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CHEMISTRY OF AQUEOUS URANIUM (V) SOLUTIONS.

III. THE URANIUM (IV)-(V)-(VI) EQUILIBRIUM IN PERCHLORATE AND CHLORIDE SOLUTIONS

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CHEMISTRY OF AQUEOUS URANIUM (V) SOLUTIONS.

III. The Uranium (IV)-(V)-(VI) Equilibrium in Perchlorate and Chloride Solutions

F. Nelson and K. Kraus

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CHEMISTRY OF AQUEOUS URANIUM (V) SOLUTIONS

III. The Uranium (IV)-(V)-(VI) Equilibrium in Perchlorate and Chloride Solutions[1]

Frederick Nelson and Kurt A. Kraus

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(1) This document is based on work performed for the Atomic Energy Commission at the Oak Ridge National Laboratory.

In previous papers[2a,b] it was shown that uranium (IV), uranium (V) and

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(2) K. A. Kraus and F. Nelson, J. Am. Chem. Soc. (a) 71,2510(1949); (b) 71,2517(1949).

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uranium (VI) form equilibrium mixtures - at times metastable - according to the equation

$$2U(V) \rightleftharpoons U(IV) + U(VI) \qquad (1)$$

The corresponding equilibrium constant

$$\underline{K}'_{eq} = \frac{(U(IV))(U(VI))}{(U(V))^2} \qquad (2)$$

(parentheses indicate molar concentrations) is strongly pH dependent. At low acidities $\underline{K}'_{eq}$ is of the order of unity and preparation of equilibrium mixtures containing a large fraction of uranium (V) is feasible.

In the work here reported, equilibrium (1) was studied as a function of acidity and ionic strength μ, in perchlorate and chloride solutions. The equilibrium constant

$$\underline{K}_{eq} = \frac{(UO_2^{++})(U^{+4})}{(UO_2^{+})^2(H_3O^{+})^4} \qquad (3)$$

for the reaction

$$2UO_2^{+} + 4H_3O^{+} \rightleftharpoons UO_2^{++} + U^{+4} + 6H_2O \qquad (4)$$

was evaluated using estimates of the stability constants of the chloride complexes and the previously determined[3] values of the acid constant of U^{+4}

(3) K. A. Kraus and F. Nelson, Report ORNL-496 (October, 1949).

$$\underline{K}(\underline{IV})_a = \frac{(H_3O^+)(UOH^{+3})}{(U^{+4})} \tag{5}$$

for the reaction

$$U^{+4} + 2H_2O \rightleftharpoons UOH^{+3} + H_3O^+ \tag{6}$$

Through the use of a modified Debye-Hückel expression[3] it was possible to extrapolate the values of $\underline{K}_{eq}$ to $\mu = 0$ and to obtain the activity constant

$$\underline{K}^o_{eq} = \underline{K}_{eq} \frac{\gamma_{UO_2^{++}}\gamma_{U^{+4}}}{\gamma^2_{UO_2^+}\gamma^4_{H_3O^+}} \tag{7}$$

Experimental - Techniques and Materials

Equilibrium mixtures of uranium in the various oxidation states were prepared a) by mixing stock solutions of uranium (IV) and uranium (VI), b) by dissolving anhydrous uranium tetrachloride in uranium (VI) solutions, c) by dissolving anhydrous uranium pentachloride in the supporting electrolyte,[4] and d) by addition of acid to

(4) Uranium pentachloride reacts instantaneously with water to form equimolar amounts of uranium (IV) and uranium (VI) which then react to attain equilibrium.[2b]

uranium (V) solutions causing (limited) disproportionation into uranium (IV) and (VI). The uranium (V) solutions used in the last method were prepared by electrolytic reduction of uranium (VI) solutions of low acidity (ca. 10^{-3} $\underline{M}$ H_3O^+)[2a]. In the experiments with uranium pentachloride this salt was sometimes added to uranium (VI) solutions to vary the uranium (IV) - uranium (VI) ratio from unity. Preparation of solutions and purity of materials were discussed earlier.[2a,b][3] The experiments

were carried out in a thermostated room at 25 ± 1°C. The temperature of most solutions was maintained at 25.0 ± 0.2°C.

