order of 8 for the lighter members and 15 for the heavier members of the rare earth sequence. Likewise, k_4 should be of the order of 2 to 3 for all of the rare earths. The ratio k_1/k_2 for the complexes at μ equal to 0.1 compare well with those obtained at μ equal to 2.0.

Variations in the acetate stability constants of the rare earths, as one proceeds through the series, are very interesting. From lanthanum through samarium there is a definite rise in the first complexation constant which may be explained by the decrease in the ionic radius of the central atom. The europium constant is about the same as samarium. Since the ionic radius of europium is smaller than that of samarium, this constant is lower than expected from the previous trend. If the generally observed trend for rare earth stability constants were followed, one would expect the constant to drop at gadolinium and then rise again at terbium. However, with the acetates the constant for terbium drops below that of gadolinium and the downward trend continues through holmium. The erbium constant is about the same as that of holmium, but a small rising trend is noted throughout the remainder of the series. With the second constant, k_2, the anomaly disappears and the trend more or less substantiates the ionic radii concept. Variations are noted, but it is difficult to say whether these are real or simply due to experimental error. The k_2 values of holmium, erbium, and thulium, for example, appear to be slightly depressed. Similar trends have been found at μ equal to 2.0, lending credence to the observed variations.

Sodium perchlorate was used as the supporting electrolyte in this work. Quite frequently other highly ionized salts are used. That the constants obtained in this work are applicable to solutions containing other supporting electrolytes is indicated by a comparison of the ionization constants of acetic acid obtained in various media. The constant found using sodium perchlorate was 2.799×10^{-5} at μ equal to 0.1, whereas Harned and Owen list values of 2.874, 2.891, and 2.850 $\times 10^{-5}$ at μ equal to 0.11 using lithium chloride, sodium chloride, and potassium chloride, respectively.[11] The behavior of acetate complexes in the different solutions should be similar to acetic acid.

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(11) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1958.

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Cerium(IV) Gluconate Complexes

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The cerium(IV) ion forms extremely stable complexes with sodium gluconate in basic solutions. Spectrophotometric, polarimetric, potentiometric, polarographic, and *p*H measurements have been used to study these complexes. At *p*H 14 and 0.08 *F* sodium gluconate the molar absorptivity for the complex is 4200 at 288 mμ, the absorption maximum. Addition of excess cerium(IV) to a basic gluconate solution intially forms soluble polymers containing approximately six ceric ions per gluconate ion. The polymers hydrolyze slowly to give ceric hydroxide plus a stable gluconate complex. A number of independent studies have been used to establish that the most stable complex contains two cerium(IV) ions per three gluconate ions; at *p*H 7.3 the formula for this complex is $Ce_2(GH_4)_3(OH)_9^{-4}$ and at *p*H 11 it is $Ce_2(GH_4)_3(OH)_{11}^{-6}$. Potentiometric measurements plus several assumptions permit a reduction reaction to be proposed for the complex at *p*H 11; $Ce_2(GH_4)_3(OH)_{11}^{-6} + 2e^- = Ce_2(GH_4)(OH)_6^- + 2GH_4^- + 5OH^-$, where the cerium(IV) complex is reduced to the cerium(III) complex. Tentative formation constants have been estimated for both the cerium(IV) and the cerium(III) complexes on the basis of the potentiometric data together with a series of assumptions.

Gluconic acid has been shown to be an effective complexing agent for a number of metal ions. Cannan and Kibrick[1] investigated the complexes formed between ions of the Group II elements and gluconic acid, but only observed weak complexes. The gluconate chelates of copper(II), iron(III), lead(II), and cadmium(II) have been studied by Pecsok and co-workers,[2] and the

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[1] R. K. Cannan and A. Kibrick, *J. Am. Chem. Soc.*, **60**, 2314 (1938).

glucono–ruthenium(III) system has been discussed recently by our group.[3] This latter group of metal gluconate complexes all have been found to be extremely stable, particularly in strongly basic solutions. Because cerium(IV) has many similarities to iron(III), ruthenium(III), and uranium(VI), all of which form strong gluconate complexes, there appeared to be a strong possibility for complexing between cerium(IV) and gluconate ion. The present discussion is concerned with the solution chemistry of the cerium(IV)–gluconate complexes.

