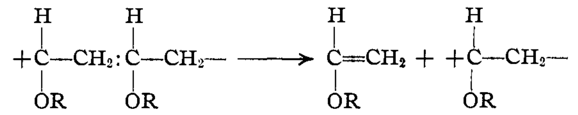
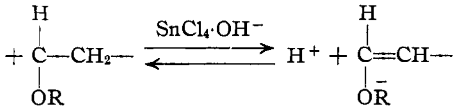


$$+\underset{OR}{\overset{H}{C}}-CH_2:\underset{OR}{\overset{H}{C}}-CH_2- \longrightarrow \underset{OR}{\overset{H}{C}}=CH_2 + +\underset{OR}{\overset{H}{C}}-CH_2-$$

etc.

Cessation:



$$+\underset{OR}{\overset{H}{C}}-CH_2- \underset{}{\overset{SnCl_4 \cdot OH^-}{\rightleftarrows}} H^+ + \underset{\overline{O}R}{\overset{H}{C}}=CH-$$

By this mechanism both monomer and low polymers are produced. The monomer which is known to be easily hydrolyzable can then split into alcohol and aldehyde. Thus, all products of degradation can be accounted for.

The stabilizer acts on the carbonium ion in exactly the same fashion as in the cessation of a polymerization chain. The alkyl ether carbonium ion should behave sterically in a similar fashion to styrene. It is not surprising, therefore, that secondary amines are better stabilizers than primary amines. Finally, since benzoyl peroxide and light catalyze the aging, it may be that a radical depolymerization occurs side by side with the carbonium ion chain.

Experimental

Nitrobenzene, carbon tetrachloride, styrene and the amines were purified as described in the preceding paper. α-Methylstyrene (Dow) was distilled under reduced pressure through an all-glass apparatus, b. p. 43° (2 mm.).

Polymerizations were carried out as described in the preceding paper, bromine addition being used to determine both residual styrene and α-methylstyrene.

Tetraethylammonium chloride was prepared as follows: Commercial triethylamine was purified by double distillation. It was refluxed in benzene with an equimolar amount of ethyl iodide for a period of thirty minutes. The mixture was then cooled and filtered. The solid was washed with benzene and ether, then dried in vacuum.

$N(C_2H_5)_4I$ was dissolved in water and shaken for one-half an hour with a slight excess of silver chloride. After filtering, the filtrate was distilled to dryness in vacuum. The solid residue was recrystallized twice from ethyl acetate to which a few drops of alcohol had been added, then filtered and dried in vacuum. The amount of chlorine was determined by dissolving part of the sample in water and titrating against standardized mercuric nitrate using *s*-diphenylcarbazone as an indicator; Cl found, 21.05; Cl calcd. 21.40.

The quaternary chloride does not melt but, rather, decomposes slowly on heating.

Summary

1. Tin tetrachloride dibutylamine complex inhibits Friedel–Crafts polymerization as much as the amine itself.

2. Chloride ion inhibits the polymerization of styrene, thus adding weight to the proposed mechanism of polymerization of Polanyi and coworkers. Chloride ions, however, are not responsible for inhibition by tin tetrachloride–amine complexes.

3. The inhibiting efficiency of amines toward α-methylstyrene has been found to differ from styrene and to follow the order $C_4H_9NH_2 < (CH_3)_2NC_6H_5 < (C_4H_9)_3N < (C_4H_9)_2NH$. This order is explained in accordance with the general mechanism of inhibition.

4. An explanation is offered for the relative efficiency of stabilizers in the aging of polyalkyl vinyl ethers by assuming a carbonium-ion mechanism of degradation.

BROOKLYN 2, N. Y. RECEIVED OCTOBER 7, 1949

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, OAK RIDGE NATIONAL LABORATORY]

Hydrolytic Behavior of Metal Ions. I. The Acid Constants of Uranium(IV) and Plutonium(IV)[1]

BY KURT A. KRAUS AND FREDERICK NELSON

In the course of a study of the hydrolytic behavior of metal ions the existence of the species U^{+4} was confirmed and the equilibrium constants (acid constants) for the reaction

$$M^{+4} + 2H_2O \rightleftarrows MOH^{+3} + H_3O^+ \qquad (1)$$

for uranium(IV) and plutonium(IV) were determined. In addition to reaction (1) which was found to be practically instantaneous, slow hydrolytic reactions were also observed. These are probably due to aggregation of hydrolysis products. The aggregates, which will be called "polymers," reach colloidal size, their composition approaches that of the hydroxide, and they greatly affect the chemistry of uranium(IV) and plutonium(IV) systems.[2,3,4] They will be considered in some detail in later papers. The oxygenated species MO^{++} ($M(OH)_2^{++}$) were not observed.

