

On the $\text{UO}_2^{2+}/\text{U}^{4+}$ Redox Potential

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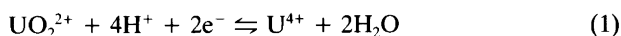
The redox potential (E°) of the couple $\text{UO}_2^{2+}/\text{U}^{4+}$ and the equilibrium constant (K°) for the reaction $\text{UO}_2^{2+} + 2\text{H}^+ + \text{H}_2(\text{g}) \rightleftharpoons \text{U}^{4+} + 2\text{H}_2\text{O}$ have been determined at 25 and 45 °C in various (H,Na)ClO₄ media $\{[\text{H}^+] = 0.25\text{--}3 \text{ m (mol kg}^{-1})\}$ by direct potentiometric determinations.

The results have been extrapolated to a common reference state (that of pure water) by using the Brönsted–Guggenheim–Scatchard specific interaction theory (SIT) to make the necessary activity factor corrections (Whitfield, M. In: Pytkowicz, R. M., Ed., *Activity Coefficients in Electrolyte Solutions*, CRC Press, Boca Raton, FL 1979, Vol. 2, Chap. 3).

The values obtained at the pure water state are $\log K^\circ = 9.1 \pm 0.2$ ($E^\circ = 269 \pm 6 \text{ mV}$) at 25 °C and $\log K^\circ = 7.0 \pm 0.1$ ($E^\circ = 221 \pm 3 \text{ mV}$) at 45 °C. The time taken to attain the equilibrium potential was strongly affected by the acidity of the test solution and increased with the proton concentration.

Previous investigations have also been reviewed and evaluated. Data from previous investigations made at 25 °C were corrected by us for hydrolysis, chloride complexation and the rather strong effect of sulphate complexation, and gave (together with the data at 25 °C from the present investigation) a consistent result. A common treatment of all these data according to the SIT method resulted in $\log K^\circ = 9.04 \pm 0.05$ ($E^\circ = 267.4 \pm 1.5 \text{ mV}$) at the pure water reference state for the reaction above.

The standard potential for the $\text{UO}_2^{2+}/\text{U}^{4+}$ couple, i.e. reaction (1), is an important thermodynamic quantity; never-



theless its value seems not to be precisely known. The standard potential is used to calculate other thermodynamic quantities, notably the standard free energy of formation of $\text{U}^{4+}(\text{aq})$, cf. Fuger and Oetting.¹ It is thus a critical datum for all thermodynamic data bases for uranium, and also for practical applications such as the modelling of uranium mobility in natural waters, as this is strongly dependent on the redox state.

Fuger and Oetting¹ have discussed some experimental determinations of the standard $\text{UO}_2^{2+}/\text{U}^{4+}$ redox potential made by Sobkowski and Minc² and Nikoaleva,³ and give $273 \pm 5 \text{ mV}$ for the potential. These and other previous determinations are summarized in Table 1. The reviewers have not discussed the quality of the experimental data and the extrapolation to zero ionic strength (I) only includes part of the experimental studies.

Comments on previous experimental determinations of the $\text{UO}_2^{2+}/\text{U}^{4+}$ standard potential. The measurements made in H_2SO_4 media are affected by the rather strong complexation of UO_2^{2+} and U^{4+} with SO_4^{2-} . The formal potentials in

sulfate media should be higher than the standard potential because U(IV) forms stronger sulfate complexes than U(VI). The chloride complexes of U(IV), and especially the U(VI) complexes, are weak, but should in any case affect the measurements made in chloride media significantly and result in formal potentials which are higher than the standard potential.

Many authors have observed that the equilibrium potential is established very slowly. This is often the case for processes involving a two-electron transfer with major structural reorganization. The exchange current density at the inert electrode surface is then low, which means that the measured potential may be influenced by other redox couples and the surface state of the electrode. However, faster and more reproducible equilibrium potentials are attained at lower acidities and/or in the presence of strong complexing agents.

