of the questionable assumptions, but also because of the approximate nature of the data. However they probably give some indication of the stability for these gluconate complexes.

The polarographic characteristics of the cerium-(IV)–gluconate complex indicate that the system has limited potential as an analytical procedure for cerium. The drawn-out wave, the absence of a diffusion plateau under all but the best of conditions, and the relatively small diffusion current emphasize the polarographic limitations.

In summary, cerium(IV) forms an extremely stable complex with gluconate ion. The complex should prove useful for the prevention of precipitation of cerium(IV) under basic conditions, and also as a means of inactivating ceric ion in basic solutions.

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Uranium(VI) Gluconate Complexes[1]

BY DONALD T. SAWYER AND RICHARD J. KULA

The gluconate ion forms stable complexes with uranium(VI), particularly under basic conditions. Spectrophotometric, polarographic, polarimetric, and pH measurements have been used to study these complexes. At pH 12 and 0.07 F sodium gluconate the complex obeys Beer's law up to 1.5×10^{-2} F uranium(VI); the molar absorptivity is 129 at 435 mμ, the absorption maximum. The continuous variations method and mole ratio method have been used to establish that the most stable complex contains one uranium(VI) per gluconate ion. In the presence of sodium gluconate solutions uranium(VI) gives a well defined polarographic wave at pH 12 with a half-wave potential of -1.26 volts $vs.$ S.C.E.; for a supporting electrolyte consisting of 0.1 to 0.5 F sodium gluconate and 0.1 F NH_4ClO_4 which has been adjusted to pH 11, the diffusion current constant (maximum current), I, is 2.27 and the half-wave potential is -1.17 volts $vs.$ S.C.E. On the basis of the entire group of studies a formation reaction can be proposed for the one-to-one complex: $(UO_2)(OH)^+ + GH_4^- + OH^- = (UO_2)(GH_4)(OH)_2^-$. The average formation constant evaluated for this reaction is 1.8×10^6.

Numerous metal ions are strongly complexed by gluconic acid, especially under basic conditions. The previous paper in this series has reviewed the known studies of metal–gluconate systems.[2] Reference to this earlier work, as well as our own experience, has indicated that many of the higher valent transition metal ions form stable gluconate complexes. Because uranium(VI) ions have many similarities in solution to iron(III) and ruthenium-(III) ions, the possibility of a strong uranium(VI)–gluconate complex appeared sufficiently probable to warrant a study of the system.

The solution chemistry of uranium was extensively reviewed and investigated during World War II; much of this work subsequently was summarized in Rodden's compilation of the work of the Manhattan Project.[3] Although numerous complexing agents have been suggested as supporting electrolytes for polarographic studies of uranium(VI), more selective and useful complexing agents (particularly at high pH values) are desirable. This is true not only in terms of polarographic studies, but also as a means for separating uranium from other ions and for keeping it in solution at high pH values. The present discussion summarizes a study of the complexes formed between uranium(VI) and gluconate ion. Because of the complex nature of the system and the slow rate of equilibration for many of the solutions, many of the data are approximate. However, by considering many pieces of data obtained by independent methods a general understanding of the system can be obtained.

(1) Presented before the Pacific Southwest Regional Meeting of the American Chemical Society in Los Angeles, December, 1960.

(2) D. T. Sawyer and R. T. Ambrose, *Inorg. Chem.*, **1**, 296 (1962).

(3) C. J. Rodden, "Analytical Chemistry of the Manhattan Project," McGraw-Hill Book Company, Inc., New York, N. Y., 1950.

Experimental

Equipment.—Polarographic measurements were made with a Sargent Model XV recording polarograph, using a modified type of H-cell to prevent attack of the agar in the salt bridge by strongly basic solutions.[4] All solutions were deaerated with purified nitrogen and thermostated to $25.0 \pm 0.1°$ prior to making measurements. Diffusion currents were measured using the tops of the oscillations (maximum current) and were corrected for residual current. The reported potentials were measured vs. the saturated calomel electrode (s.c.e.). The rate of flow of mercury was 1.75 mg./sec., and the drop time was 4.26 sec. at -1.20 volt applied potential. Half-wave potentials were measured to an accuracy of ± 0.01 volt. To obtain reproducible results, all polarograms were recorded for equilibrated solutions (usually several hours old).