Experimental

Uranium(IV) stock solutions were prepared by reduction of uranium(VI) chloride or perchlorate solutions with known amounts of zinc or by electrolytic reduction. The uranium(IV) concentration and completeness of reduc-

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(1) This document is based on work performed under Contract No. W-7405 eng 26 for the Atomic Energy Commission at Oak Ridge National Laboratory. Part of this work has previously been published in the project reports CN-2289 (November, 1944), MonN-370 (September 1947), CNL-37 (April 1948) and AECD-1888 (April 1948). Part of the material was included in a paper presented at the meeting of the American Chemical Society on April 21, 1948.

(2) K. A. Kraus, F. Nelson and G. L. Johnson, THIS JOURNAL, **71**, 2510 (1949).

(3) K. A. Kraus and F. Nelson, *ibid.*, **71**, 2517 (1949).

(4) For a summary of some observations on polymeric plutonium(IV) see K. A. Kraus, National Nuclear Energy Series (NNES) Division IV, Vol. 14B 3.16, McGraw-Hill Book Co., Inc., New York, 1949; (b) K. A. Kraus and F. Nelson, Report AECD-1888 (April, 1948).

tion was determined by cerate oxidimetry. A few stock solutions were prepared by dissolving uranium tetrachloride in oxygen-free acids of known strength. These were also polarographically analyzed for uranium(VI). The uranium(VI) solutions were prepared from spectroscopically pure[5] uranyl nitrate hexahydrate, using several ammonia precipitations to remove nitrate.

Plutonium(IV) chloride solutions were prepared by dissolving the freshly precipitated hydroxide in strong hydrochloric acid and heating to remove possible small concentrations of polymeric plutonium(IV). Since each oxidation state has a characteristic spectrum, purity of the solutions was checked spectrophotometrically using a Beckman Model DU quartz spectrophotometer. Standard radiochemical techniques were used to determine the concentration of plutonium (Pu^{239} α-emitter, $t_{1/2} = 24110$ y[6]).

Aliquots of the stock solutions were diluted with potassium chloride, sodium chloride or sodium perchlorate of known ionic strength and acidity. These were analyzed spectrophotometrically. Readings were started less than one minute after mixing to permit extrapolation to zero time (time of mixing). The acidity of the solution was measured with a vibrating reed electrometer assembly[3,7] using a glass-calomel (satd. KCl) electrode system standardized with solutions of known acidity. The method used in confirming the species U^{+4} will be described below.

Measurements were carried out in a thermostated room at 25 ± 1°. The temperature of most solutions was maintained at 25 ± 0.2°. The experiments with uranium were carried out under nitrogen (purified over copper shavings at 500°).

Results and Discussion

Acidity of UCl_4 Solutions—Identification of the Species U^{+4}.—Although many data[8] suggested that the species of uranium(IV) in acid solutions is $U^{+4}(U(H_2O)_n{}^{+4}$ where $n = 6$ or 8 is most probable[9]) the existence of this ion was still controversial. Thus, the invariance of the potential of the uranium (III)/(IV) couple with acidity[10,11] can be interpreted either by assuming that both uranium(III) and uranium(IV) are hydrolyzed to the same extent[10,11] or by assuming that both species are the non-hydrolyzed U^{+3} and U^{+4}. Conclusions from the potentials of the uranium (IV)/(VI) couple as a function of acidity are somewhat more decisive, since the species $UO_2{}^{++}$ for U(VI) is reasonably well established. The potentials of this couple in chloride and perchlorate solutions between pH 1 and 3 are consistent with the assumption of the species U^{+4}, UOH^{+3} and $UO_2{}^{++}$ and of equilibrium (1).[3,12]

The existence of the species U^{+4} was confirmed through measurement of the amount of acid liberated on dissolving samples of anhydrous uranium tetrachloride. This salt was contained in small glass capsules (filled under nitrogen) which were broken in acids of known strength. From the ensuing potential change (ΔV) of the glass-electrode assembly the change in acid concentration was calculated by the approximate equation

$$\Delta V = S \log (m_2/m_1) \qquad (2)$$

where m_1 and m_2 are the initial and final molarities of acid, respectively, and where S is ideally 0.05915 v. at 25°. This equation applies only if the changes in liquid junction potentials and activity coefficients are negligible, which was assumed since m_2/m_1 was close to unity and μ (*ca.* 0.5) large compared with the final uranium concentration (*ca.* 10^{-3} *M*). The slope S was determined experimentally and found to be dependent on acidity and ionic strength, but at most a few per cent. less than the theoretical value.

It was found that less than 1 mole of acid was liberated per mole of uranium dissolved. The acid constants calculated from these experiments were in reasonable agreement with those determined spectrophotometrically. While the spectral data only permit conclusions regarding changes in species, the agreement with these "absolute" measurements establishes the existence of the species U^{+4}.