Analysis for the relative amounts of uranium in each oxidation state at equilibrium was carried out primarily polarographically and spectrophotometrically. The polarographic equipment and method of determining the concentrations in the various oxidation states from the diffusion currents of uranium (V) and (VI) were described earlier.[2a] Additional diffusion current data are given below. Spectrophotometric measurements were used to determine the concentration of uranium (IV). The equipment and "calibration" data are described elsewhere.[3] Acidity of the solutions was measured potentiometrically with a glass-calomel (saturated KCl) electrode assembly and the vibrating reed recorder for which performance data have been given.[5]

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(5) K. A. Kraus, R. W. Holmberg and C. J. Borkowski, Anal. Chem. 22,341 (1950).

General Discussion of Analytical Methods

To obtain the equilibrium constant K'_{eq} (equation 2) the concentrations of uranium in the various oxidation states at equilibrium must be obtained. This can be done from a knowledge of the initial concentrations and determination of the equilibrium concentration in one oxidation state. The determination of the equilibrium concentrations in more than one oxidation state thus usually affords a check on the precision of the method.

Polarography of uranium (VI) and uranium (V). The uranium (VI) and uranium (V) concentrations were usually determined polarographically. The diffusion current

constants K_6 of uranium (VI)[6] and the ratio $R = K_5/K_6$ of the diffusion current

(6) The diffusion current constant K (with subscript to indicate the oxidation state) is given by the Ilkovič equation $K = i_d/C\, m^{2/3} t^{1/6}$. For methods of measurement see ref. 2a.

constants of uranium (V) and (VI) were obtained as a function of ionic strength, acid concentration and uranium concentration and are summarized in Tables 1 and 2. Table 1 shows that for a given ionic strength K_6 is essentially constant in the acid range 0.001 to ca. 0.1 M and in the uranium (VI) concentration range 0.5×10^{-3} to 4.5×10^{-3} M. At acidities considerably above 0.1 M K_6 increases, probably because of appreciable disproportionation of uranium (V) during the life of a mercury drop as suggested by Harris and Kolthoff[7]. Below $\mu = 0.5$, K_6 is approxi-

(7) W. E. Harris and I. M. Kolthoff, J. Am. Chem. Soc. 67, 1484 (1945).

mately the same in chloride and perchlorate solutions and does not change appreciably with ionic strength[8]. An increase in diffusion current constants at low concen-

(8) It had previously been shown[2a] that the diffusion coefficients D_6 calculated from this and the earlier work are in agreement with those calculated by Harris and Kolthoff[7] for chloride solutions, but not with those of Kern and Orlemann (J. Am. Chem. Soc. 71, 2103 (1949)) for perchlorate solutions. Since our new measurements show little difference between chloride and perchlorate solutions, this disagreement thus persists. Kritchevsky and Hindman recently re-evaluated D_6 in perchlorate solutions (J. Am. Chem. Soc. 71, 2096 (1949)) and found agreement with the value of Kern and Orlemann. However, since they do not give the capillary constant on which the value of D_6 depends[2a] no further comparison can be made.

tration of supporting electrolyte ($\mu < 0.1$) was avoided by using proportionately lower concentrations of uranium, thus keeping the concentration of supporting electrolyte

Table 1

Diffusion Current Constants of Uranium (VI) in Potassium Chloride and Sodium Perchlorate Solutions
($25 \pm 0.2°C$, $m^{2/3}t^{1/6} = 2.465\ mg^{2/3}m^{-1/2}$ at -0.4 v. vs S.C.E.)