Measurements of optical rotation were made with a Rudolph Precision polarimeter, No. 70, to a precision of $\pm 0.01°$ of arc, using a 100 mm. polarimeter tube. pH measurements were made with a Beckman Model G pH meter (with Type E-2 glass electrodes for high pH), which was standardized with N.B.S. buffers.

Spectrophotometric data were obtained either with a Cary Model 14 recording spectrophotometer or a Beckman Model DU spectrophotometer.

Reagents.—Uranium(VI) solutions were prepared from reagent grade uranyl perchlorate (G. Frederick Smith Chemical Co.). The nitrate salt was unsatisfactory because of a catalytic polarographic wave resulting from nitrate ion reduction. Uranyl sulfate was also unsatisfactory because of the formation of a sulfate complex of the uranium(VI) ion. The solutions prepared from uranyl perchlorate were standardized by dichromate titration, first reducing the uranium to the $+4$ state, and using diphenylamine sulfonate as the indicator.[5] The analyses were checked by polarographic analysis using the conditions and constants of Kern and Orlemann.[6]

Sodium gluconate solutions were prepared determinately from D-glucono-δ-lactone (Matheson Coleman and Bell) which had been recrystallized twice from ethylene glycol monomethyl ether. The purity of the lactone was determined by back-titrating, with standard acid, a sample to which excess standard base had been added. The lactone was found to be 99.7% pure, and to have a melting point of 152–153°. All other materials were reagent grade.

To study the characteristics of the uranium(VI)–gluconate complex as a function of pH, a buffer system was necessary. An important consideration was that the buffer must not interact with the uranium(VI) ions, especially at high pH values. Buffers containing phosphate, borate, acetate, and carbonate ions were all unsatisfactory. However, ammonium perchlorate did satisfy the necessary conditions, and was used for those systems requiring a buffered condition. Sodium hydroxide and perchloric acid were used to adjust the buffer-containing solution to the desired pH.

Results

Spectrophotometry of Uranium(VI).—A solu-

(4) R. L. Pecsok and R. S. Juvet, Jr., *Anal. Chem.*, **27**, 165 (1955).

(5) I. M. Kolthoff and J. J. Lingane, *J. Am. Chem. Soc.*, **55**, 1871 (1933).

(6) D. M. H. Kern and E. F. Orlemann, *ibid.*, **71**, 2102 (1949).
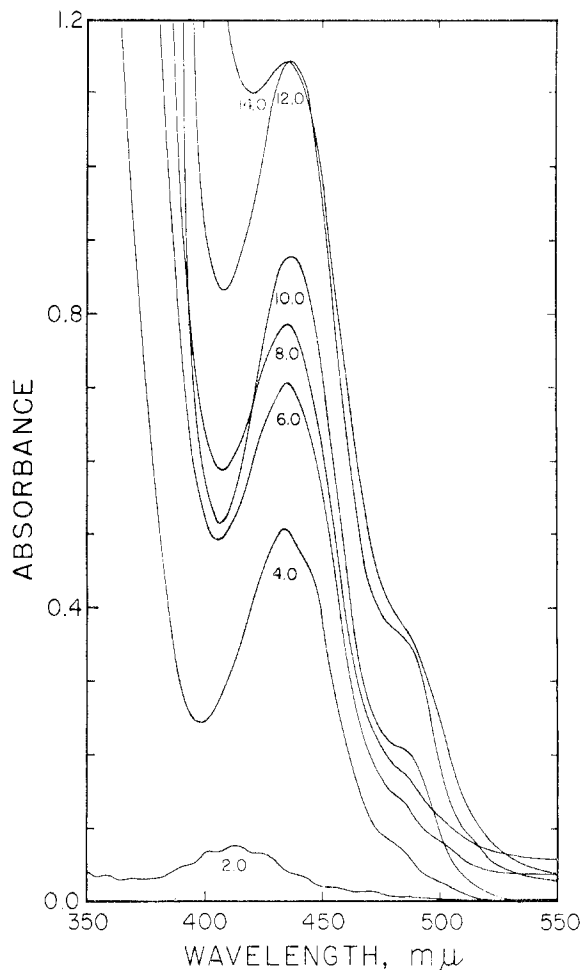
Fig. 1.—Absorption spectra of uranium(VI)–gluconate solutions at various pH values. All solutions were 8×10^{-3} F in uranium(VI) and 8×10^{-2} F in sodium gluconate, and were equilibrated for one month before the spectra were recorded. The pH values of the equilibrated solutions are indicated on the spectra.