In order to decide whether one measures an equilibrium potential or a "mixed" potential, one should ascertain both that the absolute value of the measured EMF is independent of the electrode material used in the inert electrode, and that the electrode gives a Nernstian response to changes in the concentrations of the reduced and oxidised forms. Luther and Michie⁴ made an accurate investigation in sulphate media. They used platinized and bright platinum electrodes. The presence of a Nernstian response was checked at each sulfuric acid concentration. Corrections for sulfate complexation were not made. The same comments also hold for the studies made by Titlestadt,⁵ Khlopin and Gurevich⁶ and Gurevich.⁹ Taylor and Smith⁷ reported prob-

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Table 1. Formal potentials (E') at 25 °C on the normal hydrogen electrode scale of the UO₂²⁺/U⁴⁺ couple in media of various compositions. No corrections for activity coefficients and complex formation have been made. The uncertainties reported in the formal potentials refer to the observed variations as the ionic medium is varied in the range given in the third column. The uncertainty reported by Kraus and Nelson is discussed in the text. Some of the potentials have been extrapolated to $I = 0$; these are also discussed in the text.

Author(s)	Year	Medium	E' /mV	Ref.
Luther, Michie	1908	0.05–0.5 M H ₂ SO ₄	419 ± 1	4 ^a
Tittlestadt	1910	0.05–0.5 M H ₂ SO ₄	420	6 ^a
Khlopin, Gurevich	1943	0.05–0.5 M H ₂ SO ₄	420	6
Taylor, Smith	1944	0.2–2 <i>m</i> HCl	322–337	7
Kraus, Nelson	1949	→1 <i>m</i> HCl	310 ± 30	8
Gurevich	1957	→0	407	9 ^b
Sobkowski, Minc	1960	→0	329	2
Sobkowski	1961	→0	328.8	10 ^c
Grenthe, Varfeldt	1969	4 M (NaClO ₄ , HClO ₄)	348	11
Stabrovskii	1971	0.1–1.1 M Cl	304–344	12 ^d
Nikolaeva	1973	→0	273	3
Gorong <i>et al.</i>	1985	→0	330	13 ^e
Bruno <i>et al.</i>	1985	→0	260 ± 3	14

^aMeasurements made at approximately 18 °C. ^bMeasurements made in sulfate media. ^cData from HCl and H₂SO₄ media also given.

^dRecalculated using $E' = E_{\text{meas}} - 29.58 \log ([\text{H}^+][\text{UO}_2^{2+}]/[\text{U}^{4+}])$. ^eMeasurements made at 30 °C.

lems with reversibility at high concentrations. Different electrodes showed values that differed by several millivolts. Corrections for chloride complexation and hydrolysis were not made, and the reported potentials should therefore be too high. Only Pt electrodes were used, and the Nernstian response was tested only at the 0.2 *m* HCl level. Kraus and Nelson,⁸ in their polarographic study, report an estimated error of ±30 mV. This error seems mainly to be due to shortcomings in the measuring and extrapolation procedures. Sobkowski and Minc² have tested two different electrode materials, smooth platinum and electrolytically deposited platinum black. However, they did not ascertain that the electrodes gave a Nernstian response, and only one [UO₂²⁺]/[U⁴⁺] ratio was measured at each perchlorate level. The extrapolation to $I = 0$ was made by plotting the data against $I^{1/2}$. Sobkowski¹⁰ reports experimental data that were obtained by the same methodology as reported by Sobkowski and Minc. The results in HCl media were not corrected for chloride complexation, and the results from H₂SO₄ media were not corrected for sulfate complexation. Stabrovskii¹² did not test for Nernstian response and used only Pt electrodes. Nikolaeva³ tested three electrodes (one polished Pt and two Pt-black) and varied the UO₂²⁺/U⁴⁺ ratio from 3:4 to 30:1. The different electrodes gave the same readings, and the author reports that a Nernstian response was obtained. Guorong *et al.*¹³ used only platinized Pt electrodes and did not test for Nernstian response. Furthermore, they used the same kind of empirical method for extrapolation to the pure water reference state as that used by Sobkowski and Minc.²

In order to avoid excessive hydrolysis of U⁴⁺(aq), the redox potential measurements must be made at a fairly high acidity. This may cause problems with the liquid junction potentials between the test solution and the reference half-cell if a cell with a liquid junction is used. Taylor and

Smith,⁷ Sobkowski and Minc² and Sobkowski¹⁰ have avoided this problem by using a cell with a liquid junction but with the same concentration of H⁺ throughout. The liquid junction will in this way only be influenced by the changes in the concentration of UO₂²⁺ and U⁴⁺ in the solution. We have evaluated this effect and estimated it to be 1 mV or less. Strabovskii¹² did not give the composition of the junction electrolyte. If the reference electrode was standardized against a normal hydrogen electrode in a medium significantly different in composition from the test solution, this could result in a systematic error of 10–20 mV (vide infra). Nikolaeva³ used a cell where the test solutions contained HClO₄ as the ionic medium and where the reference half-cell was Ti(Hg)–TiCl–saturated KCl. This choice is unfortunate, as KClO₄ will precipitate in the liquid junction and the diffusion potential will be very large because of the large differences in the concentrations of H⁺ between the test solution and reference half-cell. It is unlikely that this liquid junction potential is reproducible, and the value of the measured UO₂²⁺/U⁴⁺ potential may thus be in error. Guorong *et al.*¹³ used a reference half-cell filled with a 1 M KCl solution which gave same kind of problem as in the case of Nikolaeva.

