ±0.000	0.0583 ±0.0001	0.0113 ±0.0003
Calculated extraction coefficient			
γ_U	0.682	0.690	0.690
E'	0.00221 ±0.00011	0.0301 ±0.0007	1.15 ±0.12

Table 1 (continued)

Series 4

Experiment number	4a	4b	4c
Concentrations of solutions prepared			
Benzene - TTA	0.465	0.465	0.465
UO_2K_2	0	0	0.002054
Aqueous - $UO_2(ClO_4)_2$	0.0168	0.00215	0
$HClO_4$	0.0960	0.00592	0.00100
$LiClO_4$	1.755	1.890	1.896
Concentrations after equilibration			
Benzene - TTA	0.450	0.450	0.454
Total U	0.00223 $\pm$0.00002	0.00200 $\pm$0.00002	0.00202 $\pm$0.00003
Aqueous - Total U	0.0146	0.00015	0.00003
$HClO_4$	0.1005 $\pm$0.0004	0.00992 $\pm$0.00004	0.00094 $\pm$0.00006
Calculated extraction coefficient			
γ_U	0.47	0.47	0.47
E'	0.0718 $\pm$0.0008	6.27 $\pm$1.04	32

Table 1 (continued)

Series 5

Experiment number	5a	5b	5c
Concentrations of solutions prepared			
Benzene – TTA	0.0215	0.0256	0.0256
UO_2K_2	0	0.00177	0.00177
Aqueous – $UO_2(ClO_4)_2$	0.0720	0	0
$HClO_4$	0.00592	0.00240	0.00011
$LiClO_4$	1.68	1.87	1.90
Concentrations after equilibration			
Benzene – TTA	0.0192	0.0269	0.0255
Total U	0.00094 ±0.00005	0.00095 ±0.00005	0.00154 ±0.00005
Aqueous – Total U	0.0711	0.00082	0.00023
$HClO_4$	0.00780 ±0.00010	0.00076 ±0.00010	0.0000
Calculated extraction coefficient			
γ_U	0.97	0.93	0.93
E'	0.0128 ±0.0007	1.08 ±0.13	6.23

The material collected in Table 1 is largely self-explanatory.

The preparation of the initial solutions has been described, and the data concerning their concentrations require no comment.

The concentration of TTA after equilibration was obtained in every case by subtracting from the initial concentration the amount per liter extracted into the aqueous phase (one part in forty, according to King and Reas[2], and by further subtracting the amount required for the chelation of the uranium found in the benzene phase. The value was checked by observing the absorption spectrum of a sample of the benzene phase diluted about ten thousand fold, or to the point where the peak of the TTA spectrum could be measured. The only significant disagreement has been discussed in the case of experiment 3b.

The total uranium concentration in the benzene phase could not be determined directly from its absorption spectrum because it consisted not only of uranyl chelate whose spectrum was known, but also, in part, of a new species, best described as uranyl chelate complexed by the addition of a molecule of TTA. By diluting a sample of the benzene phase one hundred-fold, the amount of this complexing became negligible and the uranium could be determined from its absorption, which was due to uranyl chelate only. The details of the procedure by which the values given were obtained, together with most of the absorption data and a discussion of the probable errors, is the subject of Appendix C.

The total uranium in the aqueous phase was determined by taking the difference between that found in the benzene phase and the total present before equilibration. Thus the error which is indicated for the concentration of uranium in benzene applies equally to the value

of its aqueous concentration.

The final concentration of perchloric acid was determined by adding to the initial concentration the amount per liter formed in the chelation reaction, i.e., two moles of acid per mole of uranium extracted.

The quantity, γ_U, is the activity coefficient of uranium in benzene solutions of TTA. The values given in the table are taken from the data plotted in Fig. 8, page 56. The symbol $\gamma_{UO_2K_2}$ was used for this quantity in the Introduction, but is given another meaning in Part II, hence γ_U seems more appropriate. It is the coefficient which multiplies total uranium concentration (whether or not some of it is complexed by TTA) and not the concentration of the chelate species alone.

The quantity, E', is the corrected extraction coefficient referred to in the Introduction, Equation (4). Its value is obtained by multiplying the total uranium concentration in benzene by γ_U, and dividing by the total uranium concentration in the aqueous phase.

Table 2

Data plotted in Fig. 4

Experiment Series No.	Concentration of TTA	Υ_{HK}	$\log(HK)\Upsilon_{HK}$	$\log E'$
1	1.56	0.690	0.032	-0.175
4	0.450	0.827	-0.429	-1.145
3	0.170	0.898	-0.817	-1.840
2	0.165	0.900	-0.829	-1.905

The values of $\log E'$ are read from Fig. 2. They are the ordinates of the four curves at the value of $\log(HClO_4) = -1$.

C. Conclusions

The extraction experiments which have been described demonstrate that satisfactory results may be obtained from the spectrophotometric method of analysis for uranium in benzene - TTA solutions.

The results show conclusively that the charge on uranium(VI) is plus two in perchloric acid solutions ranging in concentration from 0.01 molar to slightly above one molar. Isotopic exchange experiments by Crandall[5] have shown that two of the oxygen atoms of uranyl ion do not exchange with the oxygens of the solvent water. This evidence denies the correctness of the formula, $U(OH)_4^{++}$, where four oxygens should be equivalent, and thus indicates as correct the other doubly charged form, UO_2^{++}.

The exact second power dependence on TTA activity of the extraction of uranium(VI) into benzene has been confirmed.

The deviations from these results that had been indicated by similar work using an oxidation-reduction titration procedure for the uranium analysis have not been found.

Part II. Molecular Species in
Solutions Containing TTA and Uranium(VI)

In the development of the spectrophotometric method of analysis used in the extraction experiments of Part I, information was obtained concerning the molecular species present in the solutions studied. The following is a discussion of these species, their absorption spectra, and their importance in the analytical method used to determine uranium(VI).

Of particular interest is the species, $UO_2K_2 \cdot HK$, whose existence explains the remarkably low values previously reported[1] for the activity coefficient of uranium(VI) in benzene solutions of high TTA concentration.

A. Species in Benzene Solutions

1. HK

The absorption spectrum of TTA in dry benzene has been measured from 280 mμ, below which benzene solutions are effectively opaque, to 440 mμ, where the value of the molar extinction coefficient falls below 0.01 and the determination becomes highly inaccurate. The principal portion of this spectrum had been previously reported[2], but the absorption at higher wavelengths was of interest to the problem of uranium analysis, and data for this region were not available. The molar extinction coefficient is shown as a function of wavelength in Fig. 5, and is tabulated in Table 3.

The TTA used for these determinations was a freshly prepared sample of the material used in the extraction experiments and described in Part I. The benzene was similar to that previously described. It was dried by being kept in contact with sodium metal.

The wavelength scale of the Beckman spectrophotometer was checked at the wavelength of the 656.3 mμ line of the hydrogen emission spectrum, where the error was zero. Errors elsewhere in the calibration of the instrument were assumed to be reproducible and were neglected. The same instrument, Serial No. D-437, was used throughout all experimental work.

The nature of the molecular species which occurs in dry benzene has been discussed by King and Reas[2]. They have shown it to consist largely or entirely of the enol form of the β-diketone.

The curves of Fig. 5 are drawn to a highly condensed logarithmic scale in order to collect all of them on a single page for ready comparison. This scale expands the curves at low values of ϵ, and greatly flattens the principal peaks. The dashed portion of the curve for

Species in Benzene

Species in dilute perchloric acid
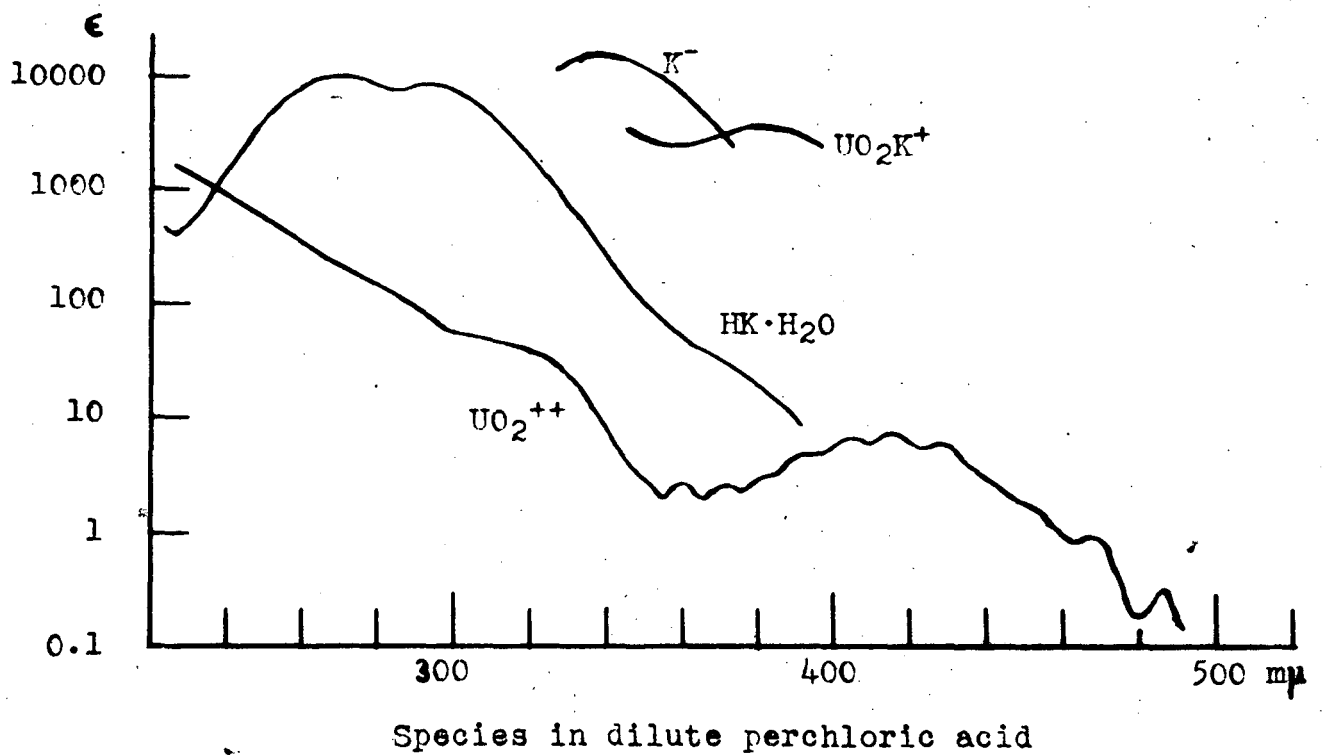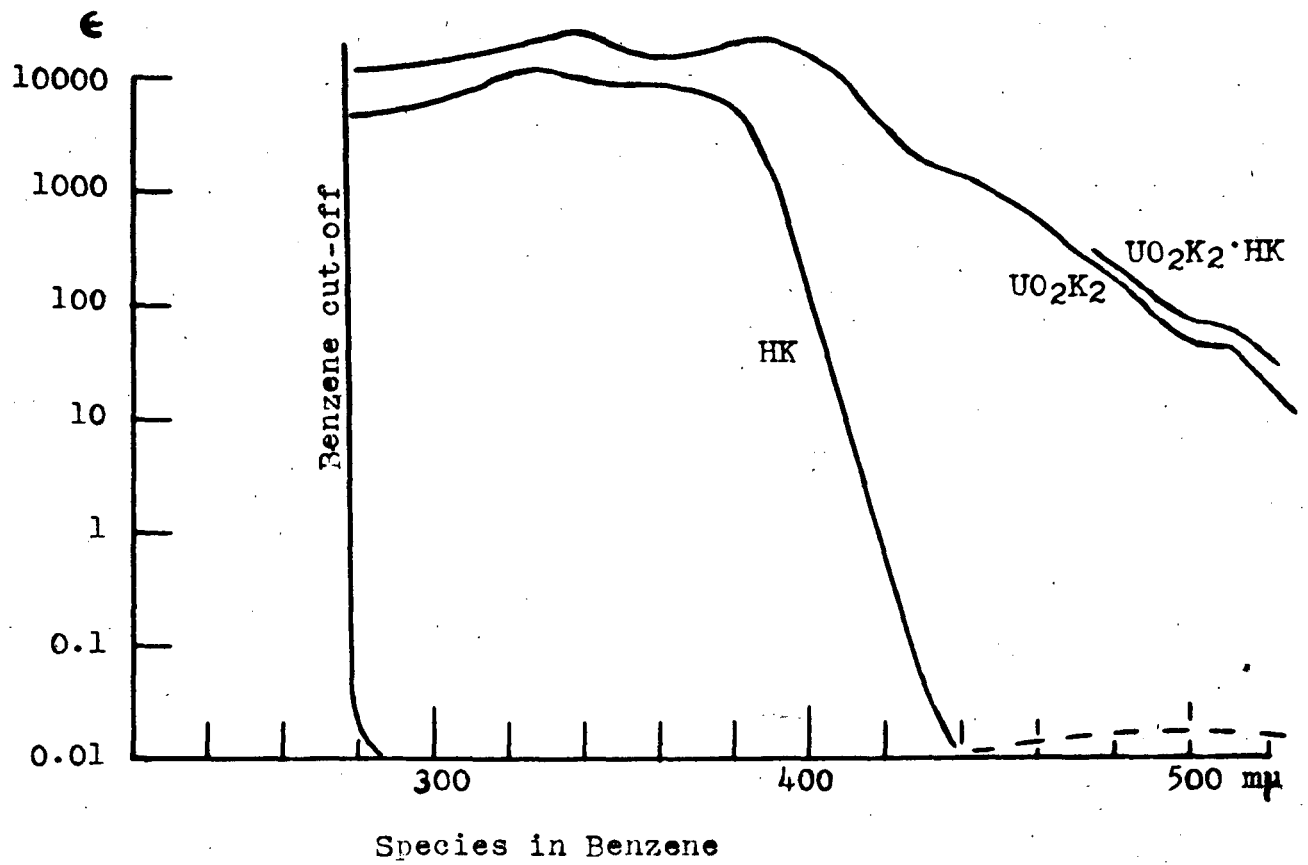
Figure 5

