and B_5H_9 in tetrahydrofuran. The reaction proceeded to completion at a moderate to slow rate at −63°.

Preparation of LiB_6H_9.—In a typical reaction, 1.00 ml of an ethyl ether solution, 1.5 *M* in $LiCH_3$, was syringed in the drybox into a 20–25-mm diameter reaction tube containing a Teflon-covered stirring bar. The reaction tube was fitted with a stopcock adapter, attached to the vacuum line, cooled, and evacuated. Hexaborane(10) was measured in a calibrated volumetric tube at 0° (0.69 g/ml)[20] and 0.163 ml (1.50 mmol) was distilled into the reaction flask at −196°. The reaction vessel was warmed until the B_6H_{10} melted (near −62°) and dissolved in the ether; then it was thermostated at −78°. The reaction was immediate and vigorous; a quantitative amount of methane was evolved in minutes. Samples no larger than 3 mmol were prepared by the procedure. This reaction was also carried out in methyl ether and glyme by removing ethyl ether from the $LiCH_3$ and replacing it with an equivalent volume of the new solvent.

Preparation of KB_6H_9 and NaB_6H_9.—A quantity of KH or NaH, 1–3 mmol, was accurately weighed in a 20–25-mm diameter reaction tube as previously described in the preparation of KB_5H_8 and NaB_5H_8. An equimolar amount of B_6H_{10} was distilled into the reaction tube and allowed to melt and run to the bottom. One milliliter of solvent per millimole of hydride was then added and the mixture was warmed to an appropriate reaction temperature and stirred. Reaction temperatures suitable for 1–2-mmol preparations are as follows: KH in $(CH_3)_2O$, −78°; KH in THF, −78°; KH in glyme, −50°; KH in $(C_2H_5)_2O$, −50°; NaH in THF, −63°; NaH in glyme, −45°; NaH in $(C_2H_5)_2O$, −45°.

KB_6H_9 and NaB_6H_9 were isolated as white, free-flowing, fine powders from $(CH_3)_2O$ or $(C_2H_5)_2O$ by pumping away the solvent at −45°.

X-Ray powder diffraction pattern data for KB_6H_9, *d* (relative intensity): 8.9 (m), 5.72 (w), 5.11 (vs), 4.42 (m), 3.82 (s, b), 3.36 (vw), 2.95 (m) 2.55 (m), 2.45 (vw), 2.24 (vw), 2.03 (w), 1.93 (w), 1.90 (w).

Infrared spectrum of KB_6H_9 (cm^{-1}): 2540 (s, sh), 2490 (s, b), 1995 (w, b), 1890 (w), 1060 (m), 1005 (m), 820 (m), 795 (m), 763 (m), 726 (m), 682 (w), 618 (m), 575 (m).

KB_6H_9 was analyzed by decomposition in a mixture of concentrated hydrochloric acid and methanol at 100° for approximately 1 day. The per cent boron was determined by titration of the boric acid–mannitol complex according to standard procedures. The hydrogen was measured in the Toepler system. *Anal.* Calcd for KB_6H_9; B, 56.8; H, 8.03. Found: B, 57.4; H, 7.93.

Regeneration of B_6H_{10} from KB_6H_9 and LiB_6H_9.—Excess HCl was added to 0.67 mmol of LiB_6H_9 in $(CH_3)_2O$ at −196°. The mixture was warmed to −78° and stirred for 1 hr. Volatile materials were then slowly passed through traps maintained at −95 and −196°. The reaction flask was not allowed to warm over −45°. In the −95° trap was found 0.62 mmol of B_6H_{10} (93% recovery) identified by mass spectrometry. A similar reaction with 0.68 mmol of KB_6H_9 in $(CH_3)_2O$ yielded 0.56 mmol of B_6H_{10} (82% recovery).

Reactions using DCl were carried out in the same fashion. The mass spectrum of B_6H_9D formed had the peak of maximum intensity in the B_6 mass region at *m/e* 72 (compare B_6H_{10} at *m/e* 71) in agreement with its average composition. The infrared spectrum of B_6H_9D contained an absorption at 1125 cm^{-1} not found in the infrared spectrum of B_6H_{10}. No absorption indicative of terminal deuteration was seen.

Acknowledgment.—We wish to acknowledge, gratefully, the support of this work by the National Science Foundation. H. D. J. is grateful for support from The Ohio State University Graduate School in the form of a dissertation fellowship.