Although several inorganic complexes of cerium(IV) are known in acidic solutions,[4] organic complexes are virtually unreported. The latter is not surprising since acidic cerium(IV) is an effective oxidizing agent for many organic substances that can function as ligands.[5] Three exceptions to this generalization have been reported; a cupferron complex, $Ce(IV)[C_6H_5N(NO)O]_4$[6]; an oxime complex, $Ce(IV)(C_9H_6ON)_4$[7]; and an acetylacetonate complex, $Ce(IV)(C_5H_7O_2)_4$.[8] Apparently the covalent character of these three complexes accounts for the inactivation of the strong oxidizing tendencies of the ceric ion.

The cerium(IV)–gluconate system is complicated and the rates of equilibration for many of the solutions are slow. As a result many of the data are approximate and less reliable than would be desired. However, by considering data from several independent methods a consistent, general understanding of the system can be obtained.

Experimental

Equipment.—Spectrophotometric data were obtained either with a Cary Model 14 recording spectrophotometer or a Beckman DU spectrophotometer. For many of the solutions a preliminary centrifugation or dilution was necessary before making spectrophotometric measurements.

Polarographic data were recorded with a Sargent Model XV polarograph or with a previously described instrument,[9] using a modified type of H-cell to prevent attack of the agar salt bridge by strongly basic solutions.[10] Measurements were made at 25.0 ± 0.1°; the diffusion currents were determined for maximum current (using the tops of the oscillations) and were corrected for residual current. All potentials were measured and reported *vs.* the saturated calomel electrode (s.c.e.). The rate of flow of mercury was 2.04 mg./sec., and the drop time was 3.32 sec. at −0.7 v. applied potential.

Measurements of optical rotation were made with a Rudolph Precision polarimeter, No. 70, to a precision of ±0.01° of arc, using a 200-mm. polarimeter tube. For many of the measurements it was necessary to centrifuge and dilute the solutions just prior to making a reading.

Potentiometric and *p*H measurements were made with either a Beckman Model G *p*H meter or a Leeds and Northrup line-operated *p*H meter. A Beckman Type E-2 glass electrode was used for *p*H measurements of basic solutions and a 1 cm.^{2} platinum electrode was used for potentiometric measurements. Both electrodes were referenced to a saturated calomel electrode.

Reagents.—Cerium(IV) solutions were prepared from reagent grade ceric sulfate, $Ce(HSO_4)_4$, and from primary standard ceric ammonium nitrate, $Ce(NH_4)_2(NO_3)_6$ (both from G. Frederick Smith Chemical Co.). The latter salt generally was more satisfactory because of its solubility in neutral solutions and also because of the ability to prepare standard solutions determinately. The ceric sulfate solutions were standardized with primary standard ferrous ammonium sulfate using a potentiometric end-point.

Sodium gluconate solutions were prepared determinately from D-glucono-δ-lactone (Matheson Coleman & 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 solution 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.

Results

Spectrophotometry of Cerium(IV).—Absorption spectra for cerium(IV) in sodium gluconate solutions at various *p*H values are shown in Fig. 1. A stable cerium(IV)–gluconate complex appears to be formed in basic solutions above *p*H 7.5. The absorption maximum for the *p*H 14 solution occurs at 288 mμ, where, in the presence of 0.08 *F* sodium gluconate, the molar absorptivity, ϵ, is 4200. The isosbestic point at 250 mμ for the spectra of the three most basic solutions indicates a single complex is formed in the region from *p*H 9 to 14 with a hydroxide ion being added to the complex at the higher *p*H values. These spectra are impressive as well as indicative of the stability of the complex when the extremely low solubility of ceric hydroxide is recalled (ceric ion normally precipitates if the solution is less than 1 molar in hydrogen ion). Thus, in the absence of gluconic acid all of the spectra in Fig. 1 would show

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(2) (a) R. L. Pecsok and R. S. Juvet, Jr., *J. Am. Chem. Soc.* **77**, 202 (1955); (b) R. L. Pecsok and J. Sandera, *ibid.*, **77**, 1489 (1955); (c) R. L. Pecsok and R. S. Juvet, Jr., *ibid.*, **78**, 3967 (1956); (d) R. L. Pecsok and J. Sandera, *ibid.*, **79**, 4069 (1957).

(3) D. T. Sawyer, R. S. George, and J. B. Bagger, *ibid.*, **81**, 5893 (1959).

(4) J. Bjerrum, G. Schwarzenbach, and L. G. Sillén, "Stability Constants. Part II: Inorganic Ligands," Special Publication No. 7, The Chemical Society, London, 1958.