tion containing uranium(VI) and an excess of sodium gluconate absorbs in the near ultraviolet region. The resulting spectra are characteristic of the gluconate complex, especially at high pH values where free UO_2^{++} ion is precipitated. Freshly prepared solutions of the complex at different pH values show a maximum absorbance for the pH 12 solution. After the solutions have equilibrated for one month the spectra shown in Fig. 1 are obtained; uranium(VI)–gluconate complexes appear to be formed above pH 4. The absorbance of the pH 14 solution has increased from an initial absorbance of 0.85 after the solution was one week old to an absorbance equal to that of the pH 12 solutions. For solutions more basic than pH 12, the gluconate complexes of uranium(VI) slowly decompose as demonstrated by spectra for three-month-old solutions. An equilibrated pH 12
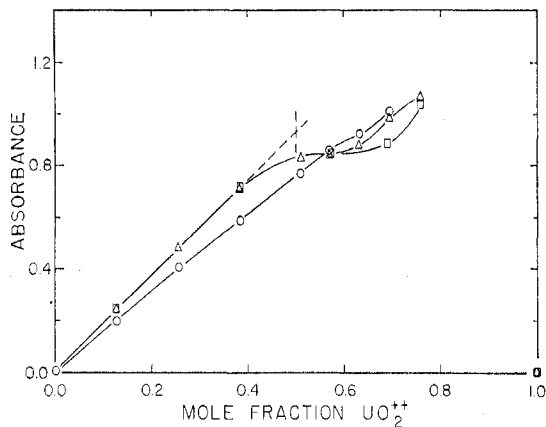
Fig. 2.—Continuous variations study of the uranium (VI)–gluconate system and the effect of time on the absorbance. The sum of the uranium(VI) concentration plus the sodium gluconate concentration was 16.3×10^{-3} F for all of the solutions and each was adjusted to pH 12. The mole fraction of uranium(VI) for the solutions is indicated on the graph. The solutions were allowed to equilibrate for the indicated periods and centrifuged just prior to measuring the absorbance: 0, immediately after preparation of the solutions; △, 7 days after preparation; □, 30 days after preparation. All measurements were made at 435 mμ.

solution containing 0.07 F sodium gluconate and uranium(VI) has an absorption maxima at 435 mμ and obeys Beer's law for uranium(VI) concentrations up to 1.5×10^{-2} F. Under these conditions, the molar absorptivity for the complex, ϵ, is 129.

Job's method of continuous variations[7] has been applied to the complex at pH 12; Fig. 2 shows the resulting curves at different times of equilibration. After one month the absorbances of the solutions ceased to change. The one-month-old solutions show an inflection at a uranium(VI) mole fraction of 0.5 and a second inflection at 0.75 (higher mole fractions give precipitates). This would indicate two or more complexes are formed, with uranium mole ratios relative to gluconate ion of 1 to 1 and 3 to 1, respectively. A series of solutions at pH 12 containing 1×10^{-2} F sodium gluconate and uranium concentrations from zero up to 6×10^{-2} F uranium(VI) exhibit increasing absorbance at 435 mμ with increasing uranium concentration. When the absorbances of one-month-old solutions are plotted $vs.$ the mole ratio of uranium to gluconate, an inflection of decreasing slope is shown at a mole ratio of 1, and precipitate is formed in the solutions with mole ratios greater than 3.

(7) P. Job, *Ann. chim.*, [10] **9**, 113 (1928).