The Acid Constant of U^{+4}—Estimation of the Activity Constant.—The absorption spectrum of uranium(IV) in acid solution ($HClO_4$ and HCl) is characterized by a number of sharp bands in the visible region[13] as shown in Fig. 1. Most of this work was carried out in the region 600–700 mμ since the most prominent band is located near 648 mμ.

The spectrum is strongly dependent on the acidity of the solution and at low acidities also dependent on time. To separate the instantaneous reactions from the (slow) polymerization reactions the data were extrapolated to "zero time" (time of mixing) whenever necessary. The observed (extrapolated) extinction coefficients[14] at 648 mμ (E_0 (648)) decrease with decreasing acidity and a plot of E_0 (648) *vs.* log m_2 has the characteristic "*S*" shape of a simple hydrolytic reaction

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(5) We are indebted to Mr. C. Feldman of the Chemistry Division, Oak Ridge National Laboratory for the spectrographic analyses.

(6) J. W. Stout and W. M. Jones, *Phys. Rev.*, **71**, 582 (1947).

(7) K. A. Kraus, R. W. Holmberg and C. J. Borokowski, *Anal. Chem.*, **22**, 341 (1950).

(8) L. Brewer, L. A. Bromley, P. W. Gilles and N. L. Lofgren, Report BC-82 (April, 1947).

(9) Although extrapolations from crystal structure data to structure of ions in solutions are of questionable validity, a coördination number of 8 is preferred since Pu(IV) has this coördination number with respect to oxygen in the dioxide (W. H. Zachariasen, Report MDDC-67, June 1946).

(10) I. M. Kolthoff and W. E. Harris, THIS JOURNAL, **67**, 1484 (1945).

(11) H. G. Heal, *Trans. Far. Soc.*, **45**, 1 (1949).

(12) F. Nelson and K. A. Kraus, Report ORNL-286 (September, 1949).

(13) The sharpness of these bands is reminiscent of rare earth spectra. This characteristic supports the assumption that uranium (IV) contains two 5 f electrons, although the extinction coefficients of uranium(IV) as well as those of similar "actinides" are at least an order of magnitude larger than those of the rare earths. The other members of the isoelectronic sequence U(IV), Np(V), Pu(VI) also have similar sharp bands. In particular this series appears to have in common an infrared transition whose wave length decreases with increasing atomic number (U(IV), 1075 mμ; Np(V), 985 mμ; Pu(VI), 831 mμ). If less than two "f" electrons were present, rare earth-like spectra would not be expected, (see *e. g.*, S. Freed, *Phys. Rev.*, **38**, 2122 (1931), S. Freed and R. J. Mesirow, *J. Chem. Phys.*, **5**, 22 (1937), and J. H. van Vleck, *J. Phys. Chem.*, **41**, 67 (1937)) as corroborated by the absence of sharp absorption bands in uranium(V) and neptunium(VI) both of which could have only one "f" electron.

(14) The extinction coefficient (E) is defined by the equation $E = (\log I_0/I)/m$, where m is the molarity, l the cell length and I_0/I the ratio of intensity of incident to transmitted light.