HK is not due to TTA itself, but is found in solutions of TTA which have been exposed to light. The longer the exposure, the higher is this absorption, so it may be concluded that it arises from photodecomposition products. Its only importance to the present work is as a source of possible error in absorption measurements made on uranyl chelate solutions in this region. A satisfactory correction can usually be applied, but at wavelengths above 500 mµ, there is usually some uncertainty arising from this source.

Table 3

Molar extinction coefficient of HK in

benzene solution

mµ	ϵ_{HK}	mµ	ϵ_{HK}	mu	ϵ_{HK}
280	6400	334	11760	388	1860
282	6460	336	11500	390	1290
284	6550	338	11300	392	848
286	6640	340	11130	394	534
288	6790	342	10980	396	330
290	6950	344	10870	398	198
292	7130	346	10750	400	116.5
294	7310	348	10680	402	69.0
296	7550	350	10580	404	42.4
298	7800	352	10480	406	25.5
300	8110	354	10440	408	15.3
302	8410	356	10370	410	9.5
304	8810	358	10280	412	5.8
306	9180	360	10140	414	3.5
308	9600	362	9820	416	2.2
310	10070	364	9440	418	1.4
312	10520	366	8970	420	.90
314	10950	368	8540	422	.56
316	11170	370	8100	424	.35
318	11770	372	7650	426	.23
320	11890	374	7230	428	.15
322	12090	376	6730	430	.10
324	12190	378	6150	432	.07
326	12200	380	5380	434	.05
328	12120	382	4470	436	.035
330	12070	384	3520	438	.02
332	11960	386	2650	440	.01

2. UO_2K_2

The absorption spectrum of uranyl TTA chelate has been measured in dry benzene. The molar extinction coefficient as a function of wavelength is shown in Fig. 5, and tabulated in Table 4.

Slight traces of water in the benzene were found to cause a slow falling of the absorption peaks in a freshly prepared solution, accompanied by other changes in the spectrum which could be accounted for with reasonable success by assuming the appearance of a small amount of TTA. To reduce the extent of this apparent hydrolysis in the solutions used for determining the absorption of the chelate, the benzene, which had been dried over sodium, was further dried by shaking with a liquid alloy of two parts potassium to one part sodium. This procedure gave solutions which changed only very slowly, and on which reproducible measurements could be made.

The chelate was prepared as described in Part I. In addition to being crystallized from benzene, it was dried for twelve hours in a high vacuum shortly before the measurements were made. This drying procedure appeared to have no very great advantage over less extreme measures, since the spectra observed were the same for samples not so treated.

It should be observed that the portion of the spectrum in the neighborhood of 500 mμ, which is the region of particular interest in the analysis for uranium, was measured with solutions of 0.001 molar concentration and higher. Such concentrations are large compared to that of water in well-dried benzene, so no particular difficulty was encountered.

Table 4

Molar extinction coefficient of UO_2K_2 in

benzene solution

mμ	ϵ	mμ	ϵ	mμ	ϵ	mμ	ϵ
280	13400	340	26100	400	16200	460	553
282	13600	342	25760	402	14660	462	516
284	13900	344	23670	404	13050	464	479
286	14150	346	21930	406	11450	466	435
288	14450	348	19870	408	9680	468	382
290	14700	350	18150	410	8250	470	324
292	15100	352	16770	412	6950	472	276
294	15300	354	15910	414	5840	474	231
296	15650	356	15340	416	4920	476	195
298	15920	358	15110	418	4120	478	165
300	16240	360	15230	420	3520	480	140
302	16540	362	15570	422	3010	482	124
304	16850	364	16020	424	2540	484	110
306	17200	366	16540	426	2200	486	98.5
308	17530	368	17300	428	1925	488	87.6
310	17830	370	18040	430	1775	490	76.0
312	18280	372	18830	432	1650	492	65.3
314	18680	374	19630	434	1550	494	56.4
316	19140	376	20270	436	1420	496	50.1
318	19710	378	20900	438	1305	498	47.2
320	20260	380	21400	440	1170	500	45.8
322	20980	382	21630	442	1100	502	45.8
324	21780	384	21870	444	1050	504	46.0
326	22690	386	21800	446	1022	506	45.4
328	23600	388	21520	448	980	508	43.0
330	24050	390	21080	450	920	510	37.9
332	25200	392	20490	452	824	512	31.2
334	25700	394	19700	454	721	514	25.0
336	26200	396	18700	456	645	516	20.6
338	26450	398	17500	458	597	518	17.2
						520	14.5

3. $UO_2K_2 \cdot HK$

In the extraction experiments of Part I, the concentration of TTA was usually in excess of one-tenth molar, whereas the uranium concentration in the benzene phase was always less by a factor of ten or a hundred. From the curves of absorption spectra collected in Fig. 5 it may be noted that the molar extinction coefficient of the chelate, UO_2K_2, is higher than that of TTA in the region of principal absorption, but by a factor of not more than three at any wavelength below 370 mμ. As the concentration of TTA exceeds that of the chelate by a much larger factor than three, the chelate will contribute only a small fraction to the total absorption which one measures in this region, and such measurements will be subject to relatively large errors if used as a means of quantitatively determining uranium. At wavelengths above 380 mμ, the extinction coefficient of TTA falls off rapidly, and the ratio between the two absorptions becomes more and more favorable. At 450 mμ, the chelate absorbs about 100,000 times as much per mole as TTA, so it was in this region of the spectrum that most of the measurements for analytical purposes were made. From 500 mμ to 506 mμ there is a step,[*] or

---

[*] When the spectrum is plotted on a vertical scale less condensed that that of Fig. 5, it becomes easy to see that this step is only the most prominent one of several equally spaced waves on the side of the band in this region. From its general similarity to the much more pronounced fine structure of the uranyl ion spectrum, it seems reasonable to conclude that this structure has its origin in the same vibrations of the uranyl oxygens against the uranium, although modified, of course, by the presence of the chelating groups in the molecule. (See also the section on the spectrum of UO_2^{++}.)

shoulder, where the chelate curve is almost level. This provides a useful region where a slight inaccuracy in wavelength setting can be tolerated. Elsewhere, since the slope of the curve is fairly steep, an error in wavelength setting results in an error in the correlation between the absorption measured and the concentration.

Following the measurement of the spectrum of the chelate, as reported in the preceding section, some preliminary extraction experiments were begun. Measurements on benzene phases containing TTA were soon found to disagree with expected results. It was then shown that the presence of TTA was causing an apparent rise in the molar extinction coefficient of uranyl chelate. Adding TTA to a benzene solution of the chelate increases by an appreciable factor the absorption in the region of 500 mμ, although the absorption due to TTA itself is entirely negligible in this region. Several series of experiments have been conducted to investigate this phenomenon, of which only the last will be discussed.

The absorption from 470 mμ to 520 mμ was measured for each of five benzene solutions containing 0.002 molar uranyl chelate, and in addition, TTA ranging in concentration from 1.045 molar in the first solution to 0.0302 molar in the fifth. The data are given in Table 5a, where the concentrations used are also shown.

The data in the columns of Table 5a which are marked with the letter A result from measurements made on the same five solutions after shaking each for one hour with a small quantity of 0.01 molar perchloric acid. This procedure was adopted when it was observed that the apparent increase in ϵ under investigation was less when an aqueous phase was present.