(5) G. F. Smith, "Cerate Oxidimetry," The G. Frederick Smith Chemical Co., Columbus, Ohio, 1942.

(6) V. Auger, L. Lafontaine, and C. Caspar, *Compt. rend.*, **180**, 376 (1925).

(7) T. I. Pistea, *Bul. chim. soc. romăne chim.*, **39**, 83 (1937–8); *Chem. Abstr.*, **34**, 2277 (1940).

(8) A. Job and P. Goissedet, *Compt. rend.*, **157**, 50 (1913).

(9) D. T. Sawyer, R. L. Pecsok, and K. K. Jensen, *Anal. Chem.*, **30**, 481 (1958).

(10) R. L. Pecsok and R. S. Juvet, Jr., *ibid.*, **27**, 165 (1955).

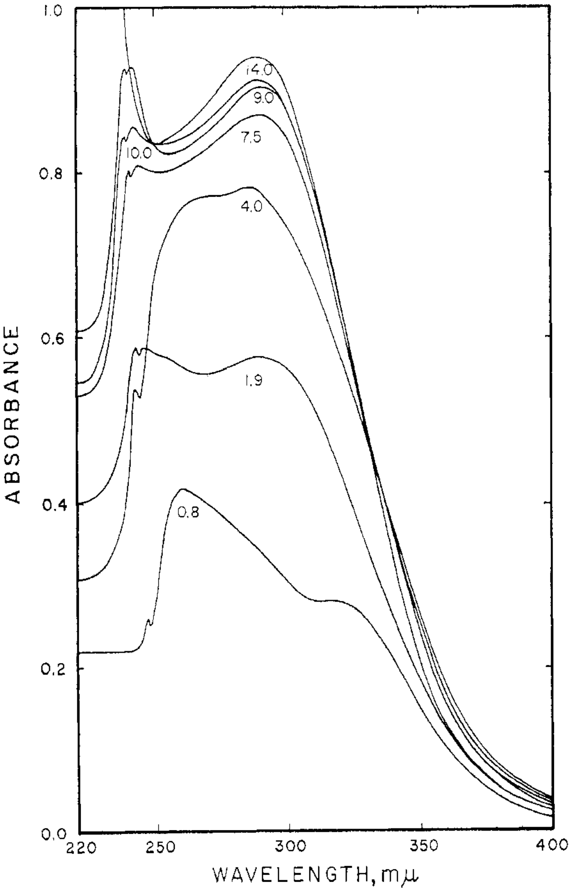

Fig. 1.—Absorption spectra of cerium(IV)-gluconate solutions at various *p*H values. All solutions were 2.24 × 10^{-4} *F* in cerium(IV) and 8 × 10^{-2} *F* in sodium gluconate, and were equilibrated for two days before the spectra were recorded. The *p*H values of the equilibrated solutions are indicated on the spectra.

zero absorbance because of precipitation of ceric hydroxide. The spectra at the lower *p*H values apparently represent protonated forms of the cerium(IV)-gluconate complexes.

The method of continuous variations[11] has been applied to the cerium(IV)-gluconate system in an effort to establish the formula of the complex. The results of this study are shown in Fig. 2. After one day of equilibration the data indicate a mole ratio of 6 cerium ions per gluconate ion. As the solutions continued to equilibrate precipitation occurred in the solutions with a high cerium-to-gluconate ratio. As indicated in Fig. 2, the solutions finally equilibrated after 17 days to approximately one cerium(IV) ion per gluconate. Additional equilibration was not satisfactory because of the slow deterioration of the solutions; this became noticeable after 50 days

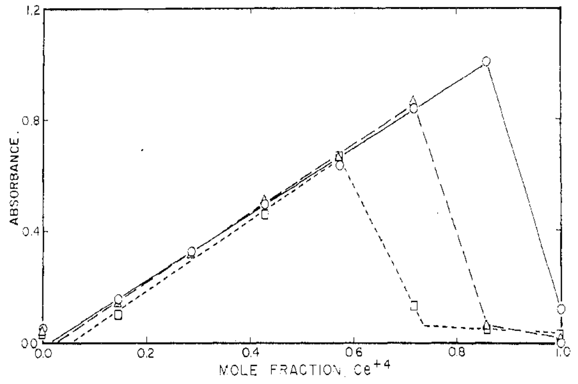

Fig. 2.—Continuous variations study of the cerium(IV)-gluconate system and the effect of time on the absorbance. All measurements were made at 288 mμ. The sum of the cerium(IV) concentration plus the sodium gluconate was 2.80 × 10^{-4} *F* for all of the solutions and each was adjusted to *p*H 14. The mole fraction of cerium(IV) in the solutions is indicated on the graph. The solutions were allowed to equilibrate for the indicated period and centrifuged just prior to measuring the absorbance: ○, 1 day after preparation of the solutions; △, 8 days after preparation; □, 17 days after preparation.