M Salt	M H_3O^+	M U(VI) x 10^3	K_6	K_6(S)
potassium chloride solutions				
0.011	.001	0.227	-	1.48
0.023	.001	0.454	-	1.52
0.055	.001	2.268	-	1.52
0.10	.001	1.982	1.52	1.52
0.10	.003	1.982	1.51	-
0.10	.003	0.855	1.51	-
0.10	.003	1.666	1.52	-
0.10	.002	2.268	1.53	1.52
0.10	.002	2.268	1.52(a)	1.52
0.10	.004	4.536	1.52	-
0.09	.01	1.666	1.52	1.51
0.09	.011	1.666	1.54	-
0.09	.34	1.815	1.58	-
0.09	.53	1.720	1.71	-
0.49	.003	1.666	1.53	-
0.49	.01	1.666	1.61(m)	1.53
0.50	.002	2.268	1.52	1.52
1.00	.001	2.268	1.54	-
1.00	.003	1.666	1.64(m)	1.55
0.99	.01	1.666	1.56	1.56
1.97	.003	2.268	1.58	1.57
3.51	.002	2.268	1.57	-
3.51	.002	2.268	1.61(a)	1.60
sodium perchlorate solutions				
0.025	.001	1.029	1.49	-
0.028	.002	0.515	1.47	-
0.055	.001	1.029	1.51	-
0.10	.005	2.454	1.53(a)	1.52
0.11	.002	2.058	1.52	1.52
0.25	.002	2.058	1.52	-
0.50	.002	2.058	1.52	-
1.00	.001	1.029	1.49	1.49
2.00	.001	1.029	1.46	1.46
3.73	.001	2.058	1.33	-
3.73	.005	2.058	1.33	-
8.3	.005	2.406	1.29(a)	1.29

(a) with a capillary for which $m^{2/3}t^{1/6} = 2.212\ mg^{2/3}sec^{-1/2}$ at -0.4 v. vs. S.C.E.

(S) 2×10^{-4}% thymol added as suppressor.

(m) pronounced maxima appeared.

Table 2

Ratio R of Diffusion Current Constants of Uranium (V) and Uranium (VI) in Chloride and Perchlorate Solutions

($T = 25 \pm 0.2^{\circ}C$; pH = 2-3; 1 to 5×10^{-3} MU; $m^{2/3}t^{1/6} = 2.465\ mg^{2/3}sec^{-1/2}$ at -0.4 v vs. S.C.E.)

M $NaClO_4$	R	M KCl	R
		0.026	1.03
0.08	1.02	0.097	1.01
0.11	1.04	0.10	1.02 ± .01 (a)
0.25	1.05		
0.31	1.05		
0.53	1.01	0.50	1.04 ± .03 (b)
1.02	1.04	1.00	1.02 ± .01 (c)
2.0	1.04 ± .02 (c)	2.00	0.98 ± .01 (c)
3.73	1.04 ± .02 (c)		

(a) data from ref. 2a. Average of 3 determinations with maximum deviation given.
(b) average of 6 determinations with standard deviation given.
(c) average of 2 determinations with maximum deviation given.

Table 3

Effect of Viscosity on Diffusion Current Constants

μ	sodium perchlorate solutions			potassium chloride solutions		
	K_6	η (a)	$K_6\eta^{1/2}$	K_6	η (b)	$K_6\eta^{1/2}$
0.25	1.52	1.02	1.53			
0.50	1.52	1.02	1.53	1.53	0.997	1.53
1.00	1.49	1.034	1.52	1.55	0.995	1.55
2.0	1.46	1.160	1.57	1.57	1.002	1.57
3.51				1.60	1.034	1.63
3.73	1.33	1.506	1.63			

(a) Viscosity data of sodium perchlorate solutions by J. H. Edgerton, Chemistry Division, Oak Ridge National Laboratory.
(b) Viscosity data of potassium chloride solutions from International Critical Tables, Vol. V, p. 17.

at least fifty times that of the uranium (VI).[9]

(9) I. M. Kolthoff and J. J. Lingane, "Polarography", Interscience Publishers, Inc., New York, New York, revised reprint, 1946 p. 83.

Above $\mu = 0.5$, K_6 decreases appreciably in perchlorate solutions and increases slightly in chloride solutions. The capillary constant ($m^{2/3}t^{1/6}$) was found to be independent of ionic strength (within ca. 1%) for sodium perchlorate solutions of ionic strength $\mu = 0.1$, 2.0, 3.8 and 8.4. At first glance the difference in K_6 for chloride and perchlorate solutions might be attributed to chloride complexing of uranium (VI). This interpretation, however, appears unlikely since the product $K_6\eta^{1/2}$ (where η is the viscosity of the solutions) is approximately the same for the two media at the same ionic strength as shown in Table 3.[10] It is of interest that the

(10) According to the Ilokvić equation K_6 is proportional to the square root of the diffusion coefficient. If Stokes' law holds the latter is proportional to the viscosity and hence one might expect $K_6\eta^{1/2}$ to be a constant.

observed increase of $K_6\eta^{1/2}$ is parallelled by similar increases of diffusion coefficients of some electrolytes and uncharged molecules.[11]

(11) See ref. 9 pp. 50 and 52.

