acid solutions are equal; however, it appears that in spite of the fact that the ionic strength was held at unity, the activity coefficient product is significantly different in molar perchloric acid as compared with the more dilute acid solutions.

Experimental

The electromotive force of the cells was measured to the nearest 0.1 microvolt with a type K Leeds and Northrup potentiometer. The hydrogen used for the hydrogen electrodes was purified with alkaline permanganate, sulfuric acid, alkaline pyrogallol and heated copper. Mallinckrodt analytical reagent grade sodium sulfate was used. The sodium perchlorate was prepared by the reaction between C.P. sodium carbonate and perchloric acid. The perchloric acid was standardized against mercuric oxide. The temperature of the cells was maintained at 25.00 ± 0.05° by circulating thermostated water in the jacket of the cell container. Initially no sodium sulfate was present in the right compartment of the cell and the measured e.m.f., which should have been zero, was generally less than 20 microvolts. Two hydrogen electrodes were used in each half of the cell and these were intercompared by means of a switching arrangement. Standardized sodium sulfate solution was added in small increments from a weight buret. The solutions were stirred with magnetic stirrers and the cell e.m.f. was recorded after each addition of sodium sulfate.

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Uranium(III) Cupferrate[1]

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Uranyl ion forms an insoluble cupferron salt in neutral solution; this compound, $UO_2NH_4(Cup)_3$, is insoluble in organic solvents.[2] A second, ether- and chloroform-extractable form appears to exist in acid media, but only in small proportions in very concentrated uranium solutions.[2c] Uranium(IV) forms brown $U(Cup)_4$ which is insoluble in up to 8% sulfuric acid solution, but is quantitatively extractable into ethyl ether.[2c]

Polarographic and other studies in this Laboratory indicate the existence, also, of a very stable, ether-soluble uranium(III) cupferrate. While it has not been recognized so far as is known, there is some independent evidence both that U(III) does form a cupferrate and that this compound must be chloroform- and ether-soluble. The reported work on cupferron extraction of U(IV) has involved both the use of Jones reductors without a subsequent aeration step and extraction in the presence of liquid amalgams. The presence of some U(III) might be expected in either case and quantitative extraction of the uranium is claimed.[2c] Grimaldi[3] is one of the few authors to indicate that U(III), as well as U(IV), cupferrate is involved and that U(III) is quantitatively precipitated by cupferron in 10% hydrochloric acid.

Experimental.—Conventional polarographic techniques were employed, involving manual measurement with a Fisher Elecdropode. The polarographic cell-compartment was jacketed and thermostatically regulated at 25.0 ± 0.1°; a fritted disk and agar plug junction connected to a saturated calomel reference electrode. Distilled water and reagents of C.P. or reagent grade were employed. Oxygen removal was accomplished by purging with tank nitrogen.

Discussion.—The polarographic behavior of uranium in its various oxidation states has been very thoroughly studied and is well summarized by Rodden.[4] In general, aqueous solutions of U(VI) in dilute mineral acid exhibit the reduction pattern shown on curve ABC of Fig. 1. A medium of 0.1 N sulfuric acid and 0.1 N potassium chloride was employed in the present study. Wave A is primarily due to the one-electron reduction of U(VI) to U(V). However, the U(V) disproportionates

$$2\text{U(V)} \longrightarrow \text{U(VI)} + \text{U(IV)} \qquad (1)$$

to reform some U(VI) and to give some U(IV); consequently, the wave is larger than required for a one-electron reduction. Wave BC represents the two-electron reduction of U(V) to U(III); the intermediate (IV) stage demarcating B from C appears only at higher acidities. Wave A is always larger than B, and C(IV to III) is approximately equal to one-half of A plus B(VI to IV). In 6 N acid the B wave coalesces with A.