Polarography of Uranium(VI).—In the presence of basic 0.1 F gluconate solutions uranium(VI) exhibits a well-defined irreversible reduction wave; at pH 12 the half-wave potential is -1.26 v. Before polarographic studies could be made of this system it was necessary to find an inert anion for the uranium salt and an inert buffer system. We have found that sulfate ions, phosphate ions, carbonate ions, and acetate ions all interfere by complexing the uranium(VI); and that nitrate ions are catalytically reduced in the presence of uranium(VI). Similar observations have been reported and summarized by Rodden.[3] Sodium perchlorate and ammonium perchlorate have proved to be inert supporting electrolytes, and the latter is an effective buffer system at high pH values. Polarographic studies concerned with the effect of pH, gluconate concentration, and uranium(VI) concentration have been made, all using 0.1 F ammonium perchlorate as the supporting electrolyte and uranium(VI) perchlorate as the source of uranium(VI) ion.

Below pH 5 uranium(VI) in a 0.1 F ammonium perchlorate solution gives a reversible, one-electron reduction wave with a half-wave potential of -0.16 v. From pH 5 to 6.6 the half-wave potential shifts to -0.42 v.; precipitation of UO_3 reduces the uranium concentration below a detectable amount above the higher pH. Fig. 3 shows the reduction waves for uranium(VI) in the presence of 0.1 F ammonium perchlorate and 0.1 F
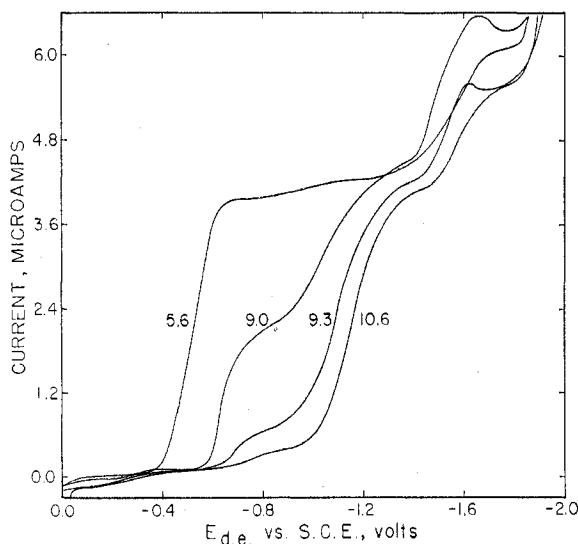

Fig. 3.—Polarograms of uranium(VI) in the presence of sodium gluconate as a function of pH; the pH values are indicated on the individual waves. All solutions were 1.0×10^{-3} F in U(VI), 0.1 F in NaGH$_4$, and 0.1 F in NH$_4$ClO$_4$.

gluconate as a function of pH. For solutions of low pH the reduction wave is almost identical to the wave in the absence of gluconate. However, as the pH is increased the height of the first wave is reduced and a second wave appears whose height increases with pH, both waves having diffusion controlled currents. (Addition of gluconate ion prevents any precipitation of uranium, even at pH 14.) Both half-wave potentials for the two waves, as shown by Fig. 3, become more negative with increasing pH. Apparently the first wave is due to uncomplexed uranium(VI) while the second wave is due to the gluconate complex of uranium-(VI). The existence of a slow equilibrium between the complexed and uncomplexed forms is indicated by the two waves for uranium(VI).

The proportionality constant for the current–concentration relation (the Ilkovic equation) can be evaluated for the uncomplexed species at a low pH where only the first wave exists, and a similar constant also can be evaluated for the complexed species at a high pH where only the second wave is present. Both constants have been evaluated using known concentrations of uranium(VI) at pH 4 and 11 for the uncomplexed and complexed forms; the first, k_s, and the latter, k_c, have values of 3900 and 3500, respectively. By assuming that these two constants do not vary with pH, and that the equilibrium between the two forms of uranium does not shift appreciably during the reduction reaction, the relative concentration of complexed and uncomplexed uranium(VI) can be evaluated as a function pH, gluconate concentration, and uranium concentration.