The apparent molar extinction coefficient, ϵ_a, is obtained by

Table 5a

Experiments on addition of TTA to UO_2K_2

Optical density of solutions

mμ	1	2	3	4	5	1A	2A	3A	4A	5A
470	1.743	1.714	1.943	1.289	1.345	1.493	1.482	1.617	1.092	1.190
474	1.317	1.279	1.465	.943	.977	1.121	1.102		.785	.860
480	.861	.824	.943	.585	.598	.710	.695	.759	.493	.534
484	.702	.672	.765	.468	.470	.566	.554		.390	.421
490	.463	.448	.512	.311	.315	.382	.374	.406	.261	.283
494	.336	.323	.368	.226	.231	.283	.275		.195	.211
498	.290	.278	.314	.192	.197	.237	.235	.255	.170	.184
500	.288	.276	.312	.191	.194	.231	.231	.252	.168	.183
502	.287	.276	.313	.192	.196	.230	.231		.169	.184
504	.280	.272	.310	.190	.194	.227	.229	.249	.168	.184
506	.255	.252	.287	.181	.187	.214	.216	.234	.160	.175
510	.190	.189	.216	.141	.150	.169	.170	.185	.126	.137
514	.120	.119	.136	.089	.096	.111	.109	.118	.079	.086
520	.066	.066	.076	.050	.054	.063	.062	.067	.044	.050

Concentrations used

	TTA	UO_2K_2
Solution 1	1.045	0.00192
Solution 2	0.625	0.00200
Solution 3	0.543	0.00225
Solution 4	0.1154	0.00172
Solution 5	0.0302	0.00195

Table 5b

Density divided by cell length

and concentration of UO_2K_2

(Cell length: 2.00 cm)

mμ	1	2	3	4	5	1A	2A	3A	4A	5A
470	454	429	432	374	345	389	370	359	318	305
474	343	320	326	274	250	292	276		228	220
480	224	206	209	170	153.2	185	174	168.5	143.3	136.9
484	183	168	170	136	120.4	147.4	138.4		113.3	108.0
490	120.6	112.0	114	90.5	80.8	99.5	93.5	90.2	75.9	72.5
494	87.5	80.8	81.8	65.7	59.2	73.7	68.8		56.6	54.1
498	75.5	69.5	69.8	55.8	50.5	61.7	58.8	56.6	49.4	47.2
500	75.0	69.0	69.3	55.5	49.7	60.1	57.8	56.0	48.9	47.0
502	74.8	69.0	69.5	55.8	50.2	59.9	57.8		49.1	47.2
504	73.0	68.0	68.9	55.2	49.7	59.1	57.3	55.4	48.9	47.2
506	66.5	63.0	63.8	52.6	48.0	55.7	54.0	52.0	46.5	44.9
510	49.5	47.2	48.0	41.0	38.5	44.0	42.5	41.1	36.6	35.1
514	31.2	29.8	30.2	25.9	24.6	28.9	27.3	26.2	23.0	22.0
520	17.2	16.5	16.9	14.5	13.8	16.4	15.5	14.9	12.8	12.8

$$D = \log (I_0/I) = lc\, \epsilon_a$$

Table 5c

The quantity in Table 5b minus ϵ

(see below for ϵ)

mμ	1	2	3	4	5	1A	2A	3A	4A	5A
470	154	129	132	74	45	89	70	59	18	5
474	131	108	114	62	38	80	64		16	8
480	92	74	77	38	21.2	53	42	36.5	11.3	4.9
484	79	64	66	32	16.4	43.4	34.4		9.3	4.0
490	50.6	42.0	44	20.5	10.8	29.5	23.5	20.2	5.9	2.5
494	35.0	28.3	29.3	13.2	6.7	21.2	16.3		4.1	1.6
498	29.5	23.5	23.8	9.8	4.5	15.7	12.8	10.6	3.4	1.2
500	29.5	23.5	23.8	10.0	4.2	14.6	12.3	10.5	3.4	1.5
502	29.0	23.2	23.7	10.0	4.4	14.1	12.0		3.3	1.4
504	27.5	22.5	23.4	9.7	4.2	13.6	11.8	9.9	3.4	1.7
506	22.5	19.0	19.8	8.6	4.0	11.7	10.0	8.0	2.5	0.9
510	16.0	13.7	14.5	7.5	5.0	10.5	9.0	7.6	3.1	1.6
514	9.2	7.8	8.2	3.9	2.6	5.9	5.3	4.2	1.0	0
520	4.4	3.7	4.1	1.7	1.0	3.6	2.7	2.1	0	0

Extinction coefficient of UO_2K_2 as corrected to include wavelength error

mμ	ϵ		mμ	ϵ		mμ	ϵ
470	300		494	52.5		506	44.0
474	212		498	46.0		510	33.5
480	132		500	45.5		514	22.0
484	104		502	45.8		520	12.8
490	70		504	45.5			

dividing the measured optical density, D, by the cell length (l = 2 cm) and the concentration of uranyl chelate, c. The marked increase in this quantity, tabulated in Table 5b, which accompanies an increase in the TTA concentration is evident for all solutions except number 3.[*] The relation which defines optical density and molar extinction coefficient is included for reference below Table 5b.

To account for the increase in absorption brought about by TTA, it is necessary to assume that a chemical change has occurred to modify the molecular species present or to create a new absorbing species. The simplest explanation is that a complex is being formed between the original absorbing species, UO_2K_2, and the TTA molecule,

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[*] An explanation for the fact that these data appear to be too high is suggested by consideration of the experimental method. Fifty milliliters of each solution were prepared using dry benzene. Forty milliliters were removed from the flask, shaken with one-half milliliter of acid (the amount of material extracted into this small aqueous phase was neglected), and the absorption of the resulting wet benzene solution measured. Thereupon, the absorption of the remaining ten milliliters of dry solution, kept meanwhile in the dark, was measured.

If it is assumed that a small crystal of uranyl chelate remained undissolved when the forty milliliters were withdrawn, its subsequent solution would cause the concentration of the remaining ten milliliters to be too high, giving high values to all the data for solution 3. Also, however, the data for solution 3A should be too low by an amount corresponding (because of the difference in volumes) to one-fourth the error in solution 3. This is observed to be the case in curve 3ₐ of Fig. 7.

HK, whose presence causes the change. Leaving the structure of such a complex unspecified for the present, let us write the formula as $UO_2K_2 \cdot HK$. The hypothesis may now be tested in the following manner.

The concentration of the new species will be denoted, x. Since c represents the total chelate concentration, the concentration of the species, UO_2K_2, becomes c-x. If ϵ is the molar extinction coefficient already measured for UO_2K_2, and if ϵ_x is taken to be that of $UO_2K_2 \cdot HK$, it follows that the observed optical density of a solution containing these species (measured in a region where TTA itself does not absorb) will be the sum of two terms:

$$D = 2x \epsilon_x + 2(c-x) \epsilon \qquad (9)$$

where two is the value of the cell length. Collecting the terms containing x and dividing through by 2c gives,

$$\frac{D}{2c} = \frac{x}{c} (\epsilon_x - \epsilon) + \epsilon \qquad (10)$$

The quantity on the left side of Equation (10) is the one experimentally determined and tabulated for various wavelengths in Table 5b.

Subtracting ϵ from both sides of Equation (10) gives,

$$\frac{D}{2c} - \epsilon = \frac{x}{c} (\epsilon_x - \epsilon), \qquad (11)$$

the right side of which consists of two factors, each a function of separate variables. Thus, x/c depends on the composition of the solution (constant for any given solution), whereas ($\epsilon_x - \epsilon$) is a function of wavelength alone and is independent of the composition of the solution.

By subtracting ϵ from the quantity tabulated in Table 5b, the function on the left side of Equation (11) is obtained. It is tabulated in Table 5c. Before the experiments here described were performed a slight mechanical displacement of the wavelength mechanism

occurred in the spectrophotometer which was not detected immediately, but which could easily be determined at the conclusion of the experiments. For this reason the reported values of wavelength shown throughout Table 5 are all slightly low, and the values of ϵ given in the lower part of Table 5c have been made to differ from the correct values shown previously in Table 4, by applying the same error to the data of that table. With this correction, amounting to 1 mμ at 470 mμ (and slightly more at longer wavelengths because of the non-linearity of the Beckman scale), the data of these experiments become entirely self-consistent, which is all that is required.

Plotting $\log(d/2c - \epsilon)$ against wavelength, according to

$$\log(D/2c - \epsilon) = \log(x/c) + \log(\epsilon_x - \epsilon), \tag{12}$$

should give a series of five curves, one for each of the five solutions, each curve having the same shape as determined by $\log(\epsilon_x - \epsilon)$, but each having a different intercept as determined by $\log(x/c)$. From the fact that many of the data consist of small differences between large numbers, errors resulting in deviations from smooth curves are to be expected. The smallest differences occur in the case of solution 5A, and the corresponding curve shows the largest deviations. The data of the first half of Table 5c are plotted in Fig. 6, and those of the second, in Fig. 7.

The latter is of the greater interest because, with an aqueous phase present, the conditions are similar to those of the extraction experiments of Part I. Let us proceed to calculate values for the intercepts, $\log(x/c)$, of the curves in Fig. 7.

If the complex obeys an equilibrium expression of the usual form,

$$K = \frac{(UO_2K_2 \cdot HK) \, \gamma_{UO_2K_2 \cdot HK}}{(HK) \, \gamma_{HK}(UO_2K_2) \, \gamma_{UO_2K_2}} \tag{13}$$
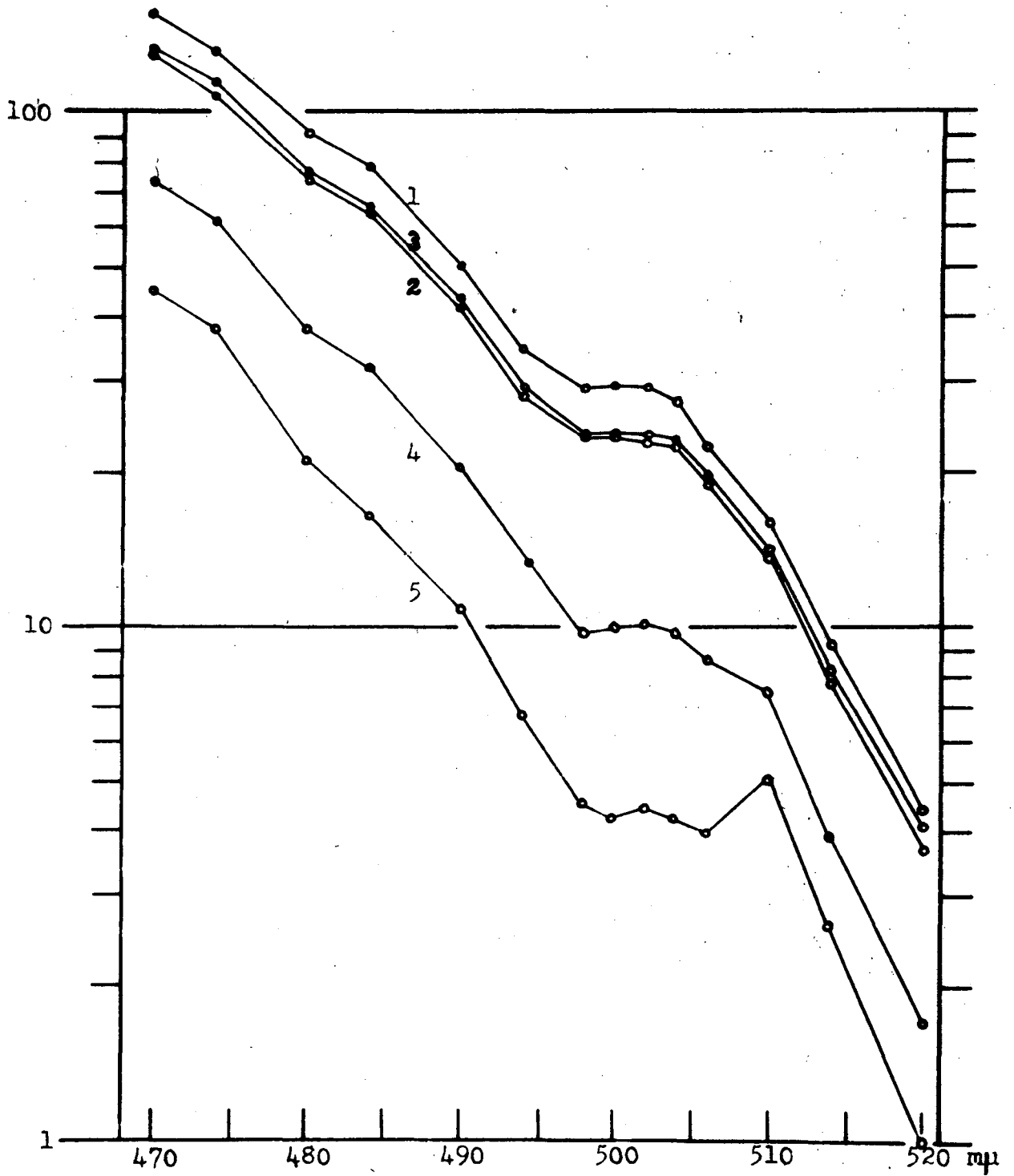
The function (D/2c - ϵ), series in dry benzene