The values of the ratios R of the diffusion current constants of uranium (V) and (VI) as a first approximation, appear to be only slightly larger than unity and the same for chloride and perchlorate solutions and independent of ionic strength (Table 2). The slight decrease of R in the concentrated chloride solutions is of questionable significance.

Spectrophotometry: For some solutions the concentration of uranium (IV) was determined by this method using the spectral data previously described.[3] Advantage was taken of the facts that U^{+4} and UOH^{+3} have the same extinction coefficient near 625 mμ, that they have equal and practically negligible extinction coefficients near 695 mμ and that uranium (V) and uranium (VI) have only negligible absorption in this wavelength range. The uranium (IV) concentration could thus readily be calculated from the difference of the observed extinction coefficients at 625 and 695 mμ. Use of differences in extinction coefficients rather than "absolute" extinction coefficients at one wavelength (e.g., 625 mμ) appears preferable since small variations in "background" absorption become less important.

Potentiometry: During the reaction of uranium (IV) with uranium (VI) as well as during disproportionation of uranium (V) to yield uranium (IV) and (VI) a change in acidity occurs which is principally determined by reactions (4) and (6). Thus knowing the initial concentrations in the various oxidation states, the change in acidity, and $\underline{K}(\underline{IV})_a$, the equilibrium constant $\underline{K}'_{eq}$ can be calculated. Although with the solutions used here the potential changes of a glass-electrode assembly usually were only a few millivolts, the values of $\underline{K}'_{eq}$ calculated by this method were in satisfactory agreement with those calculated by other methods.

Results and Discussion

Calculations: The equilibrium constant $\underline{K}'_{eq}$ represents a formal relationship between the concentrations of the various oxidation states irrespective of ionic species

present. It is thus dependent on the acidity of the solutions, on the concentration of complexing agents (chloride ions) as well as on the ionic strength.

The equilibrium constant $\underline{K}_{eq}$ (equation 2) can be calculated from $\underline{K}'_{eq}$ by evaluating the concentrations of the species UO_2^{++}, UO_2^{+} and U^{+4}. This may be done from the stoichiometric concentrations of uranium (IV), (V) and (VI) using the appropriate acid constants and chloride complex constants. Of the possible acid constants only that of uranium (IV) need be considered since uranium (V) and (VI) do not appreciably hydrolyze[2][12-14] at acidities where equilibrium measurements

(12) D. A. MacInnes and L. G. Longsworth Report A-360, Nat. Defense Res. Committee, Office of Sci. Res. and Dev. Nov. (1942).

(13) J. Sutton, J. National Res. Council of Canada No. 1612 Ontario (1947).

(14) S. Ahrland, Acta Chem. Scand. 3, 374(1949).

were made. Since uranium (V)($UO_2(H_2O)_n^{+}$) appears to have a structure similar to that of uranium (VI) ($UO_2(H_2O)_n^{++}$) but a smaller positive charge, and since furthermore uranium (VI) only forms a weak chloride complex, it appears reasonable to assume that uranium (V) is only negligibly complexed by chloride ions. Assuming also that uranium (IV) and (VI) form only the monochloride complexes UCl^{+3} and UO_2Cl^{+} at the chloride concentrations used, one can set

$$\left.\begin{aligned} (U(VI)) &= (UO_2^{++}) + (UO_2Cl^{+}) \\ (U(V)) &= (UO_2^{+}) \\ \text{and} \quad (U(IV)) &= (U^{+4}) + (UOH^{+3}) + (UCl^{+3}) \end{aligned}\right\} \qquad (8)$$