These considerations are made clearer by the reactions for complex formation and other relations

$$UO_2(OH)_z{}^{2-z} + xOH^- + yGH_4{}^- =$$
$$UO_2(GH_4)_y \, (OH)_{x+z}{}^{2-(x+y+z)} \quad (1)$$
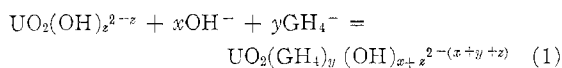
$$\frac{[UO_2(GH_4)_y \, (OH)_{x+z}{}^{2-(x+y+z)}]}{[UO_2(OH)_z{}^{2-z}][OH^-]^x[GH_4{}^-]^y} = K \quad (2)$$

$$[UO_2(OH)_z{}^{2-z}] = \frac{i_{d_1}}{k_s} \quad (3)$$

$$[UO_2(GH_4)_y \, (OH)_{x+z}{}^{2-(x+y+z)}] = \frac{i_{d_2}}{k_c} \quad (4)$$

where i_{d_1} and i_{d_2} represent the observed diffusion currents for the first and second waves, respectively, and $GH_4{}^-$ represents the gluconate ion (with the H's signifying the protons of the secondary hydroxyl groups). By rearranging eq. 2, substituting eq. 3 and 4, and taking logarithms
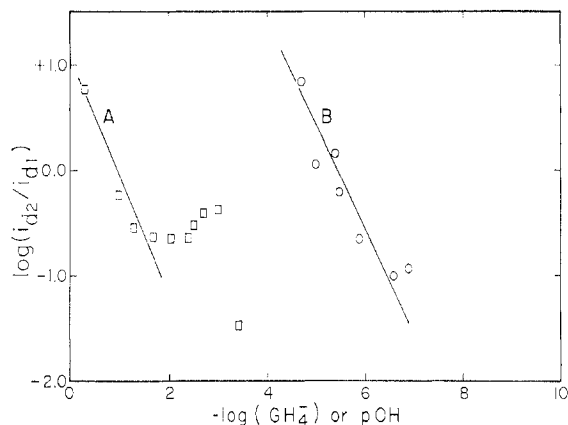

Fig. 4.—Relative diffusion currents of the first and second waves for the reduction of uranium(VI) as a function of gluconate concentration, and as a function of hydroxide concentration. All solutions were 1.0×10^{-3} F in U(VI) and 0.1 F in NH_4ClO_4. Curve A: logarithm of the ratio of wave heights as a function of $-\log (GH_4{}^-)$; all solutions were pH 8.80. Slope is equal to 1.1. Curve B: logarithm of the ratio of wave heights as a function of pOH; all solutions were 0.1 F in sodium gluconate. Slope is equal to 1.0.

$$\log\frac{i_{d_2}}{i_{d_1}} = \log\frac{k_c}{k_s} + \log K + x \log (OH^-) + y \log (GH_4{}^-) \quad (5)$$

On the basis of this equation a series of 0.1 F NH_4ClO_4 solutions was prepared in which the pH, gluconate concentration, and uranium(VI) concentrations were varied individually. Polarograms were recorded and the resulting diffusion currents were evaluated for the series. Figure 4 shows $\log (i_{d_2}/i_{d_1})$ as a function of $-\log (GH_4{}^-)$ (curve A) and pOH (curve B) for two groups within the series where the uranium(VI) concentration was held constant at 10^{-3} F. The slopes for the resulting two curves represent an evaluation of x and y in eq. 5. Although the points for the lower concentrations of gluconate deviate considerably from curve A, the data for the higher concentration are believed to be more reliable. The curves indicate values for x and y close to unity.

Assuming x and y both are unity, the data for the above series of solutions can be used in eq. 5 to evaluate K, the formation constant for the uranium–gluconate complex. On the basis of curves A and B of Fig. 4, K is calculated to have a value of $1.6_7 \times 10^6$ and $3.5_2 \times 10^6$, respectively. For the series of solutions containing various uranium concentrations in 0.1 F gluconate at pH 12, K is calculated to have a value of $1.0_2 \times 10^6$.

