the stoichiometric oxides such as MO, M_2O_3, MO_2, or M_2O_5, where there is no valence (electronic) disorder, and in which vacant lattice positions tend to arrange in ordered arrays. By contrast, for non-stoichiometric materials such as wüstite[21] ($\Delta S^0 = -27$ e.u./mole of O_2) and α Nb_2O_{5-y}[22] ($\Delta S^0 = -30$ e.u./mole of O_2) the observed ΔS^0 are numerically very small. (b) The results cited in ref. 19 represent differential molar entropy changes; in the infinitesimal reaction to which they apply neither the electronic nor the lattice disorder is changed appreciably. Hence one would expect these $|\Delta S^0|$ values to lie in the 40–50 e.u. range, as is indeed the case.

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[21] E. G. King and K. K. Kelley, U. S. Bur. Mines Rept. Invest. No. 4870 (1952).

[22] P. Kofstad and P. B. Anderson, *J. Phys. Chem. Solids*, **21**, 280 (1961).

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Osmium(VI, IV, III) Gluconate Complexes

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Osmium(VI, IV, III) ions are strongly complexed by sodium gluconate in alkaline solutions. The resultant complexes have been investigated by polarography, spectrophotometry, and optical rotation. The osmium(VI) gluconate complex gives an essentially reversible reduction wave which is independent of gluconate concentration. In 0.1 *F* sodium gluconate and 1 *F* sodium hydroxide the reduction wave has a half-wave potential of −0.495 v. *vs.* s.c.e. and a diffusion current constant, $I_{\max}$, of 2.44. Spectrophotometric measurements indicate that at least two hydrolytic species of the complex exist, one with an absorption maximum of 290 mμ for solutions of pH 7–10, and another with a maximum at 270 mμ for more alkaline solutions. The continuous variations method has been used to establish that the most stable complex contains two gluconate ions per osmium(VI). On the basis of the entire group of studies, the reactions at pH 14 for the 6-to-4 and 4-to-3 reductions can be written $Os(GH_4)_2(OH)_6^{-2} + 2e^- \rightarrow Os(GH_4)_2(OH)_3^- + 3OH^-$ and $Os(GH_4)_2(OH)_3^- + e^- \rightarrow Os(GH_4)_2(OH)_3^{-2}$, respectively.

Osmium ions have been known to be active polarographically since the work of Crowell, Heyrovsky, and Engelkemeir in 1941.[1] Later a detailed study of the polarography of osmium(VIII) in various media was reported by Meites.[2] Recently Cover and Meites[3] have presented an extensive study of the polarographic behavior of osmium(VI) and osmium(IV) in both acidic and basic media. Because osmium has many chemical properties similar to ruthenium, which has been shown to be strongly complexed by sodium gluconate,[4] the possibility of complexing osmium with gluconate appeared worth investigating, particularly by polarography.

Studies of a number of metal–gluconate complexes have been summarized in two recent papers on gluconate complexes of cerium(IV)[5] and uranium(VI).[6] In general the complexes are extremely stable in basic solutions, rather complicated, and frequently involve polymeric species and hydroxide groups. The present discussion is concerned with a detailed study of the gluconate complexes of osmium(VI), osmium(IV), and osmium(III) in alkaline solutions. Polarography, spectrophotometry, and measurements of optical rotation have been used as a means of establishing the chemical characteristics, formulas, and stabilities of the complexes.

Experimental

Equipment.—Polarographic measurements were made with a Sargent Model XV recording polarograph equipped with a three-compartment cell to prevent attack of the agar salt bridge by strongly alkaline solutions.[7] All measurements were made at 25.0 ± 0.1°, and the solutions were deaerated with pre-purified nitrogen. Diffusion currents were measured using the tops of the oscillations (maximum current) and were corrected for residual current. All potentials were measured and are reported *vs.* the saturated calomel electrode. Half-wave potentials were measured to an accuracy of ±5 millivolts. The rate of flow of mercury was 2.71 mg./sec., and the drop time was 3.13 sec. at −0.5 v. and 2.38 sec. at −1.4 v..