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[20] A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
PURDUE UNIVERSITY, LAFAYETTE, INDIANA 47907

The Thermodynamic Functions of Neptunium(V) and Neptunium(VI)[1]

BY J. R. BRAND[2,3] AND J. W. COBBLE

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The solubility and heat of solution of $NpO_2(NO_3)_2 \cdot 6H_2O$ have been measured, giving values for the free energy and heat of solution of −2940 cal mol^{-1} and 5060 cal mol^{-1}, respectively. Estimation of the entropy of $NpO_2(NO_3)_2 \cdot 6H_2O$ as 123.4 gibbs mol^{-1} then fixes the entropy of $NpO_2^{2+}(aq)$ as -20 ± 2 gibbs mol^{-1}. The heat of reduction of $NpO_2^{2+}(aq)$ to $NpO_2^{+}(aq)$ by hydrogen peroxide was found to be −10,310 cal mol^{-1} and $E°$ for the NpO_2^{2+}–NpO_2^{+} couple was measured as −1.236 V. These data permit calculation of the entropy of $NpO_2^{+}(aq)$ as -6.2 ± 2 gibbs mol^{-1}. By comparison of the $E°$ for the NpO_2^{2+}–NpO_2^{+} electrode and the formal potential reported elsewhere, corrections could be estimated for adjusting the UO_2^{2+}–UO_2^{+}, PuO_2^{2+}–PuO_2^{+}, and AmO_2^{2+}–AmO_2^{+} formal potentials to true $E°$ values. These were found to be −0.163, −1.013, and −1.70 V, respectively.

Introduction

Although a great deal of thermodynamic data are known for actinide element ions and compounds in solution, very little has been determined under conditions where the corrections to normal standard-state conditions can be made. Consequently only one experimental ionic entropy is available, for UO_2^{2+},[4] and only a few heats of formation have been extrapolated to infinite dilution. The oxygenated actinide cations are of particular interest, not only because of their importance in the chemistry of these elements, but also because of their unique structures. Only a few other

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[1] Supported by the U. S. Atomic Energy Commission.

[2] From the Ph.D. Thesis of J. R. Brand, Purdue University, Aug 1967.

[3] U. S. Atomic Energy Commission Fellow, 1963–1964.

[4] (a) L. V. Coulter, K. S. Pitzer, and W. M. Latimer, *J. Amer. Chem. Soc.*, **62**, 2845 (1940); (b) M. H. Rand and O. Kubaschewski, "The Thermochemical Properties of Uranium Compounds," Oliver and Boyd, London, 1963, pp 11–12.

elements, (*e.g.*, vanadium) in the periodic table form such stable and well-defined oxygenated cationic structures.[5]

Neptunium is almost ideal among the actinides with regard to the stability of its various ionic states in solution. In a previous communication[6] from this laboratory the standard thermodynamic functions for $Np^{3+}(aq)$ and $Np^{4+}(aq)$ have been reported. In the present research, a variety of thermochemical measurements have been used to fix experimentally the entropies of $NpO_2^+(aq)$ and $NpO_2^{2+}(aq)$, and to determine the standard potential of the NpO_2^{2+}–NpO_2^+ electrode. With such data it has been possible to estimate more reliably the standard potentials and entropies for the rest of the similar actinide element $MO_2^{2+}(aq)$ and $MO_2^+(aq)$ species than has heretofore been possible.

Experimental Section

Chemicals.—Chemicals used in this research were, unless otherwise specified, of reagent grade. Water used was twice distilled from quartz and stored in closed polyethylene containers. Perchloric acid solutions were prepared by dilution of G. Fredrick Smith double vacuum distilled 70% acid and standardized against Fisher primary standard grade THAM [tris(hydroxymethyl)aminomethane].

The Np^{237} used in this research was obtained as a nitrate solution from the Oak Ridge National Laboratory and was purified by solvent extraction[7] and ion-exchange techniques.[8,9] α-Ray spectroscopy using a solid-state detector and multichannel analysis indicated $\sim 1 \times 10^{-3}$ wt % of plutonium, largely Pu^{239}. This amount was considered insignificant for the purposes of this research.

$NpO_2(NO_3)_2 \cdot 6H_2O$.—Two methods were used for preparation of this salt. In the first, carefully washed neptunium(V) hydroxide was dissolved in concentrated nitric acid after which the solution was twice boiled to dryness. The pink residue was dissolved in water and evaporated to dryness under vacuum to remove excess nitric acid. Attempts to hydrate the resulting pink powder over 40% sulfuric acid, by the method found useful in hydrating uranyl nitrate, were not successful for $NpO_2(NO_3)_2$. The hydration method described by Laidler[10] of simply contacting the salt with laboratory air also failed, perhaps because of the relatively low-humidity conditions prevailing during the experiments. The hexahydrate was finally obtained by simply removing the red crystals formed from a saturated solution, allowing them to dry in air, and sealing the salt into sample bulbs for use in the calorimeter and for analysis. Weighed amounts of this compound (supposedly $NpO_2(NO_3)_2 \cdot 6H_2O$) were dissolved in precisely known volumes of water and triplicate aliquots of the solution used for a gross α assay of the Np^{237} content in a standardized windowless proportional counter. This analysis indicated an empirical formula of $NpO_2(NO_3)_2 \cdot (6.1 \pm 0.3)H_2O$, in agreement with previous conclusions.[10] A second preparative method[10] was also used in which neptunium(VI) hydroxide was dissolved in dilute nitric acid and evaporated to dryness under vacuum.