Grenthe and Varfeldt¹¹ made a determination of the UO₂²⁺/U⁴⁺ standard potential in connection with a study on the complex formation between uranium (U⁴⁺ and UO₂²⁺) and fluoride. They used an Ag, AgCl reference electrode connected to the solution through a salt bridge. The junction potential arising as a result of the variation in UO₂²⁺ and U⁴⁺ concentrations in the test solution was estimated to be of the same magnitude as in Sobkowski's case (1.5 mV). The determination of E° of the Ag, AgCl semicouple is more problematical, since no experimental data in 4.0 M perchlorate are available. Instead E° was calculated using tabulated data at $I = 0$ and calculating the activity factors

using the specific interaction theory (SIT).¹⁵ The error when calculating $E^\circ(\text{Ag}, \text{AgCl})$, using the SIT approach with $\epsilon(\text{Na}^+, \text{Cl}^-) = 0.03 \pm 0.01$, $\epsilon(\text{H}^+, \text{ClO}_4^-) = 0.14 \pm 0.03$ and $\epsilon(\text{H}^+, \text{Cl}^-) = 0.12 \pm 0.01$,¹⁶ in 4 M perchlorate media is at most ± 10 mV. $\epsilon(i, j)$ is the interaction coefficient for the interaction between the ions i (e.g. Na^+) and j (e.g. Cl^-) with opposite charge signs (see the section concerning the extrapolation to zero ionic strength).

A previous study of the $\text{UO}_2^{2+}/\text{U}^{4+}$ redox potential by Bruno *et al.*¹⁴ is discussed at the end of this communication. For a further discussion of previous experimental data the reader is referred to the section concerning extrapolation to the pure water reference state.

The aim of the present experimental work is to verify or reject earlier results by using experimental techniques which avoid the possible sources of error found in these investigations.

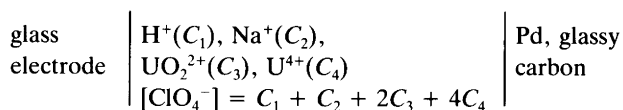
Experimental

Measurements were performed in a thermostatted air box at 25 ± 0.05 °C. The glass and glassy carbon electrodes used in the experiments were from Methrom.

Reagents, including uranium(VI) perchlorate, perchloric acid and sodium perchlorate, were prepared and analyzed as described in a previous paper.¹⁷ Uranium(IV) perchlorate solutions were prepared by reducing acidic uranium(VI) perchlorate with $\text{H}_2(\text{g})$ on a Pd catalyst. The preparation of the Pd catalyst has been described previously.¹⁸ The H_2 and N_2 gases used in the experiments were made oxygen-free by passing them through a chromium(II) chloride solution.

Method, results and calculations

In view of the experimental shortcomings mentioned, we have made a redetermination of the $\text{UO}_2^{2+}/\text{U}^{4+}$ potential by using a cell without liquid junction of the following type:



The experiments were carried out under an inert, oxygen-free $\text{N}_2(\text{g})$ atmosphere (see experimental section). The glass electrode was standardized vs. a hydrogen electrode in a separate experiment.

The $\text{UO}_2^{2+}/\text{U}^{4+}$ ratio was varied from 1:3 to 1, in order to establish whether the electrodes gave a Nernstian response. For a more detailed description the reader is referred to Ref. 19. Two different electrode materials have been used, Pd and glassy carbon. In view of our experiences from an earlier set of experiments we have used a rather high uranium concentration (0.2 mol kg^{-1}). We have also used long equilibration times (> 1 day for each $\text{UO}_2^{2+}/\text{U}^{4+}$ ratio). The kinetics of electron exchange is very slow, especially at high acidities.²⁰ Because of this we have also performed a set of

experiments at 45 °C. This should increase the electrode exchange current considerably, and hence the equilibrium potential should be attained much faster. This was verified by the experiments.