Spectrophotometric data were obtained with a Cary Model 14 recording spectrophotometer. A Leeds and Northrup line-operated pH meter equipped with a high-range glass electrode was used for measuring the pH of solutions. The meter was standardized with N.B.S. buffers.

Measurements of optical rotation were made with a Rudolph Model 70 polarimeter using 1-, 2-, or 4-dm. sample tubes. Because of the high optical absorbance of the solutions, dilution was necessary just prior to the measurement of the solution rotation.

Reagents.—Solutions of osmium(VIII) were prepared determinately from reagent grade OsO_4 (Mallinckrodt Chemical Works) which had an assay of 99.9%. Attempts to standardize the solutions gravimetrically by using the benzotriazole method[8]

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[1] W. R. Crowell, J. Heyrovsky, and D. W. Engelkemeir, *J. Am. Chem. Soc.*, **63**, 2888 (1941).

[2] L. Meites, *ibid.*, **79**, 4631 (1957).

[3] R. E. Cover and L. Meites, *ibid.*, **83**, 4706 (1961).

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

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

[6] D. T. Sawyer and R. J. Kula, *ibid.*, **1**, 303 (1962).

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gave an assay of approximately 115%. Solutions of osmium(IV) were prepared determinately from $(NH_4)_2OsCl_6$ (Johnson Matthey and Co.) which has an assay of 99.9%. Solutions of osmium(VI) were prepared by quantitatively reducing osmium(VIII) solutions with ethanol using a procedure similar to that listed by Ephraim[9]; a few drops of ethanol were added to an alkaline solution of OsO_4 and the resulting solution was heated briefly.

Sodium gluconate solutions were prepared determinately from D-glucono-δ-lactone (Pfizer), purified grade. The purity of the lactone was determined by back-titrating with standard acid a solution to which excess 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

Polarography.—Attempts to study osmium(VIII) in alkaline solutions of sodium gluconate ($(NaGH)_4$) were unsuccessful because of the reduction of the +8 species to +6 osmium by the gluconate ion. This is not surprising in view of the well established reduction of OsO_4 by alcohols.[9,10] That such a reduction actually takes place was established by placing 20 ml. of a 1 mM solution of osmium(VIII), pH 14, in the polarographic cell. The spontaneous current was 5 μa. To this solution was added 30 μl. of 0.5 F $NaGH_4$; the current decreased to 0.3 μa. within 1 hr.

Solutions of osmium(VI) in 1 F NaOH and 0.1 F $NaGH_4$ give a well defined two-step polarogram similar to that reported by Cover and Meites[3] for osmium(VI) in alkaline solutions. As in their work, an anomalous catalytic wave at −1.3 v. is observed. Variation of the height of the mercury column confirms that both osmium gluconate waves are diffusion controlled. The half-wave potentials for both waves are independent of osmium concentration. Table I summarizes the polarographic characteristics for osmium(VI) and osmium(IV) in the presence of 0.1 F $NaGH_4$ and 1 F NaOH. The diffusion current for the first reduction wave of osmium(VI) is linear with concentration from 3×10^{-5} to 3×10^{-3} F osmium(VI) and follows the relation

$$i_d = I_{max} C m^{2/3} t^{1/6} + 0.12 \qquad (1)$$

where i_d is in μa. and C is in mmoles/l. Under these conditions the diffusion current constant, I_{max}, has a value of 2.44 ± 0.01 (maximum rather than average current).

For the first wave the slope for a plot of E $vs.$ log $[(i_d - i)/i]$ is −0.048 v. Although this value is significantly greater than the theoretical value of −0.030 v. for a two-electron reversible wave, the value is sufficiently close to permit some semiquantitative conclusions concerning the nature of the complex species in solution. Similar data for the second wave indicate a slope of approximately −0.080 v. as opposed to the theoretical value of −0.059 v. for a one-electron change.