Neptunium Solutions.—Solutions of Np(V) in perchloric acid were prepared by dissolving carefully washed neptunium(V) hydroxide in previously standardized perchloric acid. The neptunium(V) concentration was determined by α counting and the hydrogen ion concentration was calculated by difference. Np(VI) solutions in perchloric acid were prepared either by dissolving $NpO_2(NO_3)_2 \cdot 6H_2O$ or neptunium(VI) hydroxide, made by ozonization of a suspension of neptunium(V) hydroxide as described by Bagnall and Laidler,[11] in standardized perchloric acid. Radiometric assay was again used to fix the concentration of Np(VI). Purity of oxidation states was checked with a Cary Model 14 spectrophotometer, using previously reported spectra.[12]

Apparatus and Procedure. Microcalorimeter.—The microcalorimeter and recent modifications and operating and calibration techniques which were used in this research have been described in previous publications.[13,14] Samples were introduced into the calorimeter in small Pyrex sample bulbs made of 3-mm tubing and having thin, flat bottoms. These were weighed, both before and after filling, on a Mettler microgram balance (sensitivity ±3 μg). Each bulb was then sealed with a small glass bead, held by a constriction in the neck of the bulb, and Apiezon W black wax.

Although there was no reason for doubt, measurements of the heat of solution of THAM in 0.10 *M* HCl[15,16] gave satisfactory results and indicated that the microcalorimeter was operating satisfactorily.

Hydrogen Electrode Measurements.—It was desirable to measure the potential of the $Pt|NpO_2(NO_3)_2$, $NpO_2(NO_3)$, $HClO_4$, $H_2|Pt$ cell to obtain standard-state free energy differences between $NpO_2^{2+}(aq)$ and $NpO_2^+(aq)$. However, there is reason to suspect that $H_2(g)$ will reduce both species at a platinum electrode. Consequently either a double cell with connecting salt bridge must be used, or an insert glass electrode must be substituted for the hydrogen electrode.

The use of a glass electrode as a thermodynamic replacement for the normal hydrogen electrode in accurate emf measurements has been described by Covington and Prue[17] and subsequently extended and improved by Zielen.[18] Essentially these previous researches indicated that there is a 1:1 correspondence between the voltage of a hydrogen electrode and a glass electrode against some reference electrode, when proper corrections are made for the slowly changing asymmetry potential of the glass system. These observations are remarkable and extremely valuable, particularly since the utility of the glass electrode was shown to extend even into concentrated solutions.

In the present research, Beckman GP 39177 glass electrodes were calibrated against hydrogen electrodes immediately prior to the emf measurements of the NpO_2^{2+}–NpO_2^+ couple, by transferring the glass electrode between various cells. Hydrogen electrodes were prepared in the manner described by Hills and Ives[19] and were used in pairs to provide additional checks on their proper operation.

Emf Measurements.—Two emf-measuring systems were used throughout the course of this work. The first was similar to that described by Zielen[18] and used a Leeds and Northrup K-3 potentiometer in series and opposing the voltage generated by the experimental cell in question. A Cary Model 31 vibrating-reed electrometer was used as a null indicator, with the glass electrode always connected to the electrometer input.

The second system, similar to the first, was one suggested by the operating manual of the electrometer supplied by the Applied Physics Corp. In this modification the electrodes of the cell in question are connected directly to the electrometer with the K-3 potentiometer placed in the electrometer feedback circuit. Both systems gave identical measurements, but the latter method was found to be less subject to stray capacitance and noise.

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(10) J. B. Laidler, *J. Chem. Soc.*, 780 (1966).

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(15) R. I. Irving and I. Wadso, *Acta Chem. Scand.*, **18**, 195 (1964).

(16) S. R. Gunn, *J. Phys. Chem.*, **69**, 2902 (1965).

(17) A. K. Covington and J. E. Prue, *J. Chem. Soc.*, 3696 (1955).

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(19) G. J. Hills and D. J. G. Ives, *J. Chem. Soc.*, 305 (1951).