The concentration of H^+ was varied from 0.25 to 2.81 *m* (25 °C) and from 0.25 to 2.98 *m* (45 °C), and the reversibility tests outlined above were made at each acidity level investigated. In all the experiments the response was Nernstian within ± 1.5 mV, and the readings for the different electrodes were within ± 1 mV, except at 25 °C and at the highest acidity, where the glassy carbon electrode did not give Nernstian response; a similar observation was made by Taylor and Smith.⁷

Correction for hydrolysis of U^{4+} according to reaction (2)



$$\log K(I)(2) = -0.51 - 6D + 0.14 \text{ m} (\text{ClO}_4^-) \quad (3)$$

was made using eqn. (3) obtained by using the specific interaction theory.²¹ $K(I)(2)$ is the equilibrium constant for reaction (2) at ionic strength I and D is the Debye-Hückel term defined below. The results are given in Tables 2 and 3.

Extrapolation to the pure water reference state using the specific interaction theory (SIT). The Brønsted-Guggenheim-Scatchard SIT approach¹⁵ assumes that the activity coefficient of a single ion i is the sum of two terms, the Debye-Hückel term, which takes into account the pure long-range electrostatic component for the non-ideal behaviour of ions in solution, and a second term $\sum \epsilon(i, j, I) m_j$, which accounts for the short-range interactions, but only between ions of opposite charge. In the second term one often assumes that ϵ is independent of concentration. This

Table 2. Experimental redox data at $T = 25$ °C for the $\text{UO}_2^{2+}/\text{U}^{4+}$ couple in perchlorate media at three different perchlorate concentration levels and three different acidities. The formal potential E' refers to the NHE scale. $\log K(I) \equiv E'/29.58$.

$[\text{H}^+]/\text{m}$	$[\text{ClO}_4^-]/\text{m}$	I/m	$E'(3)$	$\log K(I)$
0.253–0.30	0.955	1.9–1.775	339 \pm 4	11.48 \pm 0.14
1.31–1.35	1.961	2.78–2.69	334 \pm 2	11.29 \pm 0.08
2.77–2.81	3.476	4.45–4.34	346 \pm 2	11.70 \pm 0.08

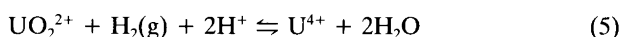
Table 3. Experimental redox data at $T = 45$ °C for the $\text{UO}_2^{2+}/\text{U}^{4+}$ couple in perchlorate media at four different perchlorate levels and three different acidities. The formal potential refers to the NHE scale. $\log K(I) \equiv E'/31.57$.

$[\text{H}^+]/\text{m}$	$[\text{ClO}_4^-]/\text{m}$	I/m	$E'(3)$	$\log K(I)$
0.25–0.43	0.955	1.9–1.5	293 \pm 2	9.29 \pm 0.06
1.26–1.39	1.96	2.91–2.59	302 \pm 2	9.58 \pm 0.06
2.89–2.98	3.54	4.37–4.14	311 \pm 2	9.86 \pm 0.06
0.25–0.38	3.97	4.92–4.61	305 \pm 2	9.67 \pm 0.06

second term is assumed to be a linear function of m , the molality of the main component of the solution, as shown in eqn. (4), where $D = 0.5091\sqrt{I}/(1+1.5\sqrt{I})$ is the Debye-Hückel term and Z_i is the charge on the ion i . By applying

$$\log \gamma_i = -Z_i^2 D + \sum \epsilon(i,j,I)m_j \quad (4)$$

this to the redox equilibrium (5), where K° is given by eqn. (6), we obtain eqn. (7). [By multiplying both sides of eqn. (7) by 29.58 (25°C) and 31.56 (45°C), respectively, we obtain the corresponding expressions for the potentials.]



$$K^\circ = K(I) \frac{\gamma(\text{U}^{4+})}{\gamma(\text{UO}_2^{2+})\gamma^2(\text{H}^+)} \quad (6)$$

$$\begin{aligned} \log K(I) - 10D &= \log K^\circ - [\epsilon(\text{U}^{4+}, \text{ClO}_4^-) - \epsilon(\text{UO}_2^{2+}, \text{ClO}_4^-) \\ &- 2\epsilon(\text{H}^+, \text{ClO}_4^-)] = \log K^\circ - \Delta\epsilon m(\text{ClO}_4^-) \end{aligned} \quad (7)$$