From an analytical consideration the best conditions for quantitative polarographic analysis of
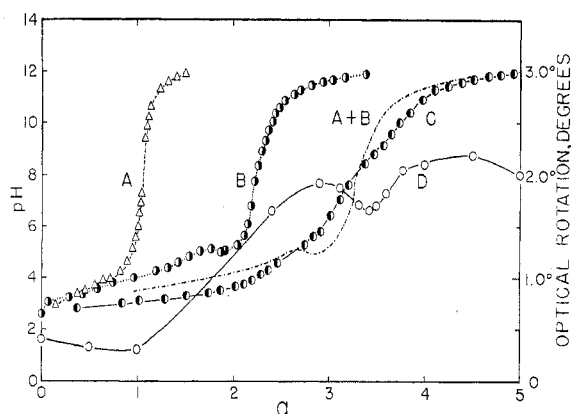
Fig. 5.—pH titrations of gluconic acid, of uranyl perchlorate, and of a one-to-one molar mixture of gluconic acid and uranyl perchlorate. The units of the abscissa represent moles of base added per mole of gluconic acid for curves A and C, and moles of base per mole of $UO_2(ClO_4)_2$ for curve B. Curve B is for the direct titration of 0.1 F $UO_2(ClO_4)_2$ with 0.1 F NaOH. Curves A and C are for the net titration where an excess of 0.1 F NaOH was first added and then back-titrated with 0.1 F HCl. Curve A, 0.1 F HGH$_4$. Curve C, 0.1 F HGH$_4$ + 0.1 F $UO_2(ClO_4)_2$. Curve (A + B) represents the sum of Curve A and Curve B, in terms of moles of base. Curve D represents the optical rotation for a series of solutions 0.1 F each in gluconic acid and uranyl perchlorate to which the indicated number of moles of base per mole of gluconic acid have been added. Each of these solutions was equilibrated for 10 days prior to making a measurement.

uranium(VI) gluconate solutions are 0.1 F ammonium perchlorate, 0.1 to 0.5 F sodium gluconate, and the pH adjusted to pH 11.0. Under these conditions the half-wave potential is -1.17 v. and the diffusion current constant, I, is 2.27 (using maximum rather than average current). This constant is applicable for 10^{-4} to 10^{-2} F uranium(VI) solutions.

pH Titrations of the Uranium–Gluconate System.—To further elucidate the formula for the uranium(VI)–gluconate complex a series of pH titrations has been performed. Figure 5 shows the titration curves for gluconic acid (curve A), uranium(VI) perchlorate (curve B), and a 1:1 molar mixture of uranium(VI) and gluconic acid (curve C). Additional titrations have been performed for mixtures of uranium(VI) and gluconic acid in which the mole ratio is 1/2:1, 3/4:1, 3/2:1, and 2:1. All of the titrations except for pure uranium(VI) perchlorate were performed as back titrations with an excess of standard base first being added and then back titrating with standard hydrochloric acid. Such a procedure was necessary to overcome the slow neutralization reaction between gluconic acid and base. Table I summarizes

TABLE I
SUMMARY OF pH TITRATIONS FOR A SERIES OF
URANIUM(VI)–GLUCONIC ACID MIXTURES[a]

| | Mole Ratio, $UO_2{}^{++}$:HGH$_4$ | | | | |
	1/2:1	3/4:1	1:1	3/2:1	2:1
OH$^-$ ions per HGH$_4$	2.18	2.70	3.48	4.59	5.68
OH$^-$ ions per $UO_2{}^{++}$	4.36	3.60	3.48	3.06	2.84
OH$^-$ ions per $UO_2{}^{++}$ minus 1 OH$^-$ per HGH$_4$	2.36	2.27	2.48	2.39	2.34

[a] Data are for pH 10, and represent the total number of hydroxides required relative to the indicated group, to reach this pH.

the number of hydroxide ions per gluconic acid or per uranium(VI) in the complex that are required to reach pH 10. The data are obtained from Fig. 5 and similar sets of curves for the other mole ratios of uranium(VI) to gluconic acid. The last line of Table I indicates the net number of hydroxide ions per uranyl ion that are taken up by the complex; the hydroxides used to titrate the proton of gluconic acid have been subtracted from the gross ratio. Reference to this last line indicates that the solution with a 1:1 mole ratio consumes the most hydroxides per uranyl ion in reaching pH 10. Maximum uptake of hydroxide ions probably occurs for the mixture having the same ratio as the correct formula for the complex. This has been shown to be true in the case of the cerium(IV)–gluconate complex.[2] Thus, at the concentrations used in the titrations the correct formula appears to have a mole ratio of one gluconate ion per uranium(VI) and 2.5 hydroxides per uranium(VI).