Using equations (2), (3), (5) and (8), letting

$$\underline{K}(\underline{IV})_c = \frac{(UCl^{+3})}{(U^{+4})(Cl^{-})} \qquad (9)$$

and

$$\underline{K}(\underline{VI})_c = \frac{(UO_2Cl^{+})}{(UO_2^{++})(Cl^{-})} \qquad (10)$$

and defining $\underline{c} = (Cl^-)$ and $\underline{h} = (H_3O^+)$ one obtains

$$\underline{K}_{eq} = \underline{K}'_{eq} \quad \frac{1}{\underline{h}^4(1 + \underline{c}\ \underline{K}(\underline{VI})_c)(1 + \underline{c}\ \underline{K}(\underline{IV})_c + \underline{K}(\underline{IV})_a/h)} \qquad (11)$$

For perchlorate solutions, where $\underline{c} = 0$, equation (11) simplifies to

$$\underline{K}_{eq} = \underline{K}'_{eq} \quad \frac{1}{\underline{h}^4(1 + \underline{K}(\underline{IV})_a/\underline{h})} \qquad (12)$$

The constants $\underline{K}(\underline{IV})_a$ and $\underline{K}(\underline{IV})_c$ were calculated as a function of ionic strength μ from the modified Debye-Hückel equation

$$\log \underline{K} = \log \underline{K}^o + 0.509\ \Delta(\underline{Z}_i^2) \quad \frac{\mu^{1/2}}{1 + 0.3286\ \mathring{a}\ \mu^{1/2}} \qquad (13)$$

where $\underline{K}$ and $\underline{K}^o$ represent the various molarity and activity constants, where $\mathring{a}$ is a parameter (distance of closets approach) and where $\Delta(\underline{Z}_i^2)$ represents the arithmetical sum of the squares of the charges of the ions involved in the equilibrium (with the product ions positive and the reagent ions negative). The following numerical values of the constants were found[3] earlier to be satisfactory:

for $\underline{K}(\underline{IV})_a$:$\underline{K}^o(\underline{IV})_a = 0.21$, $\Delta(\underline{Z}_i^2) = -6$ and $\mathring{a} = 7.5$ Å ;

for $\underline{K}(\underline{IV})_c$:$\underline{K}^o(\underline{IV})_c = 7.0$, $\Delta(Z_i^2) = -8$ and $\mathring{a} = 7.5$ Å.

The corresponding constants for $\underline{K}(\underline{VI})_c$ are evaluated below:

<u>Evaluation of the Activity Constant</u> - The results of the experiments are summarized in Tables 4a, b and c. The three methods (polarographic, spectrophotometric and potentiometric) apparently yield within the experimentsl error the same equilibrium constants $\underline{K}_{eq}$ (Table 4a) indicating that there are no systematic errors in the various experimental methods. The acid dependence of $\underline{K}'_{eq}$ at constant μ is as predicted from equations 4 and 11 (see Table 4b). This furnishes further proof that the assignment of the species U^{+4}, UOH^{+3}, UO_2^+ and UO_2^{++} and the value of the acid

Table 4

Uranium (IV)-(V)-(VI) Equilibrium Constants in Chloride and Perchlorate Solutions

(T = 25± 0.2°C)

A

Reproducibility of Methods

Solutions	$(H_3O^+) \times 10^3$ initial	final	Method	Equil. conc. $\times 10^4$ U(IV)	U(V)	U(VI)	K'_{eq}	$K_{eq} \times 10^{-7}$
1.477 x 10^{-3} M UCl_5	2.50	7.13	S	4.19	6.39	4.19	0.430	1.21
μ = 0.029 (Cl^-)			A	4.12	6.53	4.12	0.398	1.12
2.058 x 10^{-3} M U(VI)	0.77	5.52	P	2.91	9.04	23.5	0.835	10.6
1.485 x 10^{-3} M UCl_5			S	2.93	9.00	23.5	0.850	10.8
μ = 0.27 (ClO_4^-)			A	2.68	8.70	23.2	0.824*	10.4
1.372 x 10^{-3} M UCl_5	3.50	7.80	P	3.84	6.01	49.2	5.24	21.3
4.536 x 10^{-3} M U(VI)			A	3.78	6.16	49.0	4.91*	20.0
μ = 0.5 (Cl^-)								