In the SIT approach this is a linear function of $m(\text{ClO}_4^-)$, with $\log K^\circ$ as the intercept on the $[\log K(I) - 10D]$ axis and with $[\epsilon(\text{U}^{4+}, \text{ClO}_4^-) - \epsilon(\text{UO}_2^{2+}, \text{ClO}_4^-) - 2\epsilon(\text{H}^+, \text{ClO}_4^-)]$ as the slope. The experimental values of $\log K(I) - 10D$ yield an approximately linear function of $m(\text{ClO}_4^-)$, as shown in Fig. 1, and from these data we obtain eqns. (8) and (9) at 25 and 45°C, respectively.

$$\begin{aligned} \log K^\circ &= 9.1 \pm 0.2 \quad (E^\circ = 269 \pm 6 \text{ mV}) \\ \text{and } \Delta\epsilon &= -0.1 \pm 0.1 \end{aligned} \quad (8)$$

$$\begin{aligned} \log K^\circ &= 7.0 \pm 0.1 \quad (E^\circ = 221 \pm 3 \text{ mV}) \\ \text{and } \Delta\epsilon &= 0 \pm 0.1. \end{aligned} \quad (9)$$

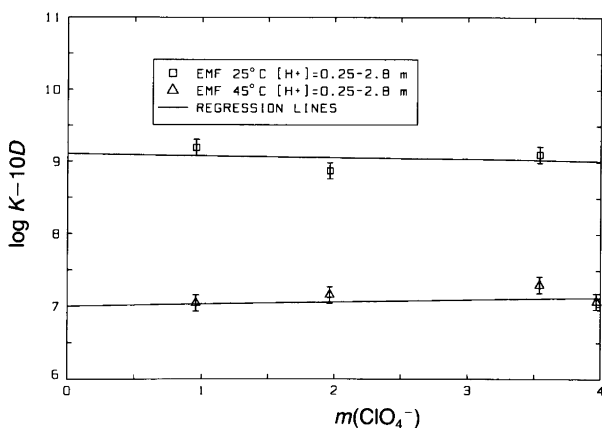


Fig. 1. Experimental data from the present investigation plotted according to SIT.

Discussion

Consistency check of experimental data for the redox potential of the UO₂²⁺/U⁴⁺ couple. A common treatment of all sets of data measured in perchlorate media at 25°C (Sobkowski and Minc,² Sobkowski,¹⁰ Nikolaeva,³ Grenthe and Varfeldt¹¹ and the present study) using the SIT approach leads to $\log K^\circ = 9.04 \pm 0.05$ ($E^\circ = 269.0 \pm 1.5$ mV) and $\Delta\epsilon = 0.02 \pm 0.03$ kg mol⁻¹ (cf. Fig. 2). These data were all corrected for the hydrolysis according to reaction (2). The linear regression treatment has been made with all the points and their individual uncertainties (95% confidence limits) included. (Figs. 2–4). The interaction coefficient $\epsilon(\text{U}^{4+}, \text{ClO}_4^-)$ can now be calculated from the experimental value of $\Delta\epsilon = 0.02 \pm 0.03$ and the known values of $\epsilon(\text{UO}_2^{2+}, \text{ClO}_4^-)$ and $\epsilon(\text{H}^+, \text{ClO}_4^-)$ (0.46 and 0.14 kg mol⁻¹ respectively).¹⁶ We obtain $\epsilon(\text{U}^{4+}, \text{ClO}_4^-) = 0.76 \pm 0.03$ kg mol⁻¹. Grenthe *et al.*²¹ studied reaction (2) in perchlorate media as a function of ionic strength, and obtained $\Delta\epsilon(2) = -0.14$. By combining $\Delta\epsilon(2)$ with a known value for $\epsilon(\text{H}^+, \text{ClO}_4^-)$ of 0.14 and a estimated value for $\epsilon(\text{UOH}^{3+}, \text{ClO}_4^-) \approx \epsilon(\text{M}^{3+}, \text{ClO}_4^-) \approx 0.49$ we obtain eqn. (10) in very