Studies of the Optical Rotation of the Uranium (VI)–Gluconate System.—Pecsok and Juvet[8] first demonstrated the application of optical rotational measurements to metal–gluconate complexes. Because of the optical activity of the gluconate ligand, a continuous variations study has been made of the uranium(VI) gluconate system at pH 12 using optical rotation as the measured quantity and is shown in Fig. 6. Where the mole fraction of uranium(VI) is zero the rotation is due to the pure gluconate solution. By assuming a 1:1 complex, correction can be made for the free gluconate ion present in the various solutions up to a mole fraction of 0.5. Such a correction is indicated in Fig. 6 by the dotted line; the corrected curve gives further support to the conclusion that the uranium(VI)–gluconate complex contains one uranium(VI) per gluconate ion.

(8) R. L. Pecsok and R. S. Juvet, Jr., *J. Am. Chem. Soc.*, **78**, 3967 (1956).
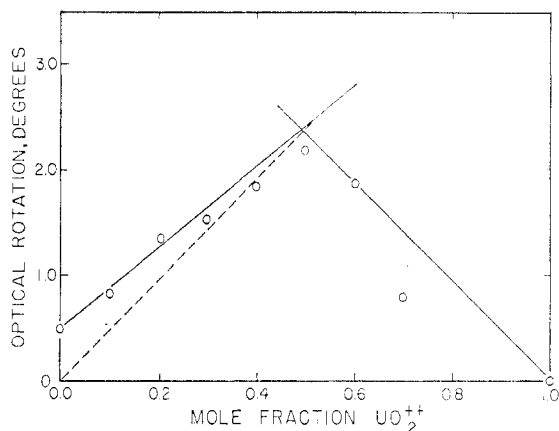
Fig. 6.—Continuous variations study of the uranium (VI)–gluconate system using optical rotation as the measured variable. The sum of the uranium(VI) concentration plus the sodium gluconate concentration was 0.2 F for all of the solutions. The solutions were equilibrated for one month, centrifuged, diluted by a factor of two, and adjusted to pH 12 prior to measuring the optical rotation.

The use of optical rotation for continuous variations studies offers the specific advantage of permitting much more concentrated solutions to be investigated. Because of the high molar absorptivity of the complex, absorbance measurements require quite dilute solutions. Conversely, the optical activity of the uranium complex is such that concentrations as high as 0.1 F can be studied polarimetrically. The measurements in Fig. 6 represent solutions for which the sum of the uranium(VI) plus gluconate concentrations is constant and equal to 0.2 F; just prior to measuring the optical rotation, each solution is diluted to one-half this concentration.

Curve D of Fig. 5 represents the optical rotation of a series of solutions, 0.1 F in uranium(VI) and 0.1 F in gluconate, as a function of the moles of sodium hydroxide added per mole of gluconic acid in the complex. All of the solutions were equilibrated for 10 days before measuring their rotation. The distinct minimum at 3.5 hydroxides per gluconic acid is taken as additional evidence that there is a net ratio of 2.5 hydroxides per complex (subtracting one hydroxide as being due to the neutralization of gluconic acid) at this level of concentrations.

A number of attempts have been made to synthesize and isolate a pure compound of the uranium(VI)–gluconate complex. Although a material has been isolated containing approximately one uranium(VI) ion per gluconic acid molecule, the isolated product is quite impure, with the con-

sistency of a glass. Our experience has been that the isolation of metal-gluconate complexes in general is extremely difficult, if possible at all. All attempts to isolate a crystalline material for the uranium complex have been unsuccessful.

Discussion and Conclusions

The continuous variations and the mole ratio studies using optical absorbance measurements both give strong support that the uranium(VI)–gluconate complex contains one uranium(VI) ion per gluconate ion. This conclusion is further supported by the continuous variations studies of the system using optical rotation as the measured variable. The fourth piece of evidence in support of this conclusion comes from the polarographic data presented in Fig. 4. Although both of the absorbance studies indicate that other complexes containing two or three uranium ions per gluconate ion also may be formed, the over-all evidence supports the conclusion that the most stable complex has a mole ratio for metal to ligand equal to one.