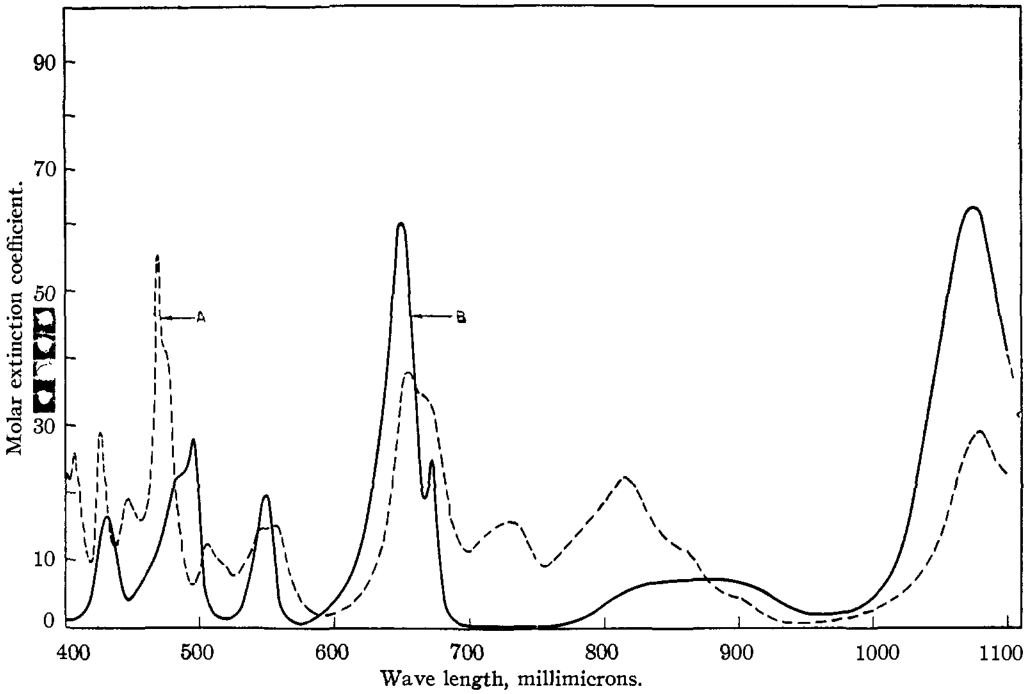

Fig. 1.—Absorption spectra of U^{+4} and Pu^{+4}: A: U^{+4}: 1 *M* $HClO_4$-1 *M* $NaClO_4$, 8.86 × 10^{-4} *M* U(IV), corrected for hydrolysis, 10 cm. cell. B: Pu^{+4}: 0.50 *M* $HClO_4$-0.015 *M* HCl, 7.3 × 10^{-4} *M* Pu(IV), corrected for hydrolysis assuming negligible absorption of the hydrolysis product, 10-cm. cell.

(see Fig. 2). At high acidity (above *ca.* 1 *M*) the observed extinction coefficients (E_0) approach asymptotically that of U^{+4} (E_1) and at low acidity that of the hydrolysis product (E_2 of UOH^{+3}).

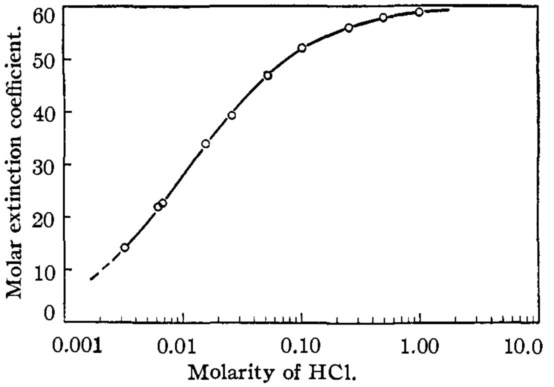

Fig. 2.—Change of extinction coefficient maximum with acidity.

The probable spectrum of UOH^{+3}, calculated from low acidity data and the acid constant, is shown in Fig. 3.

In the pertinent concentration range (using minimal slit-widths) the absorption bands of U^{+4} obey Beer's law. Since the bands of UOH^{+3} probably also obey this law, it may be assumed that the observed extinction coefficients (E_0) are a linear function of the concentrations of U^{+4} and UOH^{+3}, *i. e.*

$$E_0 = E_1M_1/M_t + E_2M_2/M_t \quad (3)$$

where E_1 and E_2 are the extinction coefficients of the species X^{+4} and UOH^{+3}, M_1 and M_2 their respective molarities and M_t the total concentration of uranium (IV). If E_1 and E_2 are known and assuming $M_1 + M_2 = M_t$ the acid constant (molarity constant) K_m can be calculated from the equation

$$K_m = [H_3O^+][XOH^{+3}]/[X^{+4}] = m_2(E_1 - E_0)/(E_0 - E_2) \quad (4)$$

where brackets indicate molar concentration and m_2 the final acidity of the solution. Actually E_1, E_2 and K_m were obtained by trial and error, using first preliminary values of K_m and the data at high and low acidities.

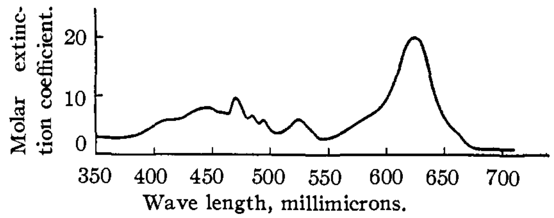

Fig. 3.—Absorption spectrum of $U(OH)^{+3}$, 8.86 × 10^{-4} *M* U(IV), 2 *M* ClO_4^-, calculated from spectrum in 8.2 × 10^{-3} *M* $HClO_4$.

The results of the experiments are summarized in Table I. It was found that at constant μ, K_m adequately describes the data over a considerable hydrolysis range and that it is practically independent of uranium(IV) concentration, thus confirming the assumed hydrolysis reaction (1).

TABLE Ia

ACID CONSTANT OF URANIUM(IV) IN PERCHLORATE SOLUTIONS

$\mu = 0.519$, 8.868×10^{-4} *M* U(IV), temperature 25 ± 0.2°.