Table I

Polarographic Data for Osmium(VI) and Osmium(IV) in 0.1 F $NaGH_4$ and 1 F NaOH

Oxidation change	Half-wave potential, volts With GH_4	Half-wave potential, volts Without GH_4[a]
VI → IV	−0.495	−0.605
VI → III	−1.465	−1.543
IV → VI	−0.447	−0.485
IV → III	−1.483	−1.520

[a] From Cover and Meites.[3]

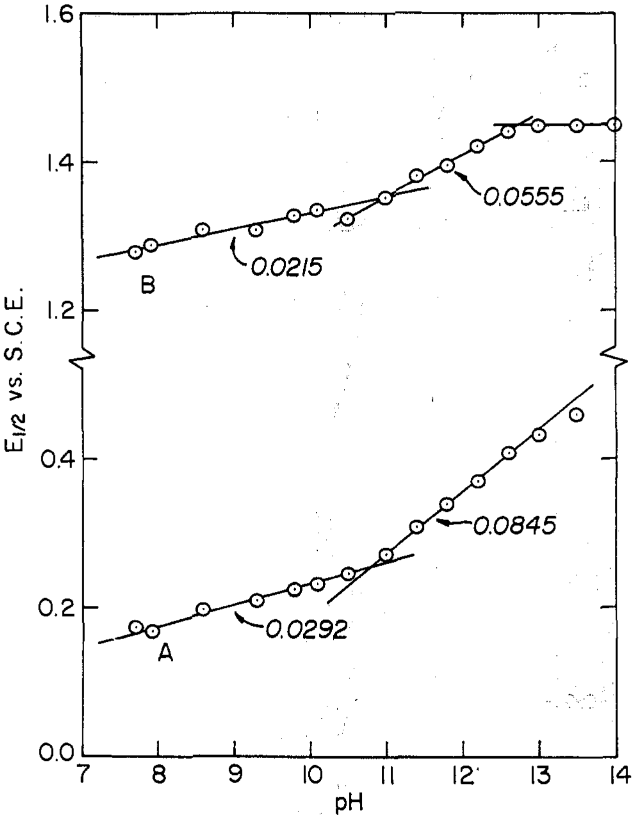

Fig. 1.—Half-wave potentials as a function of pH for the reduction of osmium(VI) in the presence of gluconate ion. Curve A is for the first reduction wave and curve B is for the second reduction wave. The slopes of the curves are indicated on the figure. The solutions contained 4.7×10^{-4} F osmium(VI) and 0.1 F sodium gluconate.

The ratio of the height of the first wave relative to that of the second wave is 0.85 in the presence of 0.1 F $NaGH_4$ and 1 F NaOH, while it is 1.05 in the absence of gluconate ion. The transitions listed in Table I are based on the coulometric data of Cover and Meites[3] and the general similarity between the reduction waves with and without gluconate ions.

The first wave for the reduction of osmium(VI) is independent of gluconate concentration at all levels of concentration while the second wave is independent below 0.2 F $NaGH_4$. Above this concentration the slope for E $vs.$ log $[GH_4^-]$, assuming a reversible wave, indicates that one GH_4^- per osmium(IV) is lost in the reduction step.

Cover and Meites[3] have shown that for unchelated osmium(VI) the half-wave potential is independent of hydroxide concentration from 1.0 to 9.4 F NaOH. The effect of pH upon the half-wave potentials for the reduction of osmium(V) in the presence of gluconate is shown in Fig. 1. Although the reduction is obviously

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(9) F. Ephraim, "Inorganic Chemistry," 6th Ed., Oliver and Boyd, London, 1954, p. 492.

(10) N. V. Sidgwick, "The Chemical Elements and Their Compounds," Vol. II, Oxford University Press, London, 1950, p. 1499.