Figure 6
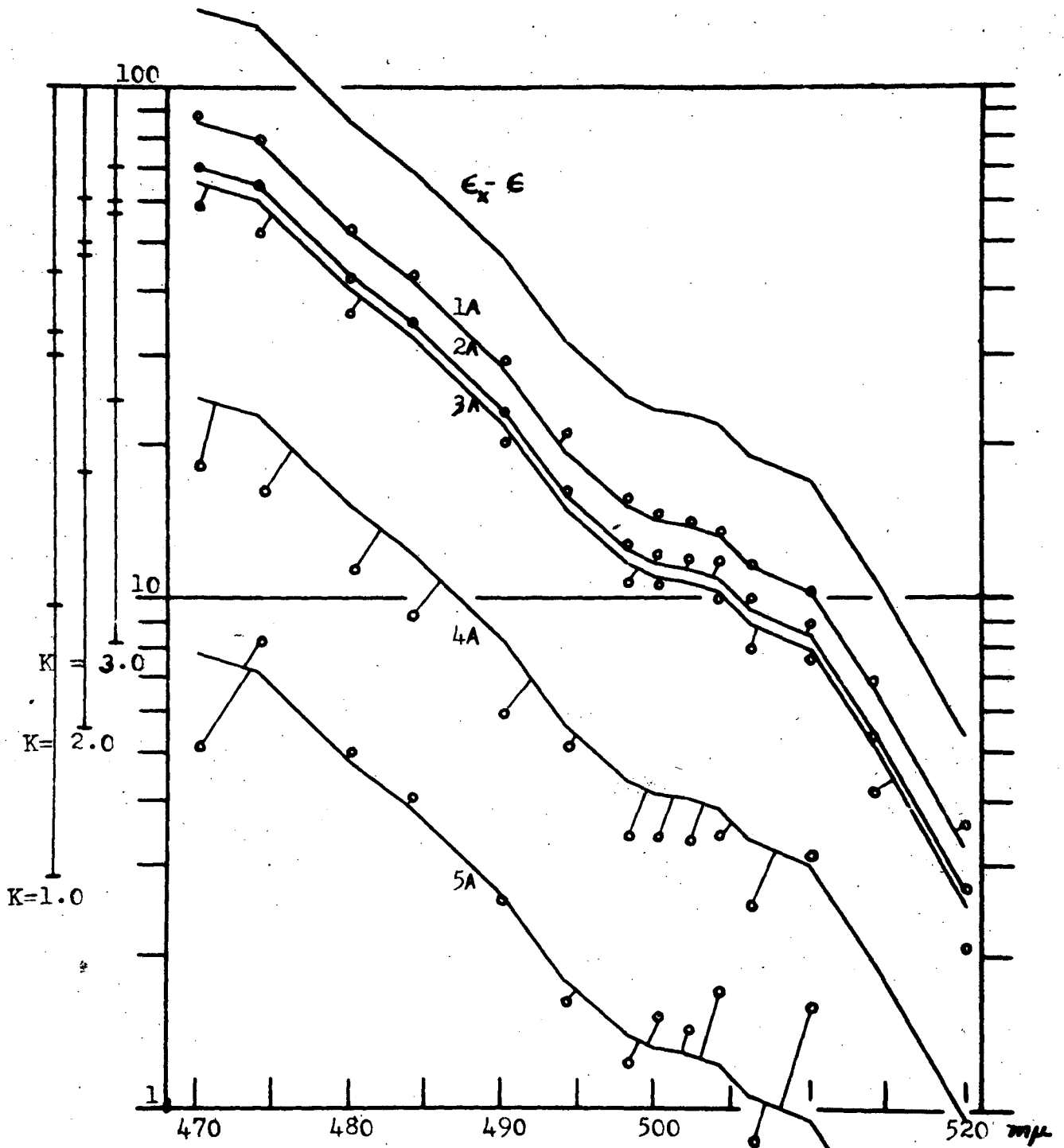
The function (D/2c - ϵ),

series with aqueous phase present

Figure 7

the ratio, (x/c), can be calculated if suitable assumptions are made. In the absence of more information, a reasonable assumption concerning the activity coefficients, $\gamma_{UO_2K_2 \cdot HK}$ and $\gamma_{UO_2K_2}$, is to regard them as equal. Thus they cancel one another. Recalling that $(UO_2K_2 \cdot HK)$ is x, and (UO_2K_2) is $c-x$, one obtains by substitution,

$$K = \frac{x}{(HK) \; \gamma_{HK}(c-x)} \tag{14}$$

which may be rearranged to yield,

$$\frac{x}{c} = \frac{1}{1 + 1/K \; (HK) \; \gamma_{HK}} \tag{15}$$

the expression desired. By assuming a value for K, one may obtain (x/c) for each of the five solutions, since (HK) is known and γ_{HK} has been measured (see Appendix A). By assuming the values 1.0, 2.0 and 3.0, for the equilibrium constant, three sets of values of (x/c) have been calculated for solutions 1A to 5A. These values have been collected in Table 6, and are marked near the left margin of Fig. 7 for easy reference.

A value of 2.0 for the equilibrium constant, K, appears to give the best fit. That is, broken-line curves vertically displaced from one another by amounts corresponding to the values of (x/c) calculated on the basis of $K = 2.0$, can be made to fit the data plotted in Fig. 7 better than those based on any other K. Such curves are the ones drawn in the figure.

The data plotted in Fig. 6, for solutions in dry benzene require some comment. The curves drawn are merely broken lines connecting the experimental points, rather than calculated curves fitted to the data as a whole, as in Fig. 7. The vertical separation between one curve and the next is not so uniform as theory predicts. It decreases, in general, at shorter wavelengths. This could be due to a difference

Table 6

The quantity (x/c), assuming

different values of K

Solution Number	(HK)	γ_{HK}	K = 1.0 (x/c)	K = 2.0 (x/c)	K = 3.0 (x/c)
1	1.045	0.746	0.438	0.610	0.701
2	0.625	0.798	0.333	0.500	0.600
3	0.543	0.811	0.306	0.468	0.569
4	0.1154	0.920	0.0960	0.175	0.242
5	0.0302	0.975	0.0286	0.0555	0.0811

$$\frac{x}{c} = \frac{1}{1 + 1/K \ (HK)\gamma_{HK}}$$

in ϵ, the extinction coefficient of UO_2K_2, which depended on the presence or absence of an aqueous phase. No such difference has been detected, however.

The fact that the curves fall closer together in Fig. 6 than in Fig. 7 merely means that the required value of the constant K for dry benzene solutions must be somewhat larger than 2.0. This is not unreasonable, and may be explained by assuming the partial hydration of UO_2K_2 when water is added.

The only serious disagreement between the two series of results is the fact that without changing some of the assumptions it is impossible to obtain from the data on dry solutions the same molar extinction coefficient for $UO_2K_2 \cdot HK$ as is obtained from the series on wet solutions. The extinction in wet solutions appears to be lower, in general, by about twenty percent. This may indicate that the species, $UO_2K_2 \cdot HK$, is hydrated to some extent.

The method of determining this extinction coefficient will now be described.

In addition to the five lower curves in Fig. 7, drawn to fit as well as possible the experimental points and to maintain at the same time the uniform vertical displacements calculated, there is shown a sixth curve of the same shape marked $(\epsilon_x - \epsilon)$. This curve is displaced vertically with respect to the others by an amount corresponding to a value of $(x/c) = 1$ on the scale at the left. By considering Equation (12), one finds that the ordinate of this curve (on the logarithmic scale used) corresponds to the function $(\epsilon_x - \epsilon)$. Values read from the curve are presented in Table 7, together with the values of ϵ_x obtained by adding ϵ. By determining ϵ_x, we have determined the molar extinction coefficient of the complex, $UO_2K_2 \cdot HK$.

Table 7

Molar extinction coefficient of $UO_2K_2 \cdot HK$

(Assumed equilibrium constant, $K = 2.0$)

mμ	$\epsilon_x - \epsilon$	ϵ	ϵ_x
470	140	300	440
474	130	212	342
480	86	132	218
484	70	104	174
490	47	70	117
494	32	52.5	84.5
498	25	46.0	71
500	23.5	45.5	69
502	23	45.8	68.8
504	22	45.5	67.5
506	19	44.0	63
510	17	33.5	50.5
514	11	22.0	33
520	5.4	12.8	18.2

In view of the errors introduced by the necessity of using small differences in the calculations, there is little justification for accepting the absolute values of ϵ_x so obtained as being very accurate. It is interesting to note, nevertheless, that the extinction coefficient has the same slope as that of uranyl chelate, and with a magnitude greater by a factor of 1.5. This could be expected if a third chelating group were being added to the uranium (the extra hydrogen being assigned to a position on one of the oxygens). It is unfortunate that the absorption of TTA hinders the study of the spectrum of the complex in the region of its principal peaks, where more useful information might be gained as to its structure.

It has been noted earlier that the activity coefficient of uranium(VI) in benzene solutions containing TTA is surprisingly low. The quantitative explanation of this phenomenon constitutes additional evidence for the hypothesis of a complex, $UO_2K_2 \cdot HK$. Let us calculate in terms of the hypothesis the activity coefficient, γ_U, and compare the result with experiment.