and may have been due to bacterial action on the gluconate molecule.

In a further effort to establish the stable cerium(IV)-gluconate mole ratio a series of solutions with a constant gluconate ion concentration of 5.0 × 10^{-4} *M* and various cerium(IV) concentrations was prepared and adjusted to *p*H 14. Measurements of the absorbance for the solutions at 288 mμ indicated, after one day of equilibration, that the mole ratio of the complex was 6 cerium ions per gluconate. After 28 days the ratio had been reduced to 2 cerium ions per gluconate as a result of hydrolysis. Thus, both spectrophotometric studies indicate that an initial complex, containing at least 6 cerium(IV) ions per gluconate ion, is formed. This polymeric complex slowly hydrolyzes to give a complex containing 1 or 2 cerium ions per gluconate.

***p*H Titrations of the Cerium-Gluconate System.**—A series of *p*H titrations of cerium(IV), gluconic acid, and various molar mixtures of cerium(IV) and gluconic acid have been performed in an effort to further elucidate the formula for the complex. $Ce(NH_4)_2(NO_3)_6$ was used as the cerium(IV) salt for all of the titration studies. With the exception of the pure cerium(IV) salt, all of the titrations were performed as back-titrations with an excess of standard base first being added and then back-titrating with standard hydrochloric acid. This procedure was necessary because of the slow rate of reaction for

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

TABLE I

SUMMARY OF pH TITRATIONS FOR A SERIES OF CERIUM(IV)–GLUCONIC ACID MIXTURES

Data represent the total number of hydroxides required per cerium(IV) in the complex

		Mole Ratio, Ce(IV):HGH_4[a]			
	Pure Ce(IV)	2:1	1:1	2:3	1:2
	pH 7				
OH^-'s per Ce(IV)	3.66	4.36	5.03	5.94	6.35
OH^-'s per Ce(IV) minus 1 OH^- per HGH_4		3.86	4.03	4.44	4.35
Theoretical (assuming a 2:3 complex)		3.92	4.18	4.44	4.44
	pH 8				
OH^-'s per Ce(IV)	3.80	4.55	5.30	6.20	6.63
OH^-'s per Ce(IV) minus 1 OH^- per HGH_4		4.05	4.30	4.70	4.63
Theoretical (assuming a 2:3 complex)		4.11	4.40	4.70	4.70
	pH 11				
OH^-'s per Ce(IV)	5.95	6.75	7.60	8.96	9.60
OH^-'s per Ce(IV) minus 1 OH^- per HGH_4		6.25	6.60	7.46	7.60
Theoretical (assuming a 2:3 complex)		6.45	6.95	7.46	7.46

[a] HGH_4 represents the gluconic acid molecule, with the first H signifying the carboxylate proton and the other H's signifying the protons of the secondary hydroxyl groups.

the gluconic acid neutralization. Titrations have been performed for mixtures of cerium(IV) and gluconic acid in which the mole ratio is 1/2:1, 2/3:1, 1:1, and 2:1. Table I summarizes the results of these titrations at various pH values and gives the number of hydroxides per cerium(IV) in the complex that are required to reach these pH values. One hydroxide ion per gluconic acid molecule is required to titrate pure gluconic acid to within the pH range from pH 7 to 11. Because this same proton would be released when titrating the complex, data are given in Table I for which the subtraction of one hydroxide per gluconic acid has been made. The pH values presented in Table I were selected on the basis of the titration curves. pH 7 and 8 are in the vicinity of the first break in the titration curve, while pH 11 represents the second break. Reference to Table I indicates that a maximum number of hydroxides per cerium(IV) in the complex (corrected for the one hydroxide consumed per gluconic acid) are consumed when the mole ratio for cerium relative to gluconic acid is 2 to 3. This is true at pH 7 and 8, while at pH 11 the number for the 1:2 ratio is essentially the same as for the 2:3 ratio.