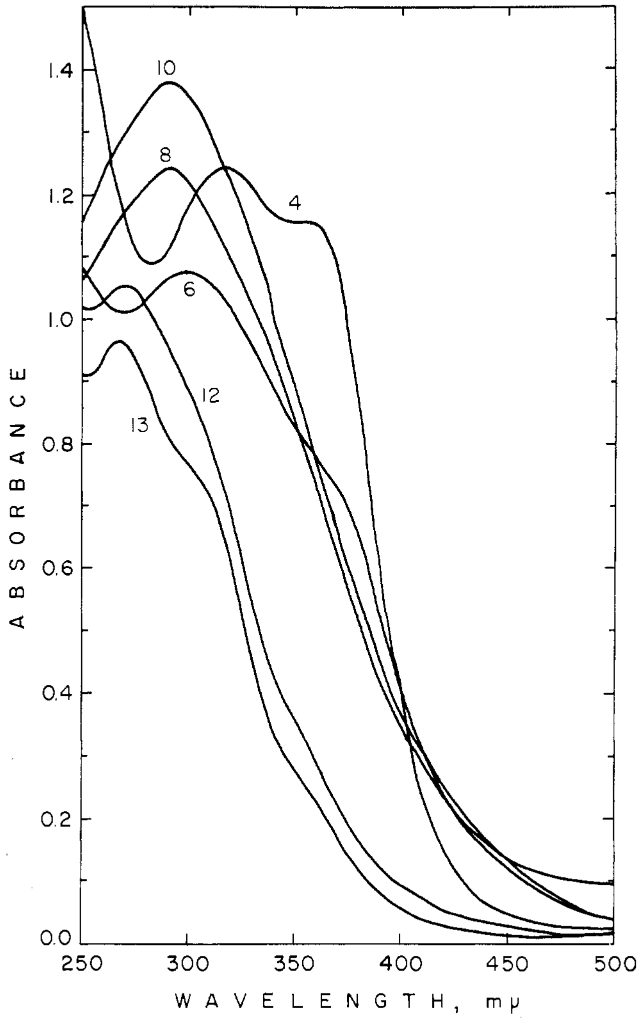

Fig. 2.—Absorption spectra of osmium(VI) gluconate solutions as a function of pH. The pH values of the equilibrated solutions are indicated on the spectra. All solutions were 2.4 × 10^{-4} *F* in osmium(VI) and 0.05 *F* ins odium gluconate and were equilibrated for 1 month before recording.

not completely reversible, it is believed that some meaningful conclusions can be made by assuming a reversible wave in terms of changes of potential with changes in pH. Curve A is for the first wave and curve B is for the second wave. The slopes indicate that one hydroxide ion per osmium(VI) ion is lost in the reduction step between pH 7 and 11, and that three hydroxide ions per osmium(VI) are lost above pH 11. For the reduction of osmium(IV) the slopes indicate that one hydroxide ion per two osmium(IV) ions is lost between pH 7 and 11, that one hydroxide ion per osmium(IV) ion is lost between pH 11 and 13, and that no hydroxide ions are lost above pH 13.

Spectrophotometry of Osmium(VI) Gluconate.—The absorption spectra for osmium(VI) in the presence of excess sodium gluconate as a function of pH are shown in Fig. 2. The pH values of the various solutions are indicated on the curves. Below about pH 4 there appears to be little tendency for gluconate to chelate osmium(VI) ion. Above pH 6 and up through pH 10 one form of the chelate appears to exist; a second form is established above pH 10 as shown by the curves at pH 12 and 13.

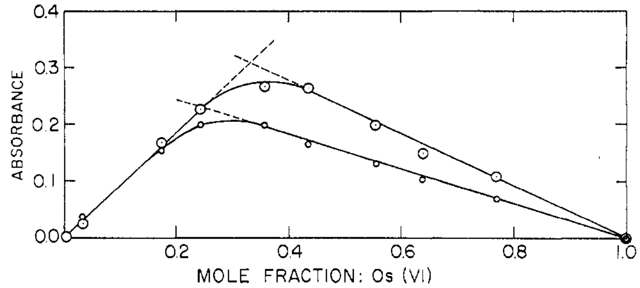

Fig. 3.—Continuous variations study of the osmium(VI)-gluconate system and the effect of time on the absorbance. The sum of the osmium(VI) concentration plus the sodium gluconate concentration was 5 × 10^{-4} *F* for all the solutions and each was adjusted to pH 10. The upper curve is for solutions which have equilibrated for 3 days; the lower curve is for 2-month old solutions.