Final H_3O^+	$E_0(648)$	$\%UOH^{+3}$	$K_m \times 10^2$
0.0096	17.1	79.9	(3.73)
.0204	27.0	61.4	3.24
.0323	32.8	50.6	3.33
.0680	43.1	31.5	3.12
.128	49.5	19.5	3.10
.250	54.0	11.2	3.16

TABLE Ib

ACID CONSTANT OF URANIUM(IV) IN PERCHLORATE AND CHLORIDE SOLUTIONS

μ	*M*U(IV) $\times 10^3$	Acidity range(*M*)	$\%UOH^{+3}$ range	$K_m \times 10^2$	No. expts.	σ[a]
			Perchlorate solutions			
2.004	0.886	0.0082–0.105	19.5–73.6	2.36	5	0.09
1.014	.886	.032 – .056	33.5–46.0	2.78	2	(.05)[b]
0.503	.183	.0107– .304	7.2–76.0	2.9	6	.33
.520	.725	.0143– .305	8.8–68.4	3.12	6	.09
.519	.886	.0204– .250	11.2–61.4	3.19	5	.09
.55	3.55	.025 – .240	12.1–61.4	3.55	7	.33
.272	0.886	.0146– .131	23.3–75.7	4.33	5	.19
.116	1.228	.0555– .105	33.4–47.8	5.17	2	(.09)
.115	1.222	.0190	75.5	5.85	1	....
.112	0.662	.0110– .0900	40.8–84.6	6.03	5	.14
.108	.616	.0160	76.8	5.30	1	....
.0634	.890	.0469	61.0	7.2	1	....
.0452	.890	.0288	73.6	7.9	1	....
.0349	.890	.019	84.6	10	1	....
.0328	.616	.0285	75.0	8.6	1	....
.0173	.616	.0134	89.9	12	1	....
			Chloride solutions			
2.004	1.00	0.0032–0.253	5.7–84.1	1.53	8	0.08
1.014	0.948	.0065– .250	7.3–76.1	1.88	7	.11
0.67	9.23	.0535– .130	17.0–32.0	2.59	2	(.07)
.519	0.932	.0064– .0550	31.4–81.9	2.62	4	.17
.529	1.34	.0181– .109	17.4–57.7	2.33	4	.11
.506	0.679	.0057– .201	11.6–80.6	2.57	6	.15
.272	.932	.0113– .0561	36.5–73.9	3.25	4	.06
.123	.932	.0165– .104	26.8–74.0	4.38	4	.29
.115	1.225	.0160– .106	32.2–72.5	4.44	7	.29
.108	1.222	.0431	51.4	4.56	1	....
.0654	1.228	.055	52.5	6.1	1	....
.0449	1.228	.0352	65.8	6.8	1	....
.0395	1.222	.0305	72.1	7.9	1	....
.0345	1.228	.0253	74.8	7.5	1	....
.0327	0.616	.0282	72.2	7.3	1	....
.0250	1.228	.0163	85.4	9.6	1	....
.0235	0.616	.0155	86.3	9.8	1	....

[a] The standard deviation σ was calculated with the equation $\sigma = \sqrt{\Sigma(x - \bar{x})^2/n}$ where x is the observed value, $\bar{x}$ arithmetic mean and n the number of observations. [b] Values in parentheses indicate deviations from the mean.

From the ionic strength dependence of K_m an attempt was made to evaluate the activity constant K_a which is given by the equation

$$K_a = K_m \gamma_{H_3O^+} \gamma_{UOH^{+3}}/\gamma_{U^{+4}} \quad (5)$$

where γ is the activity coefficient of the ion indicated as subscript. Assuming that the activity coefficients follow a Debye–Hückel limiting law of the form

$$\log \gamma_i = -0.509 Z_i^2 \frac{\mu^{1/2}}{1 + 0.3286 \mathring{a}_i \mu^{1/2}} \quad (6)$$

(where Z_i is the charge of the ion and $\mathring{a}_i$ the "mean distance of approach"[15,16,17] and assuming that an average value $\mathring{a}$ can be used instead of the different values $\mathring{a}_i$, equation (5) yields

$$\log K_a = \log K_m - 0.509 \Delta(Z_i^2) \frac{\mu^{1/2}}{1 + 0.3286 \mathring{a} \mu^{1/2}} \quad (7)$$

where $\Delta(Z_i^2) = -6$.

Using $\mathring{a} = 7.5$ Å., the perchlorate data can be fitted to equation (7) within the rather wide limits of experimental error (*ca.* ±10%) up to $\mu = 2$. The agreement is illustrated in Fig. 4 where log K_m has been plotted as a function of $\mu^{1/2}/(1 + 2.465\,\mu^{1/2})$. The solid line is drawn with the theoretical slope $-6 \times 0.509 = -3.054$. By extrapolation to $\mu = 0$, $K_a = 0.21 \pm 0.02$ is found.

The choice of $\mathring{a} = 7.5$ Å. appears reasonable since even for 2-1 electrolytes (*i. e.*, for electrolytes of considerable lower valence type than occur here) values of $\mathring{a} = 6$ Å. have been used.[15] Furthermore, it was found that $\mathring{a} = 7.5$ Å. permits a reasonable fit of the activity coefficients for 3-1 electrolytes at low molarity.