Studies of the Optical Rotation of the Cerium(IV)–Gluconate System.—The optical activity of gluconic acid and the attendant effect of coordination upon it have been used previously by Pecsok and Juvet[12] for the study of metal–gluconate complexes. Two studies of the cerium(IV)–gluconate system have been made using optical rotation.

The first involved a continuous variations study[11] using optical rotation as the measured variable and is shown in Fig. 3. The lower curve represents the corrected optical rotation assuming a one-to-one complex, which is strongly suggested by the upper curve. The solutions were made up to contain a total molar concentration of 0.100 *M* for the sum of the cerium(IV) concentration plus

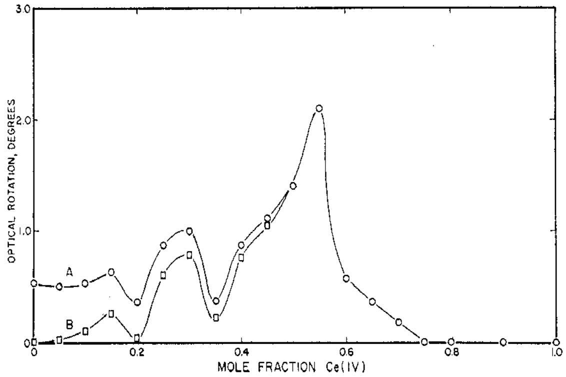

Fig. 3.—Continuous variations study of the cerium(IV)–gluconate system using optical rotation as the measured variable. The sum of the cerium(IV) concentration plus the sodium gluconate concentration was 0.10 *F* for all of the solutions. Each was adjusted to pH 13.5. The solutions were equilibrated for seven days, centrifuged, and diluted by a factor of 10 prior to measuring the optical rotation. The recorded values have been corrected to represent the rotation of solutions without dilution. Curve A represents the actual optical rotation while curve B is the optical rotation assuming that only a 1:1 complex is formed. The latter curve is obtained by subtracting the rotation due to the assumed amount of free gluconate ion.

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[12] R. L. Pecsok and R. S. Juvet, Jr., *J. Am. Chem. Soc.*, **78**, 3967 (1956).

the gluconate concentration, and each solution was adjusted to *p*H 13.5. After preparation the solutions were equilibrated for seven days, and centrifuged just prior to taking a reading. Because of the highly colored nature of the solutions, dilution by a factor of 10 was necessary to permit readings on the polarimeter through the 200-mm. sample tube. The data in Fig. 3 represent the average of five readings for each point and are corrected to indicate the rotation for a total molar concentration of 0.100 *M*. The second maximum in Fig. 3 at a mole fraction of 0.29 indicates that a second complex containing one cerium(IV) per two or three gluconate ions also is formed. Furthermore, the absence of a smooth curve with a single maximum gives added support to the conclusion that a complicated system is involved containing a number of complexed species.

The second study using optical rotation has been made for a series of solutions each containing 0.050 *M* gluconate ion and varying amounts of cerium(IV) from 0.00 to 0.30 *F*. The solutions were adjusted to *p*H 13.5 and equilibrated for three weeks. Just prior to making measurements each solution was centrifuged, and when necessary diluted by a factor of 10 to permit reading of the optical rotation. A plot of optical rotation *vs.* the mole-ratio of cerium(IV) to gluconate ion gives a smooth curve with a broad maximum at a mole ratio of one. For mole ratios higher than one the rotation decreases because of coprecipitation of gluconate ions by the ceric hydroxide resulting from the excess cerium(IV) ions. The maximum at a mole ratio of one serves as support for the conclusion that the complex contains approximately one cerium(IV) per gluconate ion.

Potentiometric Studies of the Cerium(IV)–Gluconate System.—A series of potentiometric measurements has been made of the cerium(IV)–gluconate complex. Figure 4 shows the effect of *p*H upon the potential of a solution containing equimolar concentrations of cerium(IV) and cerium(III), and 0.10 *F* gluconate ion. The transition in the region between *p*H 4 and 8 for the curve is further evidence that the cerium(IV) complex is formed in this *p*H range. The slope for the linear portion of the curve is −0.154 v. per *p*H unit; which, for a reversible process, would indicate that 2.5 hydroxides per cerium(IV) are released in the reduction reaction. Solutions more concentrated than 0.050 *F* in Ce(III) form a white precipitate which probably is cerous hydroxide. The precipitate is formed even in the presence of a large excess of gluconate ion, which implies that the cerium(III) gluconate complex is considerably weaker than the cerium(IV) complex.