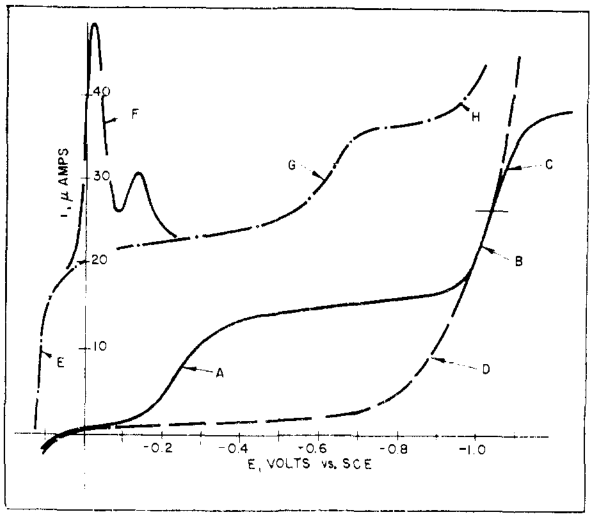

Fig. 1.—Polarographic reduction of uranium(VI) and of cupferron in dilute mineral acid solution.

Kolthoff and Liberti[5] have reported on the polarographic behavior of cupferron. The large reduction wave which occurs at more negative potentials in alkaline media, starts from about −0.8 to −0.9 v. *vs.* S.C.E. in 0.1 N acid, as shown by curve D of Fig. 1.

When a solution of 1mM uranyl ion in the presence of 10 mM cupferrate was examined, curve EFGH was obtained. The maximum at F is largely removed in the presence of 0.005% gelatin. Wave E represents the reduction of U(VI) to

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[1] This investigation was supported in part by the Air Force Cambridge Research Center under contract with the Engineering Research Institute of the University of Michigan.

[2] (a) O. Baudisch and R. Furst, *Ber.*, **50**, 324 (1917); (b) N. H. Furman and D. R. Norton, Atomic Energy Commission, Report MDDC 1623 (1947); (c) N. H. Furman, W. B. Mason and J. S. Pekola, *Anal. Chem.*, **21**, 1325 (1949).

[3] F. S. Grimaldi in "Collected Papers on Methods of Analysis for Uranium and Thorium," U. S. Geol. Survey Bull. 1006, 19 (1954).

[4] C. J. Rodden, "Analytical Chemistry of the Manhattan Project," McGraw-Hill, New York, N. Y., 1950, pp. 596–611.

[5] I. M. Kolthoff and A. Liberti, THIS JOURNAL, **70**, 1885 (1948).

U(Cup)$_4$, the extent to which the A and B waves have been made more positive (easier reduction) showing qualitatively the high stability of the complexed reduction product. Quantitatively, however, it can only be said of the E wave that its true half-wave potential is more positive than +0.1 v., the point at which the anodic dissolution of mercury in this medium permits the wave to appear. The H wave apparently represents reduction of the free excess cupferron.

The G wave must represent the counterpart of the (IV) to (III) C wave. Since it now results from a process which involves reduction beyond the complexed (IV) state, its $E_{1/2}$ should be more negative than that of the C wave if the (III) product were in a simple state. Its more positive position argues that U(III) must also form a cupferrate, whose stability is as great or greater than that of U(Cup)$_4$. In 16 mM cupferron solution the G wave is still more positive, with $E_{1/2}$ being about −0.15 v.

Studies on the current efficiencies of milligram-level electrolytic reductions of the uranyl ion in the presence of cupferron confirm the existence of a U(III) complex. It is also evident from these studies that U(III) cupferrate is readily soluble in ether.

This positive evidence for a U(III)-cupferron complex is interesting in view of the recent statement that, "Little is known about possible complex ions of U^{+3} in aqueous solution, although the general impression is that little complex-ion formation is to be anticipated."(6)

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(6) G. T. Seaborg and J. J. Katz, ed., "The Actinide Elements," McGraw-Hill Book Co., New York, N. Y., 1954, p. 162.

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The Stability of Potassium Permanganate in Alkaline Solutions Containing Telluric Acid

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The decomposition of potassium permanganate in alkaline medium and its bearing on the oxidation with that reagent was discussed by Stamm,[1] Duke,[2] Drummond and Waters[3] and Symons.[4] Decomposition in strong alkaline solutions (>3 N NaOH) is enhanced in presence of manganese dioxide and is largely inhibited in presence of telluric acid.[5] The stabilizing action of telluric acid is evidently brought about by its complexing power on quadrivalent manganese preventing the precipitation of MnO$_2$.[6] Whether or not the same stabilizing effect will be manifested by telluric acid on alkaline permanganate solutions is the aim of this investigation.