By γ_U is meant the coefficient which multiplies the total uranium concentration in benzene to give the activity. It is the quantity determined experimentally, in the absence of any hypothesis as to the activity coefficient of the uranyl chelate. Upon the assumption of the formation of a complex, $UO_2K_2 \cdot HK$, a new activity coefficient may be introduced, $\gamma_{UO_2K_2}$, referring to the species UO_2K_2, and not to the total uranium. The activity of the uranyl chelate must be the same expressed in either terms, hence, $(UO_2K_2) \gamma_{UO_2K_2}$ is equal to $c\gamma_U$, where c is total uranium concentration. Again letting x be the concentration of $UO_2K_2 \cdot HK$, one has that the concentration of the species,

UO_2K_2, is c-x, and from the above equality,

$$\gamma_U = \frac{c-x}{c} \gamma_{UO_2K_2} \qquad (16)$$

Now the function (c-x)/c may be obtained from Equation (14) in terms
of the activity of TTA and the constant of the assumed equilibrium.
Substituting the expression obtained gives

$$\gamma_U = \frac{1}{1 + K(HK)\gamma_{HK}} \gamma_{UO_2K_2} \qquad (17)$$

The remaining assumption that is required concerns $\gamma_{UO_2K_2}$. A value
must be given it, if γ_U is to be calculated from Equation (17).

It has been shown by Reas[6] that in benzene the species, UK_4,
the TTA chelate of uranium(IV), has an activity coefficient in the
presence of TTA which is equal within experimental error to that of
TTA itself. In view of the somewhat similar appearance which both
uranous and uranyl chelates present to their environment, i.e., chief-
ly the hydrocarbon portions of their large chelating groups, we shall
consider reasonable the assumption that they have the same activity
coefficient.

Writing γ_{HK} for $\gamma_{UO_2K_2}$,

$$\gamma_U = \frac{\gamma_{HK}}{1 + K(HK)\gamma_{HK}}, \qquad (18)$$

and we are in a position to calculate γ_U. This has been done for
three different choices of K, and the results are plotted as the
smooth curves of Fig. 8. The circles in the figure are the experi-
mental points obtained by King[1] in his determination of γ_U. The
value 2.0 as the choice for K gives a curve which fits all points but
the lowest. At this point the concentration of TTA is so high that
there are less than ten molecules of benzene for each of TTA in the
solution. Such altered conditions may be expected to put a severe
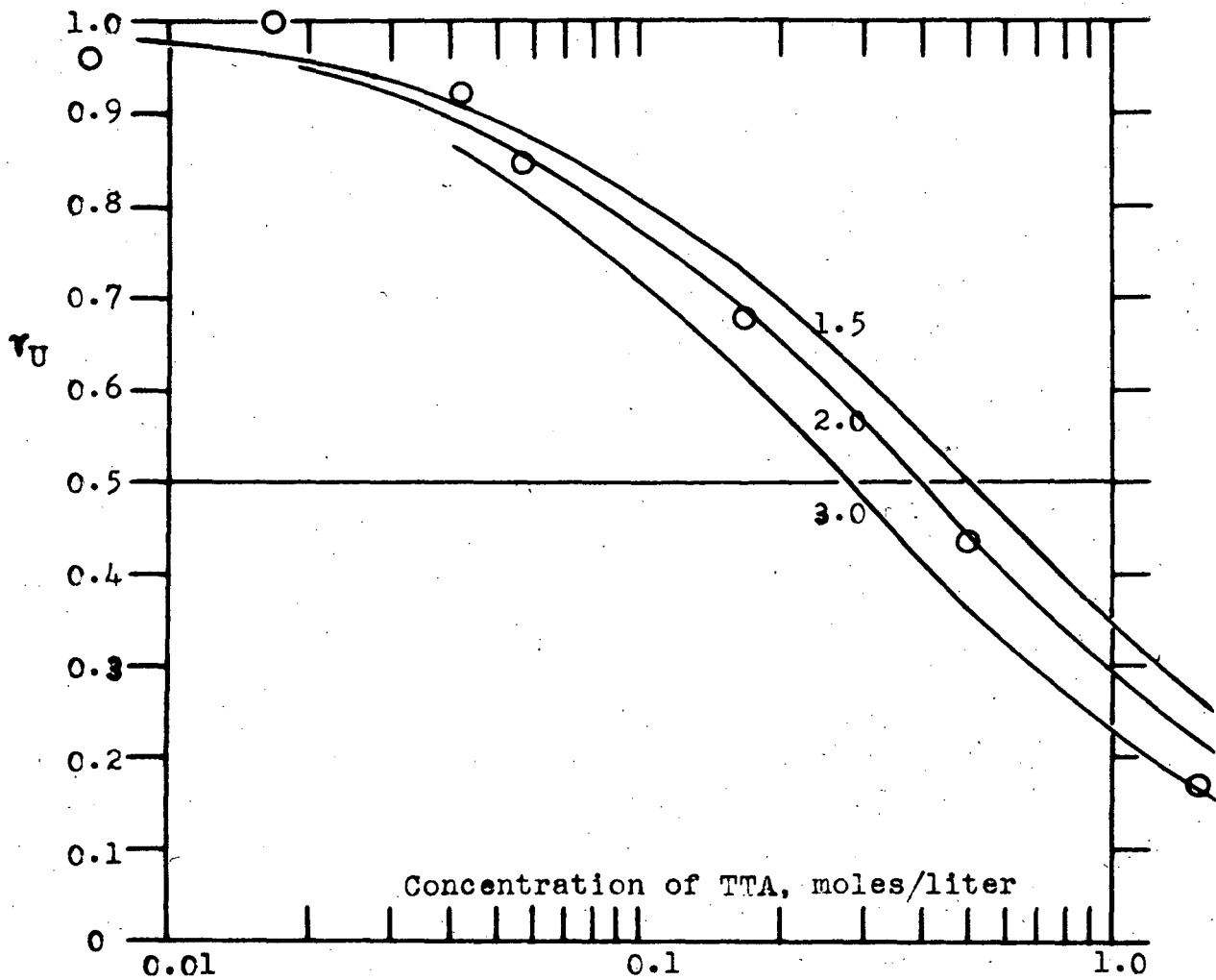
Activity coefficient of uranium(VI)

in benzene

Figure 8

strain on any assumptions based on the behavior of solutions of lower
concentration. Thus, failure to fit the data at this point should
not be regarded as a serious defect. Rather, the excellence of the
agreement elsewhere may be taken as strong support for the original
hypothesis.

It has been shown in the present section that uranyl TTA chelate
is partially complexed by TTA in benzene solution to form a new
species, $UO_2K_2 \cdot HK$, whose absorption spectrum in the region studied is
shown in Fig. 5. The extent of this complexing was found to be about
60 percent at the highest TTA concentration used (1.045 molar). The
existence of this phenomenon is demonstrated by evidence from absorp-
tion spectra and from direct measurements of the activity coefficient
of the chelate in TTA-benzene solutions.

4. $UO_2(OH)K$

When solid uranyl TTA chelate is dissolved in water-saturated benzene, a small amount of a bright yellow, finely divided solid fails to dissolve. This compound is soluble in dry benzene to which TTA is added, and slowly soluble in dilute acid.

A small amount of this yellow solid was collected, and a 5.59 mg sample was weighed and dissolved in 50 ml of $0.1\underline{M}$ perchloric acid. The absorption was that of TTA, and the concentration corresponded to a weight of 558 grams of the original compound per mole of TTA.

Forty milliliters of the acid solution were concentrated by evaporation, and the uranium was precipitated as uranate by ammonium hydroxide in the presence of ammonium chloride. The precipitate was ignited in a crucible weighing about 40 mg, and yielded 2.47 mg of U_3O_8. This corresponds to a weight of 508 grams of the original compound per gram-atom of uranium.

Comparing the two results shows that there are 0.91 moles (i.e., 508/558) of TTA per gram-atom of uranium.

In the absence of a more carefully conducted analysis, this result may be regarded as indicating a one-to-one ratio of TTA to uranium. The formula suggested for the yellow compound is $UO_2(OH)K$, which has a molecular weight of 508.

B. Species in Dilute Acid Solutions.

1. $HK \cdot H_2O$

The spectrum of TTA in aqueous solution is similar to that of TTA monohydrate dissolved in benzene or heptane[7], and hence may be regarded as being a hydrated species. From a study of the spectra of related β-diketones, and from the evidence of bromination experiments to measure enol-keto ratios, Zebroski[7] has further shown that the most likely structure for the species is

$$
\begin{array}{c}
\quad\quad\quad\; O \quad\quad\quad OH \\
\quad\quad\quad\; \| \quad\quad\quad\quad | \\
HC \overset{S}{\diagup} \; C - C - CH_2 - C - CF_3 \quad , \\
\| \quad \| \quad\quad\quad\quad\quad | \\
HC\!-\!\!-\!CH \quad\quad\quad OH
\end{array}
$$
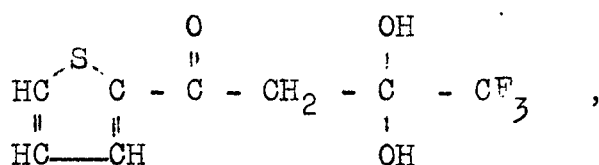
a keto hydrate.

TTA shows some of the properties of a weak acid, forming a negative ion by dissociation according to an equilibrium constant estimated by Zebroski to be $10^{-6.2}$. This species, which may be represented by K^-, is thought to be unhydrated and to be an ion of the enol form, because of the relative slowness of its ionization and the nature of its spectrum. The peak near 340 mμ shown for K^- in Fig. 5, has been observed in the course of the present work as a component of spectra measured at very low acidities.

Of chief interest, however, has been the absorption of $HK \cdot H_2O$, the principal species in the acid range of 0.01 to 0.1 molar. The molar extinction coefficient of this species has been measured as a function of wavelength from 220 mμ to 380 mμ. In the region above 340 mμ an increase in extinction coefficient accompanies an increase of acid concentration above 0.1 molar, for a reason not understood. Thus the values given for this region may not be entirely correct.

The molar extinction coefficient of $HK \cdot H_2O$ is presented in Table 8.

Table 8

Molar Extinction Coefficient of $HK \cdot H_2O$

in 0.01 Molar Acid

mμ	ϵ	mμ	ϵ	mμ	ϵ
220	685	290	7770	336	375
225	427	292	7840	338	287
230	525	294	7820	340	224
235	960	296	7700	342	174
240	1770	298	7530	344	137
245	3050	300	7290	346	111
250	4910	302	6980	348	91
255	7360	304	6600	350	76.5
260	9120	306	6160	352	66
262	9530	308	5590	354	57
264	9820	310	4830	356	50
266	9980	312	4250	358	45
267	10000	314	3700	360	41.5
268	9970	316	3200	362	37
270	9730	318	2680	364	35
272	9400	320	2230	366	33
274	8930	322	1800	368	31
276	8360	324	1450	370	29
278	7980	325	1320	372	28
280	7750	326	1180	374	26
282	7600	328	940	376	24.5
284	7570	330	774	378	22
286	7600	332	610	380	20
288	7670	334	480		

2. UO_2^{++}

The absorption of solutions of uranyl perchlorate in perchloric
acid
is due to uranyl ion in the region studied, as shown by the absence

of absorption by similar solutions of other perchlorates such as that

of lithium.