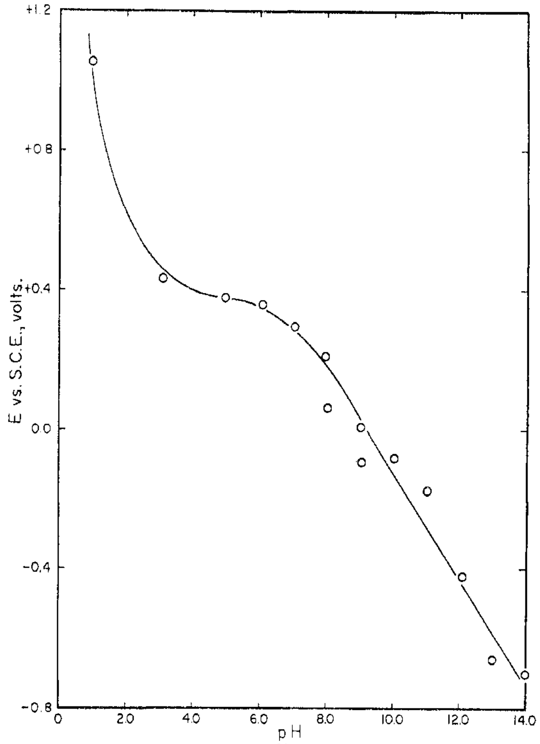

Fig. 4.—Potential of the cerium(IV)–cerium(III) couple as a function of *p*H. All of the solutions were 2.5×10^{-2} *F* each in cerium(IV) and cerium(III) and 0.10 *F* in sodium gluconate. The prepared solutions were equilibrated five days before evaluating their *p*H and measuring their potential. The slope of the linear portion of the curve at the lower right is −0.154 v. per *p*H unit.

The effect of varying the gluconate ion concentration upon the potential for solutions containing equimolar concentrations of cerium(IV) and cerium(III) at *p*H 13.5 is shown by curves A and B in Fig. 5; curve A is for solutions equilibrated for 1 day and curve B is for solutions equilibrated 42 days. Figure 5 also shows the effect upon the potential of varying cerium(IV) concentration in a series of solutions containing 0.010 *F* cerium(III) and 0.50 *F* gluconate ion, and adjusted to *p*H 13.5. Curve C is for solutions equilibrated 2 days and curve D for solutions equilibrated 40 days. The measurement of all of the potentials given in Fig. 4 and 5 is extremely difficult because of the slow equilibration of the platinum indicator electrode, particularly in the strongly basic solutions.

The potential of the platinum indicator elec-

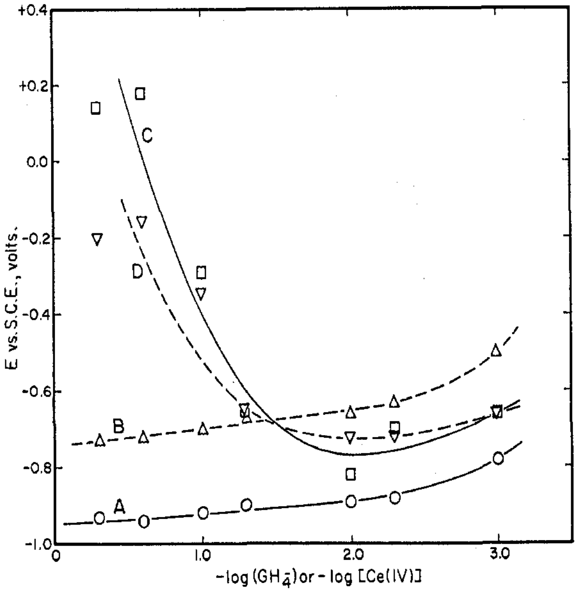

Fig. 5.—Potential of the cerium(IV)–cerium(III) couple as a function of gluconate ion concentration and as a function of cerium(IV) concentration. All solutions were adjusted to *p*H 13.5 prior to making potentiometric measurements. Curves A and B are for a series of solutions each containing 0.010 *F* cerium(IV) and 0.010 *F* cerium(III), but with varying concentrations of gluconate ion, GH$_4^-$. Curve A represents the potentials of the solutions after 1 day of equilibration. Curve B represents the potentials after 42 days of equilibration. The slope of the linear portion of curve B is 0.045 v. per $-\log(\mathrm{GH}_4^-)$ unit. Solutions containing 0.01 *F* or less gluconate formed precipitates. Curves C and D are for a series of solutions each containing 0.010 *F* cerium(III) and 0.50 *F* gluconate ion, but with varying concentrations of cerium(IV). Curve C represents the potentials of the solutions after 2 days of equilibration. Curve D represents the potentials after 40 days of equilibration.