B

Dependence on Acidity

$(H_3O^+) \times 10^3$	M U(IV) $\times 10^4$	M U(V) $\times 10^4$	M U(VI) $\times 10^4$	K'_{eq}	$K_{eq} \times 10^{-7}$	Method of Analysis	Method of Preparation
			μ = 0.10 - 0.11 (Cl^-) = ca. 0.105				
7.2	8.80	7.25	8.80	1.48	5.7	P	b
9.9	14.10	7.56	14.10	3.46	4.9	P	b
10.4	6.84	7.98	41.6	4.43	5.4	P	d
11.2	7.07	7.90	41.7	4.72	4.5	P	d
					(Ave=5.1)		
			μ = 0.49-0.51 (Cl^-)= ca. 0.50				
4.65	4.72	4.44	47.2	1.13	24.2	P	b
5.20	5.35	4.35	5.35	1.51	21.2	P	b
3.60	2.95	5.18	14.2	1.56	18.6	P	a
5.60	2.74	8.13	48.1	1.99	23.4	P	c
5.84	3.12	8.58	48.5	2.06	21.5	P	c
7.10	11.0	12.03	40.7	3.09	17.2	P	e
7.30	2.75	5.38	42.7	4.06	20.7	P	d
7.80	3.84	6.10	49.2	5.08	20.8	P	c
8.38	11.05	9.29	40.9	5.24	17.0	P	d
10.2	8.10	5.44	42.9	11.6	20.0	P	d
12.8	11.10	2.42	11.5	21.7	19.6	P	b
13.5	6.30	1.42	7.28	22.7	17.5	P	b
					(Ave=20.1)		

C

Ionic Strength Dependence

μ	(H_3O^+) x 10^3	(Cl^-)	M U(IV) x 10^3	M U(V) x 10^4	M U(VI) x 10^3	K'_{eq}	K_{eq}x10^{-7}	Method of Analysis	Method of Preparation
Chloride solutions (KCl-HCl)									
.0085	5.82	.0076	.231	5.57	0.231	0.772	0.68	S	b
.0131	8.83	.0114	.403	4.74	0.403	0.721	0.87	S	b
.0133	8.98	.0114	.403	4.78	0.403	0.711	0.82	S	b
.0260	7.75	.024	.417	11.9	2.571	0.757	1.54	P	c
.0297	7.13	.0299		See Table 3a			1.16	S,A	b
.0389	8.25	.0323	.495	15.74	4.952	0.990	1.90	S	c
.10-.11	7.2-11.2	.105		See Table 3b			5.10	P	
.49-.51	4.65-13.5	.50		See Table 3b			20.1	P	
.99	5.45	.99	.302	6.42	4.84	3.55	48.	P	c
1.97	3.87	1.97	.218	4.59	3.08	3.06	108.	P	c
1.97	6.00	1.97	.667	4.25	3.52	13.0	120.	P	c
Perchlorate solutions ($NaClO_4$-$HClO_4$)									
.115	5.00	.018	.241	8.44	2.60	0.33	4.4	P	c
.27	5.52	.018		See Table 3a			10.6	P,S,A	c
.53	6.49	.009	.484	8.17	2.54	1.84	17.1	P	c
1.02	4.36	.016	.264	7.26	2.30	1.15	41.0	P	c
1.97	4.15	.015	.255	5.32	2.32	2.09	118.	P	c
1.97	4.95	.015	.361	5.36	2.41	3.02	91.6	P	b

(a) Disproportionation of electrolytically prepared U(V) solution.
(b) Addition of UCl_5 (solid) to chloride or perchlorate solutions.
(c) Addition of UCl_5 (solid) to U(VI) chloride or perchlorate solutions.
(d) Addition of U(IV) solutions to U(VI) chloride or perchlorate solutions.
(e) Addition of UCl_4 (solid) to U(VI) chloride or perchlorate solutions.

(S) Spectrophotometric method.
(P) Polarographic method.
(A) Acid-charge method.

(*) In calculation considered small amount of hydrolysis of U(VI) in the initial solution using the value of $K(VI)_a = 6.0 \times 10^{-5}$ (μ = 0.1 Cl^-) given by MacInnes and Longsworth [12] for the reaction $UO_2^{++} + 2H_2O \rightleftharpoons UO_2OH^+ + H_3O^+$

constant $\underline{K}(\underline{IV})_a$ are correct. The ionic strength dependence of the equilibrium constant is given in Table 4c. It was found that $\underline{K}_{eq}$ increases by a factor of ca. 200 as the ionic strength increases from 0.0085 to 2.