Experimental

Potassium permanganate solutions (~0.1 N) were prepared by the procedure recommended by Stamm[1] by dissolving the appropriate amount of the solid in 200 ml. of water twice distilled from alkaline permanganate in an all glass apparatus. The solution is boiled and then left to stand for 24 hrs., after which period it was filtered twice through 1 G4 sintered glass funnel and diluted to the appropriate volume. They were stored in brown colored bottles and checked with A.R. sodium oxalate. From these concentrated (~0.1 N) KMnO$_4$ solutions, 20–4 mmolar solutions were prepared for the kinetic study by accurate dilution.

Sodium hydroxide solutions (5–16 N) were prepared from the "Analar" B.D.H. product. The solutions were kept in a thermostat adjusted at 25° and mixed only after 0.5 hr. to ensure thermal equilibrium. 0.1 gram of telluric acid dissolved in little alkali was added to the proper volume of KMnO$_4$ in a brown bottle followed by the requisite volume of alkali solution and the mixture which is made up to 100 ml. with water is thoroughly agitated. At intervals of one hour (along a period of five hours) 10-ml. portions of KMnO$_4$ were titrated potentiometrically with monovalent thallium at 1.5–2 N NaOH, after checking the decomposition by dilution with the appropriate volume of water.

Monovalent thallium was found to be a very suitable reagent for the rapid potentiometric titration of KMnO$_4$, the errors amounting only to ±0.1–0.2%. It was prepared from the B.D.H. product by dissolving in twice distilled water and standardized by titration with permanganate.[7]

Results

The stability of potassium permanganate of concentrations varying from 4–20 mmolar, in 2–10 N NaOH was studied in presence of telluric acid.

TABLE I

NaOH concn.,(b) N KMnO$_4$ = 4.5 × 10^{-3} M	Initial rate × 10^3 0–2 hr.	Final rate × 10^3 3–5 hr.	Av. rate, r × 10^3
4	0.100	0.117	0.110
5	.225	.273	.254
7	.240	.340	.300
8	.370	.390	.386
10	.455	.490	.476
KMnO$_4$ concn. (c), M NaOH = 4 N			
16.85 × 10^{-3}	0.035	0.04	0.038
14.79 × 10^{-3}	.033	.05	.045
11.16 × 10^{-3}	.047	.067	.057
7.50 × 10^{-3}	.075	.117	.100
3.50 × 10^{-3}	.235	.250	.245

The results obtained are listed in Table I and shown graphically in Figs. 1 and 2.

From these results it is apparent that the rate of decomposition is greatly inhibited by the introduction of telluric acid. A solution 0.02 M with respect to KMnO$_4$ is quite stable in 4 N NaOH for a period of 4 hours, whereas it undergoes considerable decomposition in absence of telluric acid. However, despite the lower rate of decomposition observed, the behavior is much the same in absence of telluric acid. The rate of decomposition increases with rise of alkalinity and with decrement of permanganate concentration.

These results can be made use of in determining the order of the reaction. Thus by plotting the logarithm of the average rate of decomposition r against the logarithm of the reciprocal of the permanganate concentration c at three different alkalinities, *viz.*, 4, 5 and 7 N NaOH, curves A, B and C,

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(1) H. Stamm, "Newer Methods of Volumetric Analysis," Trans. by Oesper, D. Van Nostrand Co., New York, N. Y., 1938, p. 55.

(2) F. R. Duke, THIS JOURNAL, **70**, 3975 (1948).

(3) A. Y. Drummond and W. A. Waters, *J. Chem. Soc.*, 435 (1953).

(4) M. C. R. Symons, *ibid.*, 3956 (1953); 3676 (1954).

(5) I. M. Issa, *et al.*, *Anal. Chim. Acta*, **11**, 198 (1954); **11**, 518 (1954).

(6) O. Tomicek, O. Procke and V. Pavelka, *Collection Czech. Chem. Commun.*, **11**, 449 (1939).

(7) I. M. Issa and R. M. Issa, *The Analyst*, **79**, 771 (1954); *Anal. Chim. Acta*, in press.