The most interesting detail of the spectrum is the structure of

equally spaced maxima superimposed on the broad bands, especially

near the peak at 414 mµ. This fine structure is due to the uranium-

oxygen vibrational transitions[8].

The molar extinction coefficient is plotted in Fig. 5 and tabu-

lated in Table 9.

Table 9

Molar Extinction Coefficient of UO_2^{++}

in Dilute Perchloric Acid

$m\mu$	ϵ	$m\mu$	ϵ	$m\mu$	ϵ
212	1670	360	3.07	410	6.85
220	1460	362	2.84	412	7.49
230	1135	364	2.44	413	7.75
240	833	366	2.40	414	7.86
250	538	368	2.68	415	7.83
260	332	370	2.86	416	7.62
267	250	372	2.72	418	6.92
270	220	374	2.50	420	6.15
280	145	376	2.46	422	5.80
290	90	378	2.65	424	5.90
292	82	380	2.91	426	6.09
300	62	382	3.10	428	5.90
310	53.6	384	3.26	430	5.20
320	41.5	386	3.58	432	4.33
330	19	388	4.19	434	3.67
340	7.9	390	4.73	436	3.23
342	6.93	392	5.04	438	3.02
344	5.63	394	5.09	440	2.88
346	4.20	396	5.24		
348	3.33	398	5.75		
350	3.04	400	6.55		
352	2.75	402	7.00		
354	2.40	404	7.05		
356	2.38	406	6.69		
358	2.81	408	6.54		

3. UO_2K^+

The extraction experiments conducted at low acidities gave an indication, as was pointed out in Part I, that complexing of uranium by TTA occurs to some extent in the aqueous phase. The absorption spectra of the aqueous phases, moreover, could not be interpreted in terms of known species, which suggested that a new molecule was present.

The experiments now to be described are of the nature of a preliminary investigation. Their results are quite conclusive, however, as to the existence of some sort of complex, and in all probability, the one proposed is correct.

The procedure used is essentially that which proved helpful in studying the species, $UO_2K_2 \cdot HK$.

The complex molecule which seems most likely to be the one formed in dilute acid solutions containing TTA is the ion, UO_2K^+. The expression describing its equilibrium is

$$K = \frac{(UO_2K^+)(H^+)}{(UO_2^{++})(HK)} \cdot \tag{19}$$

The experiments were performed at constant ionic strength and the concentrations which were altered were low, so activity coefficients may be omitted from the expression.

To test the behavior of the system according to this form of equilibrium constant as fully as possible in a single experiment, three solutions were prepared. All three contained the same concentration of TTA, one had three times as high a concentration of perchloric acid as the other two solutions, and all three solutions contained different concentrations of uranyl perchlorate. The exact concentrations appear in Table 10.

Table 10

Calculation of the Quantity $(D/2c - \epsilon_{HK})$

Solution 1: $(UO_2^{++}) = 0.01586$, $(HK) = 0.000513$, $(H^+) = 0.00337$

$m\mu$	D_{obs}	$D_{UO_2}^{++}$ (est'd)	D	$D/2c$	ϵ_{HK}	$(D/2c - \epsilon_{HK})$
340	2.107	0.244	1.863	1814	307	1507
350	1.366	0.094	1.272	1239	136	1103
360	1.106	0.094	1.012	985	92	893
370	1.204	0.088	1.116	1087	70	997
380	1.346	0.090	1.256	1223	53	1170
382	1.358	0.096	1.262	1229	48	1181
390	1.323	0.156	1.169	1136	26	1110
400	1.035	0.202	0.833	811	14	797

Solution 2: $(UO_2^{++}) = 0.00790$, $(HK) = 0.000513$, $(H^+) = 0.00337$

$m\mu$	D_{obs}	$D_{UO_2}^{++}$ (est'd)	D	$D/2c$	ϵ_{HK}	$(D/2c - \epsilon_{HK})$
340	1.366	0.122	1.244	1212	307	905
350	0.863	0.047	0.816	795	136	659
360	0.686	0.047	0.639	622	92	530
370	0.730	0.044	0.686	669	70	599
380	0.804	0.045	0.759	740	53	687
382	0.809	0.048	0.761	742	48	694
390	0.776	0.073	0.703	685	26	659
400	0.598	0.101	0.497	485	14	471

Solution 3: $(UO_2^{++}) = 0.00470$, $(HK) = 0.000513$, $(H^+) = 0.0100$

$m\mu$	D_{obs}	$D_{UO_2}^{++}$ (est'd)	D	$D/2c$	ϵ_{HK}	$(D/2c - \epsilon_{HK})$
340	0.618	0.074	0.544	530	280	250
350	0.332	0.029	0.303	295	109	186
360	0.259	0.029	0.230	224	72	152
370	0.258	0.027	0.231	225	54	171
380	0.271	0.027	0.244	238	41	197
382	0.269	0.029	0.240	234	37	197
390	0.252	0.044	0.208	202	14	188
400	0.204	0.061	0.143	139	--	--

The optical density of each solution was measured. The absorption due to the uranyl ion present was calculated and subtracted from the quantity measured. The difference, D, is assumed to be the absorption due to TTA and UO_2K^+, and is therefore given by an expression containing two terms,

$$D = 2y \, \epsilon_y + 2(c-y) \, \epsilon_{HK}, \qquad (20)$$

where y is the concentration of UO_2K^+, and ϵ_y is its molar extinction coefficient. The total concentration of TTA taken is c, giving (c-y) as the concentration of the species, HK.

From Equation (20) may be obtained,

$$D/2c - \epsilon_{HK} = (y/c)(\epsilon_y - \epsilon_{HK}), \qquad (21)$$

where the expression on the left may be evaluated from the experimental data and plotted logarithmically to give a curve for each solution measured. The curves should, in theory, have the same shape, and should be displaced vertically from one another according to the value of log (y/c).

These calculations result in the values presented in Table 10, and are plotted in Fig. 9. Because the apparent extinction coefficient of TTA is variable in the wavelength region used, owing chiefly to changes in the small amount of K^- which accompany changes in acidity, it was thought wise to measure it directly for each concentration used. Thus the values of ϵ_{HK} shown in the table were determined by measuring the absorption of solutions identical with those described except that they contained no uranium. It may be seen that ϵ_{HK} for solution 3 is lower than that for 1 and 2, since it contains a higher concentration of acid.

We calculate values for (y/c) from the assumed equilibrium constant expression, Equation (19), which, with the substitution of y
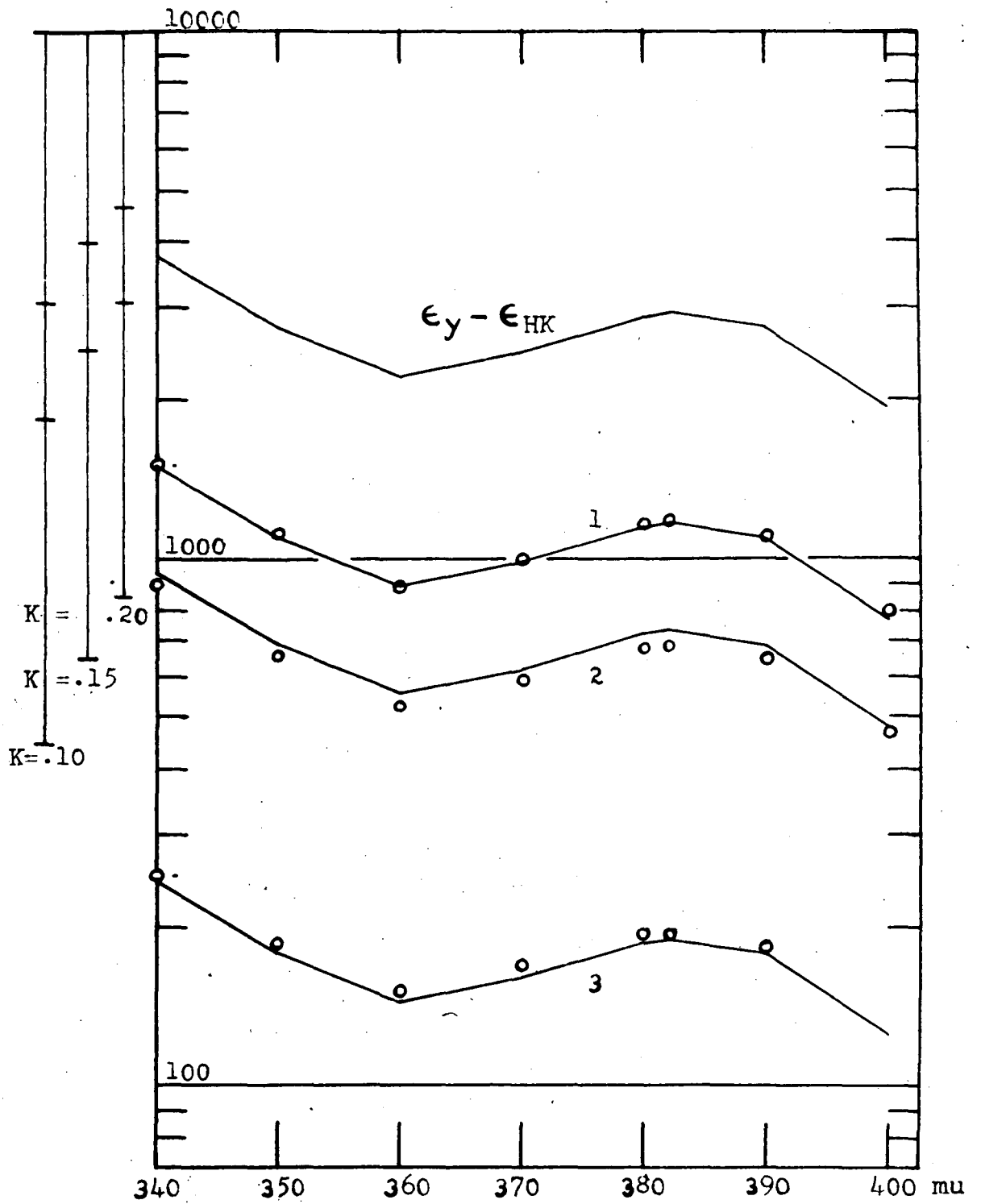
The function $(D/2c - \epsilon_{HK})$

Figure 9

for (UO_2K^+) and $(c-y)$ for (HK), is rearranged to give,

$$y/c = \frac{1}{1 + (H^+)/K(UO_2^{++})} \qquad (22)$$

By assuming values of K equal to 0.10, 0.15 and 0.20, three sets of values of (y/c) have been calculated. The results appear in Table 11, and are also marked for reference on the left side of Fig. 9. It should be observed that the values used for (H^+) and (UO_2^{++}) in making the calculation are slightly greater and slightly less, respectively, than the stoichiometric concentrations originally given. They have been corrected for the changes accompanying the reaction,

$$UO_2^{++} + HK = UO_2K^+ + H^+, \qquad (23)$$

as determined by the value of K assumed.