In view of the fact that it was possible to represent the ionic strength dependence of $\underline{K}(\underline{IV})_a$ satisfactorily by the Debye-Hückel equation[3] (equation 13) the same equation was applied to the ionic strength dependence of $\underline{K}_{eq}$. For this equilibrium $\Delta(Z_i^2)$ is 14, and a plot of log $\underline{K}_{eq}$ vs. $\frac{\mu^{1/2}}{1+0.3286\,\mathring{a}\,\mu^{1/2}}$ should have a slope of 14 x 0.509 = 7.126. By trial and error it was found that, using $\mathring{a}$ = 6.0 Å, the data (particularly for perchlorate solutions) fell along a straight line of the theoretical slope and by extrapolation to μ = 0 the activity constant $\underline{K}^{o}_{eq} = (1.7\pm0.3)\times10^{6}$ was found. (See Figure 1).

The data for chloride solutions, corrected for chloride complexing of uranium (IV), tended to be higher than those for perchlorate solutions. From the deviations the stability constant of the uranium (VI) chloride complex was estimated. Assuming again that equation 13 is applicable, $\underline{K}(\underline{VI})^{o}_{c}$ = 2.4 was found using $\mathring{a}$ = 6.0 Å and $\Delta(Z_i)^2)$ = -4. In view of the limited precision of the data, the arbitrary limitation of the complexing reactions, and the large uncertainity in the value $\underline{K}(\underline{IV})_c$ on which $\underline{K}(\underline{VI})_c$ is directly dependent (eq. 11), this stability constant can only be considered a rough approximation, showing that uranium (VI) is only weakly complexed by chloride ions.

The agreement of the data with the Debye-Hückel expression (equation 13) is surprisingly good considering that $\Delta(Z_i^2)$ is extremely large, that the ionic strength range covered is large, that highly charged ions are involved, and only one parameter ($\mathring{a}$) is used. Furthermore, the numerical value of the parameter $\mathring{a}$ = 6.0 Å is quite reasonable if compared with those used to represent activity coefficients of simple