The activity coefficient ratios $\gamma_{UOH^{+3}}/\gamma_{U^{+4}}$ and $\gamma_{UOHX_3}/\gamma_{UX_4}$ (where X denotes ClO_4^- or other non-complexing anions) were calculated assuming $\gamma_{H_3O^+} = \gamma_{\pm HCl}$ and $\gamma_{\pm HCl} = \gamma_{\pm HClO_4}$, respectively, and using the values $\gamma_{\pm HCl}$ given by Harned and Hamer[18] for 0.01 *M* HCl solutions in

TABLE II

ACTIVITY COEFFICIENTS IN THE U^{+4}–UOH^{+3} SYSTEM

μ	$\frac{\gamma_{H_3O^+}\gamma_{UOH^{+3}}}{\gamma_{U^{+4}}}$[a]	$\gamma_{\pm HCl}$[b]	$\gamma_{UOH^{+3}}/\gamma_{U^{+4}}$[c]	$\gamma^4_{UOHX_3}/\gamma^5_{UX_4}$[d]	$\gamma_{\pm UOHX_3}$[e]	$\gamma_{\pm UX_4}$[f]
0.01	1.76	0.904	1.94	2.15	0.75	0.68
.02	2.09	.873	2.39	2.74	.69	.61
.04	2.56	.836	3.07	3.67	.63	.53
.06	2.93	.815	3.59	4.41	.58	.48
.10	3.49	.790	4.42	5.60	.54	.43
.20	4.46	.752	5.93	7.90	.47	.36
.50	6.13	.706	8.67	12.30	.40	.29
1.00	7.61	.719	10.58	14.73	.36	.26

[a] Calculated using equation (7). [b] From Harned and Hamer, ref. 18. $\gamma_{\pm HCl} = \gamma_{\pm HClO_4}$ is assumed. [c] Calculated from column (2) assuming $\gamma_{H_3O^+} = \gamma_{\pm HCl}$. [d] Calculated from column (2) by diving by $\gamma_{\pm HCl}$. "X" indicates a non-complexing negative ion, particularly ClO_4^-. [e] Calculated from $\log \gamma_\pm = -0.509\, Z_iZ_j \frac{\mu^{1/2}}{1 + 0.3286\, \mathring{a}\, \mu^{1/2}}$ using $\mathring{a} = 7.5$. [f] Calculated from columns (5) and (6).

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(15) R. A. Robinson and H. S. Harned, *Chem. Rev.*, **28**, 419 (1941).

(16) Equation (6) differs from the Debye limiting law in that γ_i has been substituted for f_i, the activity coefficient on a mole fraction basis (see ref. (15)), and Z_i^2 for Z_iZ_j, the product of the charges of the positive and negative ions. In view of the limited precision of the data no distinction will be made between f_i, γ_i and y_i, the activity coefficients on a mole fraction, molality and molarity basis since the error introduced is small (less than 10% even at an ionic strength of 2). For the relationship between $f_i \gamma_i$ and y_i, see ref. (15).

(17) For values of the constants in equation (6) see G. G. Manov, *et al.*, THIS JOURNAL, **65**, 1765 (1943).

(18) H. S. Harned and W. J. Hamer, *ibid.*, **55**, 2194 (1933).

KCl. These values are given in Table II together with estimates of $\gamma_{\pm \text{UX}_4}$ which were obtained from $\gamma_{\text{UOHX}_3}/\gamma_{\text{UX}_4}$ by estimating γ_{UOHX_3}. This was done with the Debye limiting law since $UOHX_3$ can be considered a 3–1 electrolyte and since the activity coefficients of most 3–1 electrolytes differ only by a few per cent. for values of $\mu = 1$ and appear to obey this law for $\mathring{a} = 7.5$.

Estimate of the Stability Constant of the Uranium(IV)—Chloride Complex.—The values of K_m for chloride solutions are generally lower than for perchlorate solutions, which is probably due to chloride complexing of uranium(IV) according to the equation

$$U^{+4} + Cl^- \rightleftarrows UCl^{+3} \qquad (8)$$

To evaluate the stability constant K_c for this reaction (K_c^0 at $\mu = 0$) it was assumed that equation (7) with $\Delta(Z_i^2)^* = -8$ is applicable. Through trial and error $K_c^0 = 7.0$ was found to bring the acid constants for chloride solutions in line with those for perchlorate solutions (see Fig. 4). From the precision of the data it is questionable that this value of K_c^0 is better than ±30%. Complexing in 2 M Cl^- can be estimated to be *ca.* 42%. It is surprising that this large amount of complexing hardly affects the absorption spectrum.