Job's method of continuous variations has been applied in an effort to establish the formula of the osmium(VI) gluconate complex. The results of this study are shown in Fig. 3, where the upper curve represents the absorbances after the solutions have equilibrated for 3 days and the lower curve is for 2-month old solutions. Because osmium(VI) absorbs by itself, the curves in Fig. 3 had to be corrected by assuming a formula for the chelate. The curves as shown represent an assumption of two gluconate ions per osmium(VI) ion; all other assumptions for the complex gave meaningless results.

Optical Rotation of the Osmium(VI) Gluconate Complex.—To further establish the formula of the complex, the optical rotation has been measured for various mole ratios of osmium(VI) ion relative to gluconate ion. The results of such a study are shown in Fig. 4, where curve A is for the solutions after 2 hr. of equilibration and indicates 1.5 gluconate ions per osmium(VI); curve B is for 2-day old solutions and indicates both a complex with 5 gluconate ions per osmium(VI) and one with a one-to-one ratio; curve C is for the solutions after they have equilibrated for 3.5 weeks. These results indicate that the equilibration process is slow and that a number of complexes and possibly polymeric species are formed as the solutions equilibrate.

Discussion and Conclusions

By assuming that the Job's study gives the correct formula of two gluconate ions per osmium(VI) and by using the slopes of Fig. 1 to indicate the loss of hydroxide ions in the reduction steps, it is possible to propose tentative reduction reactions for the osmium gluconate complexes:

Osmium(VI) to osmium(IV); pH 11 to 14

$$\mathrm{Os(GH_4)_2(OH)_x}^{4-x} + 2e^- \longrightarrow \mathrm{Os(GH_4)_2(OH)_{x-3}}^{5-x} + 3\mathrm{OH}^- \quad (2)$$

pH 8 to 11

$$\mathrm{Os(GH_4)_2(OH)_y}^{4-y} + 2e^- \longrightarrow \mathrm{Os(GH_4)_2(OH)_{y-1}}^{3-y} + \mathrm{OH}^- \quad (3)$$

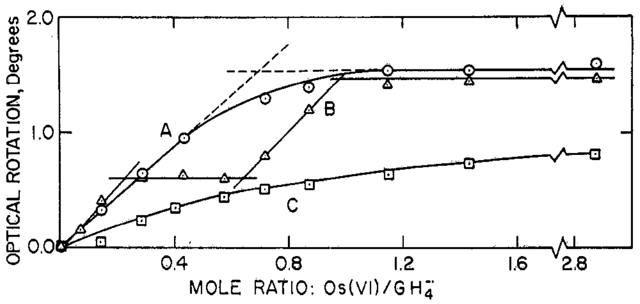

Fig. 4.—Mole-ratio study of the osmium(VI)–gluconate system using optical rotation as the measured variable. All solutions contained 2×10^{-3} F sodium gluconate and were adjusted to pH 14. The measurements were made in a 40-cm. polarimeter tube. Curve A is for 2-hr. old solutions, curve B for 2-day old solutions, and curve C for 24-day old solutions.

Osmium(IV) to osmium(III); pH 13 to 14

$$\mathrm{Os(GH_4)_2(OH)_{x-3}}^{5-x} + \mathrm{e}^- \longrightarrow \mathrm{Os(GH_4)_2(OH)_{x-3}}^{4-x} \quad (4)$$

pH 11 to 13

$$\mathrm{Os(GH_4)_2(OH)_{x-3}}^{5-x} + \mathrm{e}^- \longrightarrow \mathrm{Os(GH_4)_2(OH)_{x-4}}^{5-x} + \mathrm{OH}^- \quad (5)$$

pH 8 to 11

$$\mathrm{Os(GH_4)_2(OH)_{y-1}}^{3-y} + \mathrm{e}^- \longrightarrow \mathrm{Os(GH_4)_2(OH)_{y-1.5}}^{2.5-y} + 0.5\mathrm{OH}^- \quad (6)$$

Consideration of these five equations indicates that $x \geqq 4$; $y \geqq 1$; $y \leqq x$.