The curves drawn in the figure correspond to the value, K = 0.15. By means of this value, one can calculate the concentration of UO_2K^+ in a solution such as the aqueous phase of extraction experiment number 4b, described in Part I. Using this calculated value to correct the extraction coefficient, E', raises point 4b as plotted in Fig. 2 to the position marked x. While hardly greater than the experimental error, this displacement serves to put the point more nearly on the line.

The highest curve in Fig. 9 gives $(\epsilon_y - \epsilon_{HK})$, and from it, ϵ_y may be obtained (Table 12). The fact that two different sets of values of ϵ_{HK} were used earlier in the calculation may now be justified by observing that ϵ_{HK} is in both cases small compared to ϵ_y. Thus a variation in ϵ_{HK} for the different solutions does not greatly affect the shape of the curves of Fig. 9.

The agreement with theory of the results of these experiments appears to be good enough to warrant the conclusion that the species UO_2K^+ is present in dilute acid solutions of uranium(VI) containing TTA.

Table 11

The Quantity (y/c), Assuming

Different Values of K

Solution Number	$(UO_2{}^{++})$	(H^+)	$K(UO_2{}^{++})/(H^+)$	y/c
		Assuming K=0.10		
1	0.01570	0.00353	0.445	0.308
2	0.00781	0.00346	0.226	0.184
3	0.00468	0.01002	0.0467	0.0446
		Assuming K=0.15		
1	0.01566	0.00357	0.659	0.397
2	0.00777	0.00350	0.333	0.250
3	0.00467	0.0100	0.070	0.0654
		Assuming K=0.20		
1	0.01562	0.00361	0.866	0.465
2	0.00774	0.00353	0.438	0.305
3	0.00466	0.01004	0.0928	0.0850

Table 12

The Molar Extinction Coefficient

of UO_2K^+

$m\mu$	$\epsilon_y - \epsilon_{HK}$	ϵ_{HK}	ϵ_y
340	3750	307	4060
350	2750	136	2890
360	2230	92	2320
370	2480	70	2550
380	2900	53	2950
382	2950	48	3000
390	2750	26	2780
400	1950	14	1960

(In calculating these values it has been assumed

that the value of the equilibrium constant is

0.15.)

Appendix A

The Activity Coefficient of TTA

in Benzene Solution

Fig. 10 is a plot of the data of King and Reas[2] for the activity coefficient of TTA in benzene solution as a function of the concentration of TTA.

It was determined by measuring the distribution of TTA between benzene and $0.115\underline{M}$ hydrochloric acid solution. The extraction coefficients at various concentrations were compared with that found for the most dilute concentrations of TTA, and the activity coefficient in benzene was calculated on the assumption that the activity in the aqueous phase remained equal to the concentration.

The values of γ_{HK} used throughout the present work have been taken from these data.
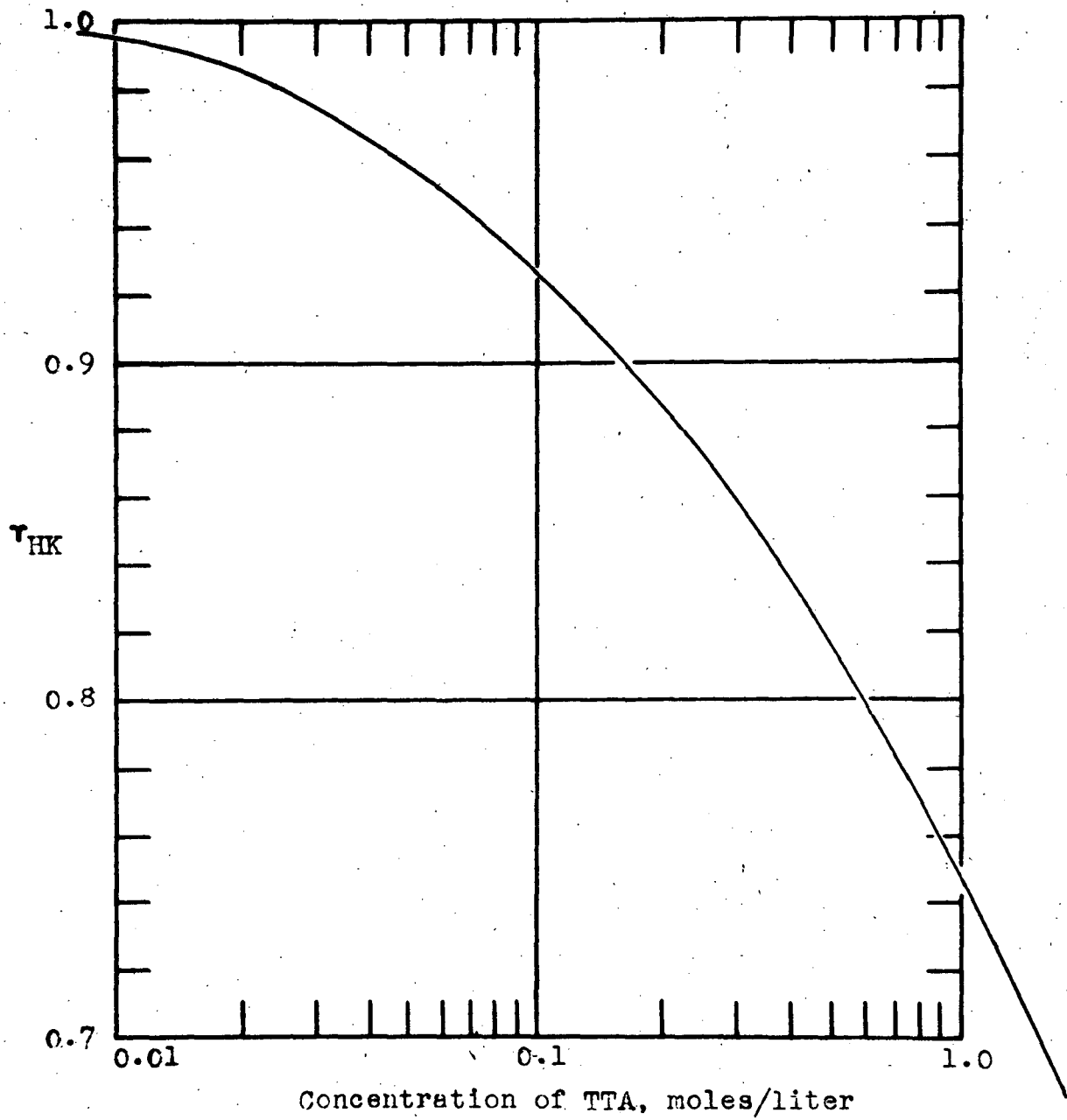
Activity coefficient of TTA in benzene

Figure 10

Appendix B

Preparation of Uranyl Perchlorate and the

Standardization of its Solutions

For reasons set forth in the Introduction it seemed desirable
to have a supply of pure solid uranyl perchlorate for use in the
extraction experiments. The following procedure was used.

A moderately dilute solution of uranyl nitrate was treated with
three percent hydrogen peroxide solution to precipitate the uranium
as a peroxide. The pale yellow precipitate was washed and heated
with slightly more than an equivalent amount of perchloric acid.
The peroxide dissolved with the evolution of oxygen, and the result-
ing clear yellow solution was concentrated by evaporation on a steam
bath. On slow cooling, large yellow needles of uranyl perchlorate
formed. These were dissolved again in water and recrystallized.
They were pressed onto a clay dish and placed in a vacuum dessicator
over concentrated sulfuric acid.

(9)

This treatment should have left the compound as the hexahydrate.
After six days an analysis was made by the procedure described below,
and three samples taken weighed respectively 567.1 g, 567.6 g and
571.1 g per gram atom of uranium. These weights correspond, respec-
tively, to 5.45, 5.47 and 5.66 moles of water in the crystal. After
six months time in the dessicator some of the crystals had changed
their appearance to that of a fine powder. Three samples analyzed
at this time showed an average weight corresponding to 4.9 moles of
water. It seems likely that the hexahydrate was slowly losing water,
probably to form the tetrahydrate.

The analytical procedure used for the determination of uranium

in a given weight of solid uranyl perchlorate, and also for the standardization of the uranyl solutions used in the extraction experiments, was the following.

By opening the weighing bottle only in a dry-box, and by keeping a drying agent in the balance case, it was found possible to weigh out one gram samples of the deliquescent perchlorate with a gain in weight of less than one part in one thousand during the process. A correction was estimated by noting the time required for the weighing and determining the gain in weight of the weighing bottle during an equal period immediately thereafter.

The solid samples were dissolved in water, and the aliquots of solutions to be standardized were diluted. Ammonium chloride was added, and then ammonium hydroxide was used to precipitate the uranium as ammonium uranate. Coagulated by heating, the precipitate was filtered, washed with water containing ammonium chloride and ignited in a porcelain crucible to the greenish gray oxide, U_3O_8. The ignition was repeated until the weight was constant.

In the case of the stock solutions from which the extraction experiment solutions were prepared, the analyses were repeated until three or more results agreed to better than three parts in two thousand.

Appendix C

Determination of the Concentration
of Uranium from Absorption Spectra of Solutions

The tables of this appendix include the optical densities measured on samples of the benzene phases diluted in benzene by a factor of 110. The sample was taken in the same pipette (0.4544 ml) for all dilutions, and raised to a final volume of 50 ml in a volumetric flask. The reason for this dilution was to reduce the fraction of the uranyl chelate complexed by TTA (as $UO_2K_2 \cdot HK$) to the point where it could be neglected. The principal disadvantages of this procedure are that, in the spectral region where measurements must then be made, a larger correction for the absorption of TTA must be applied, and greater care must be exercised in measuring wavelengths because of the steeper slope of the absorption curve.

In addition, the spectra of the original undiluted phases and solutions made by 10,000-fold dilutions of the phases were measured. The latter enabled the concentration of TTA to be checked, since it alone has a significant absorption at this dilution.

The absorptions of the aqueous phases were measured, and were used to give an approximate value for concentrations. The data appeared to contribute no increase in accuracy to the values obtained by taking the difference between the concentration in benzene and the total.