trode is essentially independent of cerium(IV) concentration when this concentration is below 0.010 *F*, but rises rapidly above this concentration. The non-linear behavior of curves C and D in Fig. 5 may indicate either that the platinum electrode has not equilibrated with the solution, or that the nature of the cerium(IV)–gluconate complex changes with cerium(IV) concentration.

Polarography of Cerium(IV)–Gluconate.—Basic solutions of cerium(IV) in the presence of excess gluconate give irreversible and poorly defined polarographic waves. Under the best of experimental conditions (namely, approximately 0.01 *F* cerium(IV), 0.1 to 0.3 *F* gluconate ion, and *p*H 12 to 13) the reduction wave has a half-wave potential of −0.6 v. *vs.* s.c.e. and a diffusion current constant, *I*, of 0.11 (maximum rather than average current). The height of this wave is approximately proportional to cerium(IV) concentration up to 0.05 *F* cerium(IV). However, deviation from these conditions causes reduction waves which are essentially undefined. The small diffusion currents exhibited by cerium(IV)–gluconate solutions tend to indicate that a large rather immobile species is present in solution.

Several efforts have been made to isolate the cerium(IV)–gluconate complex. These attempts have consisted of mixing equimolar amounts of gluconic acid and $Ce(NH_4)_2(NO_3)_6$, in this order, to an excess of base. After mixing, the solutions were evaporated slowly until sirupy, followed by the addition of 95% ethyl alcohol. A brownish-red material was isolated on several occasions, but it was impossible to recrystallize it. Analysis indicated an impure material containing approximately one cerium(IV) ion per gluconate ion, but the impure condition of the isolated material makes any conclusions questionable.

Discussion and Conclusions

Both spectrophotometric studies (the continuous variations study shown in Fig. 2 and the mole ratio study) indicate that cerium(IV) in the presence of gluconate ion initially forms a polymeric species containing at least six cerium(IV) ions per gluconate ion. This behavior is similar to that observed for the ruthenium(III)–gluconate complex.[13] In the case of the continuous variations study of the cerium(IV) complex the polymeric species slowly hydrolyze to give a stable complex containing approximately one cerium(IV) ion per gluconate ion. However, the mole ratio study indicated that a stable species containing two cerium ions per gluconate ion also is formed. The second continuous variations study for this system used optical rotation as the measured variable and the results (shown in Fig. 3) support the conclusion that the stable complex contains approximately one cerium(IV) per gluconate ion. The multipeaked plot shown in Fig. 3 also supports the conclusion that several complex species probably are formed rather than just one. The use of optical rotation as the measured variable has one distinct advantage over the spectrophotometric method; namely, much more concentrated solutions can be used with the former method and under such conditions the rate of hydrolysis of any unstable polymeric species is accelerated. Thus these three studies give support for a complex containing approximately one

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(13) D. T. Sawyer, R. S. George, and J. B. Bagger, *J. Am. Chem. Soc.* **81**, 5893 (1959).

cerium(IV) ion per gluconate ion as well as indicating that the system is complicated by other complexed species.