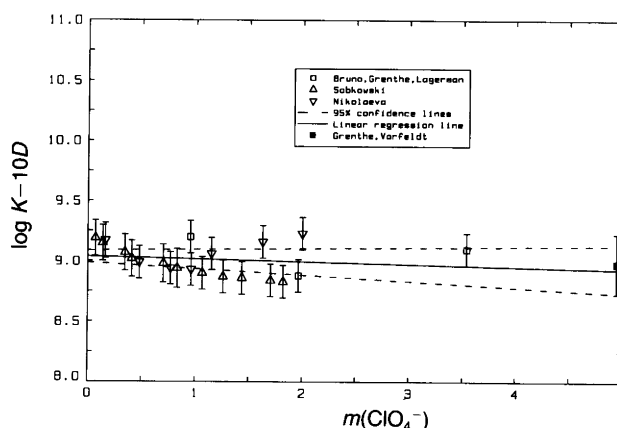


Fig. 2. Data obtained in perchlorate media plotted according to SIT.

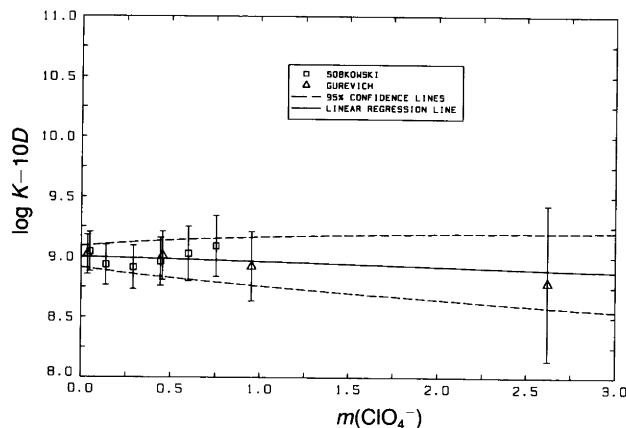


Fig. 3. Data obtained in chloride media plotted according to SIT.

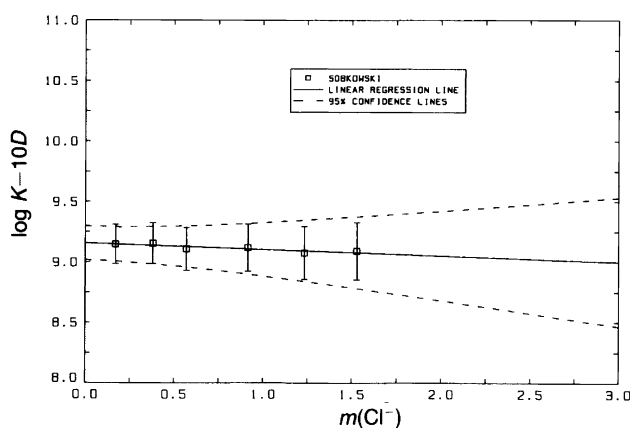


Fig. 4. Data obtained in sulfate media plotted according to SIT.

$$\varepsilon(\text{U}^{4+}, \text{ClO}_4^-) = \varepsilon(\text{H}^+, \text{ClO}_4^-) + \varepsilon(\text{UOH}^{3+}) - \Delta\varepsilon(2) = 0.77 \quad (10)$$

good agreement with the value obtained in the present investigation. The observed scatter in Nikolaeva's data at higher ClO_4^- concentrations may be due to precipitation of $\text{KClO}_4(\text{s})$ at the junction test-solution interface. However, all data were included in the least-squares analysis. The dashed lines in Fig. 2 give the 95 % confidence interval of the data.

The data of Sobkowski obtained in chloride media were corrected for hydrolysis and chloride complexation using the stability constants given in Table 4. We obtained $\log K^\circ = 9.16 \pm 0.14$ and $\Delta\varepsilon = 0.05 \pm 0.17$ (Fig. 1) in good agreement with the data measured in perchlorate media. The experimental data of Taylor and Smith give a somewhat smaller value, $\log K^\circ = 8.8$.

The reported formal potentials in sulfate media were corrected for the rather strong effect of sulfate complexation using the equilibrium constants given in Table 4. By combining the data reported by Gurevich and Sobkowski using equilibrium constants and interaction coefficients reported in Ref. 16 (with their individual uncertainties, Table

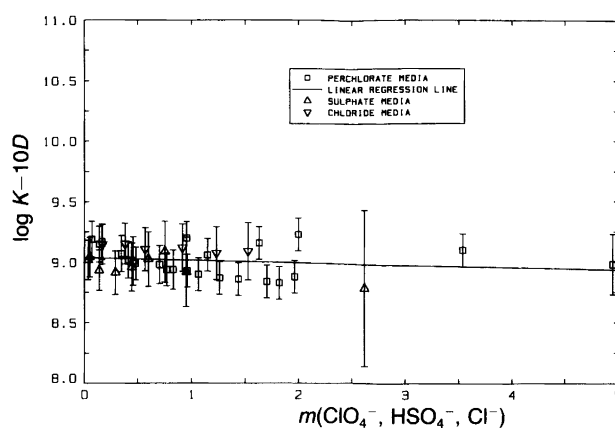


Fig. 5. Perchlorate, chloride and sulfate data plotted according to SIT.