Assignment of the Species Pu^{+4}.[19]—The evidence for the assignment of the formula Pu^{+4} ($Pu(H_2O)_n{}^{+4}$)[9] for plutonium(IV) is similar to that for uranium(IV). Thus the potential of the plutonium(III)/(IV) couple was found to be practically independent of acidity[20] (from 0.2–1 M H_3O^+) and the acid dependence of the plutonium(IV)/(VI) couple is in fairly close agreement with the assignment of the species Pu^{+4} and $PuO_2{}^{++}$.[4a] In addition, Pu(III) was found to hydrolyze near pH 7 as predicted by analogy with the rare earths.[4b,21] Since during this hydrolysis more than two hydroxide ions are picked up, the assignment Pu^{+3} for acid solutions can be made with fair certainty and hence the assignment Pu^{+4}.

The Acid Constant of Pu^{+4}.—The method and calculations for the evaluation of the acid constant K_m (molarity constant) of Pu^{+4} were very similar to those used for uranium(IV). However, plutonium(IV) polymerizes more readily than uranium(IV) and undergoes disproportionation into plutonium(III) and plutonium(VI) (with rate increasing with decreasing acidity). Thus extrapolation of the data to "zero-time" is considerably more difficult, particularly under conditions where more than *ca.* 50% of the Pu^{+4} are hydrolyzed.

The absorption spectrum of unhydrolyzed Pu^{+4} is shown as curve B in Fig. 1. The striking similarity of the absorption curves for U^{+4} and Pu^{+4} is of interest, particularly since it extends to a number of details and confirms the assumption that these elements are members of a "second rare earth series." The similarity is so great as to suggest that Pu^{+4} only has two 5 f electrons instead of the expected four.

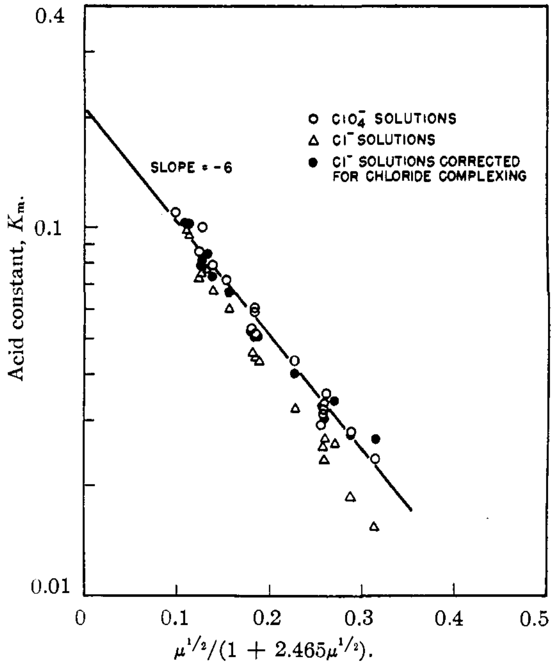

Fig. 4.—Estimation of acid (activity) constant of U(IV).

The prominent absorption band located near 470 mμ was chosen ($E_1(470) = 55$) for analysis. Deviations of this maximum from Beer's law are negligible in the concentration range of interest if the slit width used is small (*ca.* 0.04 mm.). There is no indication for an absorption maximum of the hydrolysis product in the wave length range studied (*ca.* 450–500 mμ) although absorption due to it is by no means negligible ($E_2(470) = ca.\ 17$).

The results of two series of experiments for perchlorate and chloride solutions are summarized in Table III. At $\mu = 0.5$, $K_m = 0.025$ was found for perchlorate solutions and $K_m = 0.022$

TABLE III

ACID CONSTANT OF PLUTONIUM(IV) IN PERCHLORATE AND CHLORIDE SOLUTIONS

Ionic strength $\mu = 0.5$, 7.2×10^{-4} M Pu(IV)

Perchlorate				Chloride			
Final $[H_3O^+]$	E_0 (470)	%Pu-$(OH)^{+3}$	$K \times 10^2$	Final $[H_3O^+]$	E_0 (470)	%Pu-$(OH)^{+3}$	$K \times 10^2$
0.011	25.8	76.8	(3.64)	0.011	25.3	78.0	(3.9)
.021	33.4	56.8	2.76	.031	38.9	42.3	2.27
.031	38.0	44.5	2.49	.051	43.4	30.3	2.22
.051	42.7	32.2	2.42	.091	47.3	20.2	2.30
.091	46.9	21.2	2.45	.131	49.8	13.6	2.06
.131	48.8	16.1	2.51	.500	53.3	4.5	2.35
.211	51.3	9.6	2.24			Av.	2.24
.500	53.2	4.7	2.47				
		Av.	2.49				

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[19] For a more detailed discussion regarding the evidence for this assignment see ref. 4a.

[20] J. C. Hindman, Report CN-2289 (November 1944).