Table 13

Absorption Data for Series 1

Solution 1a

$m\mu$	D	D_{HK}		$\frac{D-D_{HK}}{\epsilon}\cdot 10^5$
404	1.570	1.200	0.375	2.87
406	1.083	0.723	0.360	3.14
408	0.722	0.434	0.288	2.97
410	0.514	0.270	0.244	2.96
414	0.263	0.099	0.164	2.81
420	0.121	0.026	0.095	2.7
430	0.052	0.003	0.049	2.8
440	0.034	0.000	0.034	2.9

$$2.9 \pm 0.2$$
$$\text{x}10^{-5}\text{x}55^* = 0.0016 \ \underline{M}$$
$$\pm 0.0001$$

Solution 1b

$m\mu$	D	D_{HK}		$\frac{D-D_{HK}}{\epsilon}\cdot 10^5$
404	1.589	1.200	0.389	2.98
410	0.536	0.270	0.266	3.23
414	0.287	0.099	0.188	3.22
420	0.134	0.026	0.108	3.1
424	0.090	0.010	0.080	3.2
430	0.058	0.003	0.055	3.1
434	0.050	0.001	0.049	3.2
440	0.038	0.000	0.038	3.2

$$3.2 \pm 0.1$$
$$\text{x}10^{-5}\text{x}55 = 0.00176 \ \underline{M}$$
$$\pm 0.00006$$

Solution 1c

$m\mu$	D	D_{HK}		$\frac{D-D_{HK}}{\epsilon}\cdot 10^5$
404	1.648	1.200	0.448	3.43
410	0.579	0.270	0.309	3.75
414	0.316	0.099	0.217	3.75
420	0.153	0.026	0.127	3.61
424	0.106	0.010	0.096	3.8
430	0.067	0.003	0.064	3.6
434	0.059	0.001	0.058	3.7
440	0.042	0.000	0.042	3.6
450	0.035	0.000	0.035	3.8
460	0.020	0.000	0.020	3.6

$$3.7 \pm 0.1$$
$$\text{x}10^{-5} \ \text{x}55 = 0.00204 \ \underline{M}$$
$$\pm 0.00006$$

*The factor 55 which appears throughout these tables
is the dilution factor divided by the cell-length.

Table 14

Absorption Data for Series 2

Solution 2a

$m\mu$	D	D_{HK}		$(D-D_{HK})/\epsilon \cdot 10^5$
400	0.595	0.352	0.243	1.50
404	0.324	0.128	0.196	1.50
410	0.156	0.029	0.127	1.54
414	0.098	0.011	0.087	1.49
420	0.055	0.003	0.052	1.5
424	0.040	0.001	0.039	1.5
430	0.026	0.000	0.026	1.5
440	0.018	0.000	0.010	1.5
450	0.013	0.000	0.013	1.4

$$1.5 \pm 0.05$$

$$x10^{-5} \, x55 = 0.00083 \, \underline{M} \\ \pm \, 0.00003$$

Solution 2b

$m\mu$	D	D_{HK}		$(D-D_{HK})/\epsilon \cdot 10^5$
396	1.308	0.966	0.342	1.83
400	0.654	0.341	0.313	1.93
404	0.375	0.124	0.251	1.91
410	0.188	0.028	0.160	1.94
414	0.120	0.010	0.110	1.88
420	0.068	0.003	0.065	1.85
424	0.049	0.001	0.048	1.9
430	0.032	0.000	0.032	1.8
440	0.021	0.000	0.021	1.8
450	0.016	0.000	0.016	1.7
460	0.009	0.000	0.009	1.6

$$1.85 \pm 0.1$$

$$x10^{-5} \, x55 = 0.00102 \, \underline{M} \\ \pm \, 0.00005$$

Table 14 (continued)

Solution 2c

$m\mu$	D	D_{HK}		$(D-D_{HK})/\epsilon \cdot 10^5$
396	1.305	0.966	0.339	1.81
398	0.929	0.580	0.349	1.99
400	0.665	0.341	0.324	2.00
402	0.491	0.202	0.289	1.97
404	0.380	0.124	0.256	1.96
410	0.192	0.028	0.164	1.99
414	0.125	0.010	0.115	1.97
420	0.070	0.003	0.067	1.9
430	0.034	0.000	0.034	1.9
440	0.023	0.000	0.023	2.0
450	0.018	0.000	0.018	2.0
460	0.011	0.000	0.011	2.0

$$1.97 \pm 0.04$$

$$\times 10^{-5} \times 55 = 0.00108 \underline{M}$$
$$\pm 0.00003$$

Solution 2e

$m\mu$	D	D_{HK}		$(D-D_{HK})/\epsilon \cdot 10^5$
396	1.433	0.966	0.467	2.50
398	1.045	0.580	0.465	2.66
400	0.782	0.341	0.441	2.72
402	0.600	0.202	0.398	2.72
404	0.479	0.124	0.355	2.72
410	0.257	0.028	0.229	2.78
414	0.168	0.010	0.158	2.70
420	0.098	0.003	0.095	2.70
430	0.049	0.000	0.049	2.8
440	0.033	0.000	0.033	2.8
450	0.026	0.000	0.026	2.8
460	0.014	0.000	0.014	2.5

$$2.73 \pm 0.07$$

$$\times 10^{-5} \times 55 = 0.00150 \underline{M}$$
$$\pm 0.00004$$

The concentration of solution 2d was determined from the spectrum of the undiluted benzene phase by comparison with those of the undiluted phases 2a, 2b, 2c, and 2e.

Table 15

Absorption Data for Series 3

Solution 3b

$m\mu$	D	D_{HK}		$(D-D_{HK})/\epsilon \cdot 10^5$
410	0.454	0.030	0.424	5.14
420	0.179	0.003	0.176	5.00
430	0.088	0.000	0.088	4.95
440	0.060	0.000	0.060	5.1
450	0.046	0.000	0.046	5.0
460	0.028	0.000	0.028	5.1

$$5.05 \pm 0.1$$

$$\times 10^{-5} \times 55 = 0.00278 \pm 0.00006 \underline{M}$$

Solution 3c

$m\mu$	D	D_{HK}		$(D-D_{HK})/\epsilon \cdot 10^5$
400	1.307	0.362	0.945	5.84
404	0.892	0.132	0.760	5.82
410	0.520	0.030	0.490	5.94
414	0.349	0.011	0.338	5.79
420	0.206	0.003	0.203	5.77
424	0.153	0.001	0.152	5.98
430	0.103	0.000	0.103	5.80
434	0.092	0.000	0.092	5.94
440	0.070	0.000	0.070	6.0
444	0.062	0.000	0.062	5.9
450	0.054	0.000	0.054	5.9
454	0.044	0.000	0.044	6.1
460	0.032	0.000	0.032	5.8
464	0.029	0.000	0.029	6.0
470	0.019	0.000	0.019	5.9

$$5.9 \pm 0.2$$

$$\times 10^{-5} \times 55 = 0.00324 \pm 0.00012 \underline{M}$$

The concentration of solution 3a was determined from the spectrum of the undiluted benzene phase by comparison with those of the undiluted phases 3b, and 3c.

Table 16

Absorption Data for Series 4

Solution 4c

$m\mu$	D	D_{HK}	$(D-D_{HK})/\epsilon \cdot 10^5$	
400	1.476	0.961	0.515	3.18
404	0.807	0.350	0.457	3.50
410	0.386	0.078	0.308	3.73
414	0.240	0.029	0.211	3.63
420	0.135	0.007	0.128	3.64
424	0.097	0.003	0.094	3.70
430	0.066	0.001	0.065	3.66
434	0.058	0.000	0.058	3.7
440	0.044	0.000	0.044	3.8
444	0.039	0.000	0.039	3.7
450	0.034	0.000	0.034	3.7
454	0.026	0.000	0.026	3.6
460	0.019	0.000	0.019	3.4

$$3.67 \pm 0.06$$

$$\times 10^5 \times 55 = 0.00202 \underline{M}$$
$$\pm 0.00003$$

The concentrations of solutions 4a and 4b were determined from the spectra of the undiluted benzene phases by comparison with that of the undiluted phase 4c.

Table 17

Absorption Data for Series 5

Solution 5a

$m\mu$	D	D_{HK}		$(D-D_{HK})/\epsilon \cdot 10^5$
384	1.54	1.23	0.31	1.4
390	0.79	0.450	0.34	1.6
394	0.46	0.190	0.27	1.4
400	0.303	0.041	0.262	1.62
404	0.226	0.015	0.211	1.62
410	0.142	0.003	0.139	1.68
414	0.099	0.001	0.098	1.68
420	0.060	0.000	0.060	1.7
440	0.021	0.000	0.021	1.8

$$1.7 \mp 0.1$$

$$x10^{-5} \; x55 = 0.00094 \; \underline{M} \\ \pm 0.00005$$

Solution 5b

$m\mu$	D	D_{HK}		$(D-D_{HK})/\epsilon \cdot 10^5$
384	2.08	1.71	0.37	1.7
390	0.99	0.626	0.36	1.7
394	0.598	0.264	0.334	1.70
400	0.330	0.057	0.273	1.68
404	0.245	0.021	0.224	1.72
410	0.152	0.005	0.147	1.78
414	0.104	0.002	0.102	1.75
420	0.062	0.000	0.062	1.76
424	0.043	0.000	0.043	1.69
430	0.031	0.000	0.031	1.75
434	0.026	0.000	0.026	1.7
440	0.021	0.000	0.021	1.8
444	0.018	0.000	0.018	1.7
450	0.015	0.000	0.015	1.6

$$1.72 \pm 0.1$$

$$x10^{-5} \; x55 = 0.00095 \; \underline{M} \\ \pm 0.00005$$

Table 17 (continued)

Solution 5c

$m\mu$	D	D_{HK}		$(D-D_{HK})/\epsilon \cdot 10^5$
384	2.17	1.63	0.54	2.5
390	1.18	0.60	0.58	2.75
394	0.800	0.252	0.548	2.73
400	0.51	0.054	0.46	2.8
404	0.385	0.020	0.365	2.8
410	0.243	0.004	0.239	2.90
414	0.168	0.002	0.166	2.84
420	0.100	0.000	0.100	2.84
424	0.072	0.000	0.072	2.83
430	0.048	0.000	0.048	2.7
434	0.043	0.000	0.043	2.8
440	0.032	0.000	0.032	2.7
444	0.028	0.000	0.028	2.7
450	0.023	0.000	0.023	2.5

$$2.8 \pm 0.1$$

$$\times 10^{-5} \times 55 = 0.00154 \ \underline{M}$$
$$\pm 0.00005$$

References

(1) E. L. King, Report MB-278, August 15, 1946.

(2) E. L. King and W. H. Reas, Report BC-69, July 1947.

(3) C. W. Koch, Report CC-3323, October 30, 1945.

(4) Best, Taub, and Longsworth, Report A-380, p. 2, reported
     in PPR (National Nuclear Energy Series), Vol. XI A, Chap.
     17, p. 28.

(5) H. W. Crandall, Report BC-64, July 22, 1947.

(6) W. H. Reas, private communication.

(7) E. L. Zebroski, Report BC-63, July 1, 1947, Part II, pp.
     41-42.

(8) G. H. Diecke, Report A-3227, March 23, 1945.

(9) Gmelins Handbuch der Anorganische Chemie, 8th ed., Syst.
     No. 55, Verlag Chemie, Berlin, 1936, p. 137.

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