4) we obtained $\log K^\circ = 9.00 \pm 0.09$ and $\Delta\varepsilon = 0.04 \pm 0.18$ (Fig. 4) using the SIT method. This result is also in very good agreement with the results in ClO_4^- media. The large uncertainty at 2.7 $m \text{H}_2\text{SO}_4$ is a result of the uncertainties in the equilibrium constants of the complex formation reactions and the corresponding values of $\Delta\varepsilon$ (Table 4).

By combining the experimental information in all investigated ionic media we can, with good confidence, assert that the value for the $\text{U(VI)}/\text{U(IV)}$ couple is $267.4 \pm 1.5 \text{ mV}$ ($\log K^\circ = 9.04 \pm 0.05$) at $I = 0$, as shown in Fig. 5. The very good agreement, after corrections for hydrolysis, chloride and sulfate complexation, between the great majority of the reported values of the redox potential, confirms the consistency of the thermodynamic data used. The value obtained for $\varepsilon(\text{U}^{4+}, \text{ClO}_4^-)$ of 0.76 ± 0.03 , which is very close to the value expected for a +4 ion $\{\varepsilon(\text{Y}_2\text{CO}_3^{4+}, \text{ClO}_4^-) = 0.80,^{22} \varepsilon[\text{Fe}_2(\text{OH})_2^{4+}, \text{ClO}_4^-] = 0.82,^{23} \varepsilon(\text{Np}^{4+}, \text{ClO}_4^-) = 0.82^{24}$ and $\varepsilon(\text{Pu}^{4+}, \text{ClO}_4^-) = 1.02^{24}\}$, gives additional support. By using values of the enthalpy of formation and entropy (298 K) reported in the literature $\{\Delta_f H_m^\circ(\text{UO}_2^{2+}) = 1018.8 \text{ kJ mol}^{-1}$, $\Delta_f H_m^\circ(\text{U}^{4+}) = -591.2 \text{ kJ mol}^{-1}$, $\Delta_f H_m^\circ[\text{H}_2\text{O}(\text{l})] = -285.83 \text{ kJ mol}^{-1}$, $S^\circ(\text{UO}_2^{2+}) = -97.1 \text{ J K}^{-1} \text{ mol}^{-1}$, $S^\circ[\text{H}_2\text{O}(\text{l})] = 69.95 \text{ J K}^{-1} \text{ mol}^{-1}$ and $S^\circ[\text{H}_2(\text{g})] = 130.68 \text{ J}$

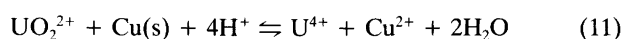
Table 4. Equilibrium constants and their ionic strength dependence taken from Ref. 16. The uncertainties in $\log \beta_n^\circ$ and $\Delta\varepsilon$ are those selected by the authors of Ref. 16. The interaction coefficients $\varepsilon(\text{UO}_2^{2+}, \text{ClO}_4^-)$ and $\varepsilon(\text{U}^{4+}, \text{ClO}_4^-)$ and the corresponding values for $\varepsilon(\text{UO}_2^{2+}, \text{HSO}_4^-)$ and $\varepsilon(\text{U}^{4+}, \text{HSO}_4^-)$ are assumed to be the same as in perchlorate media when corrections for complex formation have been made, cf. Ref. 16.