Both the pH titrations and the measurements of optical rotation shown in Fig. 5 for the 1:1 complex support the conclusion that there are 2.5 hydroxide ions per complex. However, both the polarographic and spectrophotometric studies were carried out at much lower concentrations. Hence, it seems plausible for these more dilute conditions that the complex probably contains two hydroxide ions, particularly at lower pH values. Because the polarographic data establish that x and y are both equal to unity (see Fig. 4), z must equal 1 on the basis of eq. 1. Thus, eq. 1 may be rewritten with the above evaluations of the constants included.

$$(UO_2)(OH)^+ + OH^- + GH_4^- \longrightarrow$$
$$(UO_2)(GH_4)(OH)_2^- \quad (6)$$
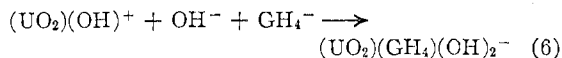
This equation is consistent with the experimental data for the complex and is concluded to be a satisfactory representation of the formation reaction for the complex. On the basis of eq. 6, eq. 2 may be rewritten to give the formation constant, K

$$\frac{[(UO_2)(GH_4)(OH)_2^-]}{[(UO_2)(OH)^+][OH^-](GH_4^-)} = K \quad (7)$$

Using eq. 7, the data in Fig. 2 can be used to determine an approximate value for K. Extrapolation of the straight-line portion of the left side of the curve in Fig. 2 represents the absorbance (and thereby the concentration) of the com-

plex if it were not dissociated at all. The difference between this extrapolated curve and the actual measured curve at a mole fraction of 0.5 should represent the uncomplexed uranium(VI). From Beer's law

$$[(UO_2)(GH_4)(OH)_2^-] = kA \qquad (8)$$

$$[(UO_2)(OH^+)] = k(A_{ext} - A) \qquad (9)$$

where k is a proportionality constant, A is the measured absorbance, and A_{ext} is the extrapolated absorbance. Substitution of eq. 8 and 9 into eq. 7 and insertion of the values for A and A_{ext} from Fig. 2 at a mole fraction of 0.5 gives a value for K equal to 1×10^6. However, it should be emphasized that this type of measurement is quite inaccurate; the calculated value can be considered only an order of magnitude estimate. At the low concentrations represented in Fig. 2 hydrolysis reactions may compete with reaction 6. Also, Fig. 2 indicates that under the conditions of measurement a higher complex involving a uranium(VI)-to-gluconate ratio equal to 3 is apparently formed. This would interfere further with an accurate evaluation of K.

Table II summarizes the values for K determined both polarographically and spectrophotometrically; the average value for K equals 1.8×10^6.

TABLE II
SUMMARY OF VALUES DETERMINED FOR THE FORMATION
CONSTANT OF THE URANIUM(VI)–GLUCONATE COMPLEX

Variable Used for Evaluation		K
Polarography:	(OH$^-$)	3.5×10^6
	(GH$^-$)	1.7×10^6
	(UO$_2^{++}$)	1.0×10^6
Spectrophotometry		$1. \times 10^6$
Av. of 4 evaluations		1.8×10^6

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The Effect of Coördination on the Reactivity of Aromatic Ligands. II. Bromination of Some Complexes of Palladium(II) Bromide with Aromatic Amines[1]

BY ROBERT L. JETTON AND MARK M. JONES[2]

A series of palladium(II) bromide complexes with aromatic amines of the type [Pd(A)$_2$Br$_2$] has been brominated using small and large mole ratios of bromine to complex. The brominated complexes have been analyzed and the ligands subsequently recovered and characterized. In each case the orientation of the bromination was *ortho* or *para* to the amino group. These results are discussed in terms of theoretical models of the coördinate bond.

Previous work in this Laboratory[1] has indicated that, contrary to the predictions which might be made on the basis of a simple picture of the coordinate bond *and* the resonance theory of the preferred positions for attack of aniline by electrophilic reagents,[3] coördination *does not* exert a

(1) Previous paper in this series: J. C. Taft and M. M. Jones, *J. Am. Chem. Soc.*, **82**, 4196 (1960).

(2) To whom correspondence concerning this paper should be addressed.

(3) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, third edition, 1960, pp. 207-208.

great effect upon the reactivity of aniline toward bromination *nor upon the orientation of substitution*. Because of the profound implications of these results, the studies have been extended to a series of complexes where it is possible to isolate and characterize the brominated complexes, *viz.*, the complexes of palladium(II) bromide with aniline and with the *ortho-*, *meta-*, and *para*-toluidines.

Because the lone pair of electrons on the nitrogen atom, which is not involved in bonding in the