The *p*H titrations, summarized in Table I, used rather concentrated solutions and actually were back titrations of solutions to which an excess of base first had been added. As a result we feel that these data are the most reliable in terms of making conclusions about the formula of the cerium(IV) complex. Because more hydroxides are consumed per cerium(IV) in the presence of gluconate ion than in its absence, it is reasonable to conclude that a maximum number of hydroxides per cerium(IV) will be consumed by the solution containing the same mole ratio of cerium(IV) to gluconate as the stable form of the complex. Thus, reference to Table I indicates that the net number of hydroxides per cerium(IV) increases as the mole ratio of cerium(IV) to gluconate is decreased. This continues until the mole ratio has decreased to 2:3; beyond this ratio there is no increase in the number of hydroxides per cerium(IV) because an excess of gluconate ion is present. The data for the 1:2 complex illustrate this point. On the basis of the number of hydroxides per cerium(IV) consumed in the absence of gluconate and the assumption that the stable complex has a mole ratio of 2:3, the theoretical number of hydroxides per cerium(IV) can be calculated for the mixtures listed in Table I. The results of such a calculation are given in Table I and the agreement between the actual number and theoretical number of hydroxides gives added support to the conclusion that the correct ratio of the stable complex is 2:3. Such a conclusion is not inconsistent with the data shown in Fig. 2 and 3 which indicate approximately one cerium(IV) per gluconate ion. The approximate nature of the data in these curves does not preclude a complex containing 2 cerium(IV) ions per three gluconate ions. Reference to the data in Table I also indicates that in the vicinity of *p*H 7.3 the formation of the stable complex consumes 4.5 hydroxides per cerium(IV). At this *p*H the ammonium ions of the ceric salt, $Ce(NH_4)_2(NO_3)_6$, are essentially all in their acidic form. The data further indicate that at *p*H 11 a net of 5.5 hydroxides per cerium(IV) are consumed in forming a hydroxylated form of the complex formed at *p*H 7.5. At this *p*H the two ammonium ions in $Ce(NH_4)_2(NO_3)_6$ have been converted to ammonia and thus 2 hydroxides per cerium(IV) must be subtracted from the 7.5 per cerium(IV) shown in Table I. From these arguments two formation reactions can be written for the cerium(IV)–gluconate complex

$$p\text{H } 7.5,\ 2Ce^{+4} + 3GH_4^- + 9OH^- \longrightarrow Ce_2(GH_4)_3(OH)_9^{-4} \quad (1)$$

$$p\text{H } 11,\ 2Ce^{+4} + 3GH_4^- + 11OH^- \longrightarrow Ce_2(GH_4)_3(OH)_{11}^{-6} \quad (2)$$

where GH_4^- represents the gluconate ion (with the H's signifying the protons of the secondary hydroxyl groups).

The slope for the lower part of the curve in Fig. 4 implies that 2.5 hydroxides per cerium(IV) are lost in the reduction reaction. In addition, the slope of curve B in Fig. 5 indicates that one gluconate ion per cerium(IV) also is lost in the reduction reaction. If these conclusions are valid a plausible reduction reaction can be written for systems at approximately *p*H 11

$$Ce_2(GH_4)_3(OH)_{11}^{-6} + 2e^- \longrightarrow Ce_2(GH_4)(OH)_6^- + 2GH_4^- + 5OH^- \quad (3)$$

Although this equation is quite tentative it does account for our observation that at *p*H 14 and in the presence of 0.20 F GH_4^-, cerium(III) remains in solution up to 0.050 F concentrations. Assuming this is the maximum formal concentration of cerium(III) possible under these conditions and using the reported solubility product for $Ce(OH)_3$ ($K_{sp} = 10^{-20}$ at 25°),[4] the free Ce^{+3} concentration at *p*H 14 can be calculated to be 10^{-20} M. Writing the formation reaction for the postulated cerium(III)–gluconate complex

$$2Ce^{+3} + GH_4^- + 6OH^- \longrightarrow Ce_2(GH_4)(OH)_6^- \quad (4)$$

permits an approximate formation constant, K_f, to be calculated for the conditions under which no precipitation of $Ce(OH)_3$ is observed. The approximate value, assuming concentration equals activity, for log K_f is 39. Reference to the data in Fig. 4 for the potential at *p*H 14 together with the assumption that the observed potential is reversible and dependent upon the cerium(IV)–cerium(III) couple (with an E^0 of 1.61 v.) leads to a calculation of the formation constant for the reaction expressed by eq. 2. For the conditions used relative to Fig. 4 it is necessary to use the formation constant for eq. 4 together with the Nernst equation to determine the free Ce^{+4} concentration. Using this and assuming concentrations equal activities the approximate formation constant for eq. 2 is calculated to have a value for log K_f equal to 63. Both of these constants are highly tentative not only because 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]

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The gluconate ion forms stable complexes with uranium(VI), particularly under basic conditions. Spectrophotometric, polarographic, polarimetric, and *p*H measurements have been used to study these complexes. At *p*H 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 *p*H 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 *p*H 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 *p*H 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 *p*H 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.

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(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.