Reaction	$\log \beta_n = \log \beta_n^\circ + \Delta\varepsilon I + \Delta z^2 D$
$\text{UO}_2^{2+} + \text{Cl}^- \rightleftharpoons \text{UO}_2\text{Cl}^+$	$(0.16 \pm 0.02) + (0.27 \pm 0.03)I(m) - 4D$
$\text{U}^{4+} + \text{Cl}^- \rightleftharpoons \text{UCl}^{3+}$	$(1.72 \pm 0.13) + (0.29 \pm 0.08)I(m) - 8D$
$\text{UO}_2^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{UO}_2\text{SO}_4(\text{aq})$	$(3.15 \pm 0.02) + (0.34 \pm 0.07)I(m) - 8D$
$\text{UO}_2^{2+} + 2\text{SO}_4^{2-} \rightleftharpoons \text{UO}_2(\text{SO}_4)_2^{2-}$	$(4.15 \pm 0.07) + (0.34 \pm 0.14)I(m) - 8D$
$\text{U}^{4+} + \text{SO}_4^{2-} \rightleftharpoons \text{USO}_4^{2+}$	$(6.48 \pm 0.23) + (0.47 \pm 0.15)I(m) - 16D$
$\text{U}^{4+} + 2\text{SO}_4^{2-} \rightleftharpoons \text{U}(\text{SO}_4)_2(\text{aq})$	$(10.42 \pm 0.24) + (0.74 \pm 0.11)I(m) - 24D$
$\text{U}^{4+} + \text{H}_2\text{O} \rightleftharpoons \text{UOH}^{3+}$	$(-0.54 \pm 0.20) + (0.44 \pm 0.14)m(\text{ClO}_4^-) - 6D$
$\text{SO}_4^{2-} + \text{H}^+ \rightleftharpoons \text{HSO}_4^-$	$(1.98 \pm 0.05) - (0.03 \pm 0.04)I(m) - 4D$

K⁻¹)^{1,16} and the value of the potential given above, one can calculate a value for S°[U⁴⁺(aq)]. The value is -416±11 J mol⁻¹ K⁻¹, in good agreement with values reported for other tetravalent actinides,¹ e.g. S°[Th⁴⁺(aq)] = -423±17 J mol⁻¹ K⁻¹.

The consistency of the E° values at 25 and 45°C can be checked using the enthalpy change of reaction (5) calculated by the known standard enthalpies of formation of the reactants and products. We find Δ_rH_m^o(5) = -148.8±3.0 kJ mol⁻¹. Assuming that Δ_rH_m^o is independent of the temperature in the interval 25–45°C we obtain log K° (45°C) = 7.5±0.2. The agreement between the experimental and calculated values of log K° at 45°C is fair, considering the overall experimental uncertainties. The largest source of uncertainty is associated with the experimental value of log K(25°C), while the enthalpy of reaction is precisely known.

Previously, we have studied equilibrium(11) in (H,Na)



ClO₄ media at 25°C.¹⁴ The experiments were made in batches and were equilibrated for approximately 1 month under vigorous shaking. The concentrations of the different species (U⁴⁺, UO₂²⁺ and Cu²⁺) were determined by either a spectrophotometric or a titrimetric technique. Knowing the Cu(s)/Cu²⁺ standard potential in the same media one can calculate the U(VI)/U(IV) potential from the experimental equilibrium constant of reaction (11). The results at low proton concentrations agree well with the present study, while the results at high acidities do not.¹⁴

Based on the experiences in the present study we are now convinced that we had not attained equilibrium in the previous experiments at high acidities, despite the fact that the EMF measurements indicated a Nernstian response (within ±1 mV!).

The factors that influence the homogeneous electron transfer process may also affect the heterogeneous processes at the electrode surface. Rona²⁰ studied the effect of the hydrogen concentration on the homogeneous exchange reaction (12) and found the rate equation (13), where K_h is



$$\text{Rate} = \text{constant} \times \frac{[\text{U(IV)}]^2 [\text{UO}_2^{2+}]}{\left(\frac{[\text{H}^+]}{K_h} + 1 \right)^2 [\text{H}^+]^2} \quad (13)$$

the equilibrium constant for reaction (2) and U(IV) = [U⁴⁺]+[UOH³⁺]. The important precursor in the exchange reaction seems to be UOH³⁺. OH⁻ and SO₄²⁻ are good bridging ligands which in general increase the rate of electron transfer and also result in a more stable redox potential.

A systematic error due to disequilibrium at high acidities resulted in a log K° value significantly lower (log K° =

8.8±0.1), and a value of ε(U⁴⁺,ClO₄⁻) = 1.5±0.1¹⁴ significantly higher, than the values proposed here. It is obvious that direct EMF measurements of the UO₂²⁺/U⁴⁺ couple are difficult to make, and that great caution must be used to eliminate systematic errors. However, the combined results of our own experimental studies and those of previous investigators give a consistent value for this important thermodynamic quantity.

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