[21] K. A. Kraus and J. R. Dam, National Nuclear Energy Series, IV, 14B no. 4.14, McGraw-Hill Book Co., Inc., New York, N. Y., 1949.

for chloride solutions. K_m was found to be independent of Pu(IV) concentration in the range 3.6 × 10^{-4} to 2.9 × 10^{-3} *M* Pu(IV). Since K_m is smaller for chloride solutions than for perchlorate solutions, weak chloride complexing of Pu^{+4} is indicated. However, the precision of the experiments is not sufficient to warrant calculation of a stability constant.

A persistence of properties with changing atomic number would be expected for a "rare-earth-like" series (actinide, thoride or uranide) of the same oxidation number. The qualitative and quantitative similarity in the hydrolytic properties thus supports the assumption that uranium and plutonium are members of such a series. The similarity of the absorption spectra with each other and with the rare earths (see footnote 13) is further confirmation as is the weakness of the chloride complexes of these elements (strong chloride complexes would be expected if they were transition elements).

Uranium(IV) ($K_m = 0.032$, $\mu = 0.5$) is slightly more acidic than plutonium(IV) ($K_m = 0.025$, $\mu = 0.5$). This difference is barely outside the experimental error but appears to be significant. On the basis of simple "coulombic arguments" the reverse would be expected, since uranium(IV) is larger than plutonium(IV) as indicated by the metal-oxygen distances of the dioxides (U-O, 2.363 Å.; Pu-O, 2.332 Å.[22]). A similar but considerably more pronounced anomalous trend was found for the MO_2^+ and MO_2^{++} ions.[23] In the case of the M^{+4} ions, however, this trend is too small to provide an adequate basis for extensive interpretation.

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Summary

1. Through *p*H measurements of UCl_4 solutions, U^{+4} was established to be the species of uranium(IV) *in* acidic solutions.

2. The acid constant of U^{+4} was determined as a function of ionic strength for chloride and perchlorate solutions through a spectrophotometric method. The molarity constants could be fitted approximately to a Debye-Hückel limiting law and the activity constant $K_a = 0.21 \pm 0.02$ was estimated for the equilibrium $U^{+4} + 2H_2O \rightleftarrows UOH^{+3} + H_3O^+$.

3. The stability constant for the reaction $U^{+4} + Cl^- \rightleftarrows UCl^{+3}$ was estimated to be K_c = *ca.* 0.63 ($\mu = 0.5$) and $K_c^0 = 7.0$ ($\mu = 0$).

4. The acid constant of Pu^{+4} ($K_m = 0.025$, $\mu = 0.5$) was found to be almost identical with though slightly smaller than that of U^{+4} ($K_m = 0.032$, $\mu = 0.5$).

5. The spectral data, the quantitative hydrolytic data and the observation that the chloride complexes of uranium(IV) and plutonium(IV) are weak, are confirmatory evidence of the hypothesis that these elements are members of a "rare-earth-like" series.

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[22] W. H. Zachariasen, Report MDDC-67 (June 1946).

[23] K. A. Kraus and F. Nelson, Report AECD-1864 (March 1948).

[CONTRIBUTION FROM RESEARCH LABORATORY, UNITED STATES STEEL CORPORATION OF DELAWARE]

The Composition of $CaO-FeO-Fe_2O_3$ and $MnO-FeO-Fe_2O_3$ Melts at Several Oxygen Pressures in the Vicinity of 1600°

BY R. W. GURRY AND L. S. DARKEN

As a step in the extension of the work on the iron-oxygen system[1,2] to steel-making slags it was thought desirable to investigate near 1600° the several ternary systems formed by the addition to iron oxides of each of the other important elements to be found in such slags. The investigations of Chipman and co-workers[3,4] on the activity of FeO in slags of the system $CaO(MgO)-SiO_2-FeO$ furnish a basis for our knowledge of slags in equilibrium with liquid iron, that is, at partial pressures of oxygen in the vicinity of 10^{-8} atmospheres at 1600°. This paper reports the results of some determinations of the composition of the liquid oxides in the systems Ca-Fe-O and Mn-Fe-O in the vicinity of 1600° at oxygen pressures up to one atmosphere. Similar data from the literature on the system Si-Fe-O have been included and tentative phase diagrams at 1600° for all three systems have been constructed. Some of the data here reported were accumulated several years ago when it was intended to make a more complete investigation; some are the recent by-product of another investigation. This partial report based on such fragmentary data is made now, since the more complete investigation is no longer planned for the immediate future.

The experimental technique including the method of analysis was substantially that reported in our earlier investigations. The vertically mounted tubular globar furnace was used

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[1] Darken and Gurry, THIS JOURNAL, **67**, 1398 (1945).

[2] Darken and Gurry, *ibid.*, **68**, 798 (1946).

[3] Fetters and Chipman, *Trans. Am. Inst. Min. Met. Eng.*, **145**, 95 (1941).

[4] Taylor and Chipman, *ibid.*, **154**, 228 (1943).