Under basic conditions it is probable that the osmium complexes would all carry negative charges. Thus, reference to eq. 2 indicates that assuming $x = 6$ gives a consistent set of equations. Also, these same conditions indicate that it is consistent to assume $y = 5$.

In summary gluconate ion forms strong complexes with osmium(VI, IV, III) in alkaline solutions. Advantage can be taken of these complexes as a means for stabilizing the ions in solution and also as a polarographic method of analysis. The use of sodium gluconate plus NaOH as a supporting electrolyte has the advantage that osmium(VIII) is spontaneously and quickly reduced to osmium(VI) by the gluconate. The resulting osmium(VI) gives a well defined and analytically useful reduction wave over a wide concentration range.

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CONTRIBUTION FROM THE LOS ALAMOS SCIENTIFIC LABORATORY,
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Preparation and Properties of Several Ammonium Uranium(IV) and Ammonium Plutonium(IV) Fluorides[1]

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A series of anhydrous fluoride complexes is formed between NH_4F and actinide tetrafluorides. Compounds with $NH_4F:MF_4$ (M = U or Pu) mole ratios of 4:1, 2:1, 7:6, 1:1, and 1:3 were prepared by reaction of stoichiometric quantities in sealed tubes or by gravimetric arrests during NH_4F distillation. X-Ray powder diffraction data are presented. Corresponding U(IV) and Pu(IV) compounds are isostructural. The $7NH_4F \cdot 6MF_4$ compounds are rhombohedral, $a_0 = 9.55$ and 9.42 Å., $\alpha = 107.4°$ and 107.4° for M = U and Pu, respectively. A method of chemical analysis for NH_4, U, and F on a single sample was developed using pyrohydrolysis, ion exchange, and volumetric techniques.

Introduction

The extensive studies of compounds formed in melts containing UF_4 and the alkali fluorides have been reviewed by Thoma,[2] who noted that several compound types are common: $3MF \cdot UF_4$, $2MF \cdot UF_4$, $7MF \cdot 6UF_4$, and $MF \cdot UF_4$. Only one corresponding compound in the NH_4F–UF_4 and NH_4F–PuF_4 systems has been reported, "NH_4PuF_5"; the occurrence of $NH_4F \cdot PuF_4$ and $7NH_4F \cdot 6PuF_4$ as separate compounds was not noted.[3-8] Prior work with ammonium fluoride complexes of U(IV) and Pu(IV) obtained by precipitation from aqueous solution or by treatment of the dioxide with NH_4HF_2 often has contained errors, primarily from the lack of recognition that "drying" can result in loss of NH_4F. Furthermore, NH_4F loss has been confused with loss of hydrate water (note the near coincidence of the formula weights of NH_4F, 37, and $2H_2O$, 36).

The direct reaction of actinide tetrafluorides with NH_4F under anhydrous conditions has not been re-

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(1) Work performed under the auspices of the U. S. Atomic Energy Commission.

(2) R. E. Thoma, *Inorg. Chem.*, **1**, 220 (1962).

(3) (a) H. A. Bernhardt, R. A. Gustison, and J. C. Posey, K-410 (June 1, 1949); (b) W. B. Tolley, HW-31211 (Mar. 16, 1954); (c) W. B. Tolley, HW-35814 (Feb. 1, 1955); (d) M. D. Alford, HW-41713 (Mar. 1, 1956). Obtainable from Office of Technical Services, Department of Commerce Washington 25, D. C.

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(8) N. P. Galkin, B. N. Sudarikov, and V. A. Zaitsev, *At. Energy*, **11**, 554 (1961).