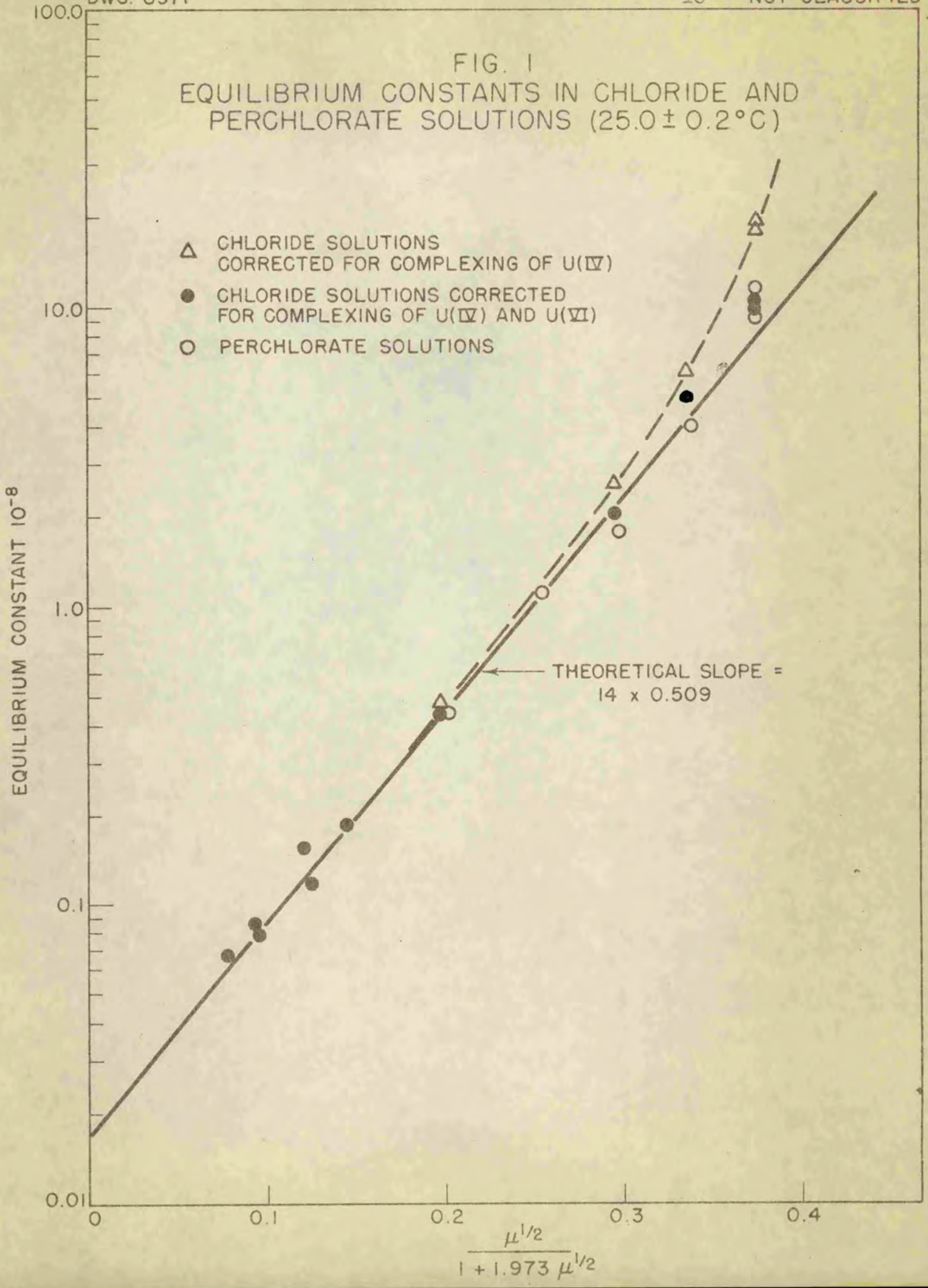
FIG. 1
EQUILIBRIUM CONSTANTS IN CHLORIDE AND PERCHLORATE SOLUTIONS (25.0 ± 0.2°C)
CHLORIDE SOLUTIONS CORRECTED FOR COMPLEXING OF U(IV)
CHLORIDE SOLUTIONS CORRECTED FOR COMPLEXING OF U(IV) AND U(VI)
PERCHLORATE SOLUTIONS
THEORETICAL SLOPE = 14 x 0.509
EQUILIBRIUM CONSTANT 10^-8
100.0
10.0
1.0
0.1
0.01
0
0.1
0.2
0.3
0.4
μ^1/2 / 1 + 1.973 μ^1/2

electrolytes and if compared with the parameter $\mathring{a} = 7.5\ \mathring{A}$ used to represent $\underline{K(IV)}_a$ where relatively more highly charged ions are involved. It thus appears that considerable confidence can be placed in the use of the Debye-Hückel expression (equation 13) for estimation of activity constants for equilibria involving highly charged ions.

Summary

(1) The equilibrium constant $\underline{K}_{eq}$ for the reaction

$$2UO_2^+ + 4H_3O^+ \rightleftharpoons UO_2^{++} + U^{+4} + 6H_2O$$

was obtained as a function of ionic strength for perchlorate and chloride solutions using polarographic, spectrophotometric and potentiometric methods.

(2) A modified Debye-Hückel expression was found to represent the data up to μ=ca.1.0 and the activity constant

$$\underline{K}^o_{eq} = \underline{K}_{eq} \frac{\gamma_{UO_2^{++}}\gamma_{U^{+4}}}{\gamma^2_{UO_2^+}\gamma^4_{H_3O^+}} = (1.7 \pm 0.3)\times 10^6$$

was evaluated.

(3) The stability constant of the uranyl chloride complex UO_2Cl^+

$$\underline{K}^o(\underline{VI})_c = \frac{(UO_2Cl^+)\ \gamma_{UO_2Cl^+}}{(UO_2^{++})(Cl^-)\ \gamma_{UO_2^{++}}\gamma_{Cl^-}} = 2.4$$

was estimated from a comparison of $\underline{K}_{eq}$ for chloride and perchlorate solutions.

(4) Some observations on the polarography of uranium (V) and uranium (VI) have been included. The diffusion current constants of uranium (VI) and the ratio of the diffusion current constants of uranium (V) and (VI) were evaluated as a function of ionic strength.