The glass and hydrogen electrodes were checked against the known potentials of the Ag–AgCl electrode[20] by measurements in 0.1022 m HCl solutions. The average of six determinations was found to be within ±0.0001 V of the value calculated from the previously accepted values at 25°. The emf standard used in these laboratories was a calibrated unsaturated Eppeley cell.

The cells used in this research are described in detail elsewhere.[2] Briefly they consisted of multicompartmented, jacketed, glass cells fitted with ground-glass jacketed covers containing ground-glass openings for insertion of various electrodes. Water from a thermostat was circulated through the jackets of both the cells and covers to provide the necessary temperature control at 25.00 ± 0.05°. The neptunium cells had a volume of 5–20 ml, and the hydrogen and silver chloride electrode cells could contain up to 200 ml of solution.

The platinum–hydrogen electrodes were constructed in the usual manner.[21] The neptunium electrode system consisted of a 0.4 × 2.0 cm piece of platinum gauze welded to a piece of platinum wire which was sealed into a length of Pyrex tubing. This electrode was inserted into the neptunium solution which was stirred by passing purified, presaturated nitrogen gas through a small bubbling tube. All of the reference hydrogen electrode potentials were corrected for barometric pressure using a table given by Bates.[22]

Reaction of Np(VI) with H_2O_2.—During the course of this research it was of interest to obtain a direct measurement of the enthalpy difference between NpO_2^{2+}(aq) and NpO_2^{+}(aq). This was due to the fact that the temperature coefficient of the NpO_2^{2+}–NpO_2^{+} electrode could not be measured with sufficient accuracy. A previous report on the stoichiometry of the reduction of Np(VI) with H_2O_2,[23] although not of sufficient accuracy for a calorimetric determination, nevertheless suggested that this reaction might be quantitative under certain conditions.

An Np(VI) solution was carefully standardized by igniting aliquots on small platinum disks to solid NpO_2 and was found to be (1.381 ± 0.004) × 10^{-2} M. A solution of H_2O_2 was standardized against standard cerate solution, which had, in turn, been standardized against primary standard grade As_2O_3 and found to be (1.972 ± 0.002) × 10^{-3} M. A Beckman Model G pH meter fitted with small platinum and calomel electrodes was used to follow the titration of the H_2O_2 solution into the Np(VI) solution. A sharp end point was observed, and by this method the Np(VI) solution was found to be (1.380 ± 0.002) × 10^{-2} M, in good agreement with the gravimetric results.

In one titration small bits of glass, Apiezon W black wax, and tantalum foil were placed in the Np(VI) solution during titration to determine any possible catalytic effect on the self-decomposition of H_2O_2. These extraneous substances are present in the calorimeter; however, no effect was observed. We conclude that, under proper conditions, the reaction of H_2O_2 with excess Np(VI) is rapid and quantitative. When a large excess of H_2O_2 is used, a very slow (at these concentrations) secondary reaction usually follows, presumably involving the further reduction of Np(V).

Results

Previous experience with $NpO_2(NO_3)_2$ gave every indication that the saturated solutions came to equilibrium rapidly with the solid phase, $NpO_2(NO_3)_2 \cdot 6H_2O$, at a concentration of 3 m.

Solubility of $NpO_2(NO_3)_2 \cdot 6H_2O$.—A solution of this compound was slowly brought to saturation in a closed container at 25.0 ± 0.2° and allowed to stand for several hours. Three 1-μl "microcap" precision-bore capillaries (Kensington Scientific Corp., Berkeley, Calif.), which had been previously weighed in a Mettler microgram balance, were used to remove samples of the saturated solution and reweighed. Each capillary was crushed in an accurately known volume of dilute perchloric acid. Aliquots of these solutions were then radiometrically assayed to determine the amount of $NpO_2(NO_3)_2$ in the saturated solution. The resulting solubility data are summarized in Table I.

Table I

Solubility of $NpO_2(NO_3)_2 \cdot 6H_2O$ at 25°

Soln wt, mg	$NpO_2(NO_3)_2$ wt, mg	Soly, m
1.748	0.915	2.79
1.849	1.032	3.21
1.738	0.919	2.85
	Av	2.95 ± 0.26

The Heat of Solution of $NpO_2(NO_3)_2 \cdot 6H_2O$.—Two small samples of the hydrated salt weighing about 11 mg were sealed in glass bulbs as previously described. The microcalorimeter was filled with 10.0 ml of water and thermostated at 25.0°. Electrical calibrations were carried out before and after each heat of solution measurement. The salt dissolved rapidly. Previous tests indicated that during the time interval involved from the preparation of the salt to the calorimetric measurements, autoreduction of Np(VI) by the α radioactivity was negligible. The results of the heats of solution are summarized in Table II.

Table II

The Heat of Solution of $NpO_2(NO_3)_2 \cdot 6H_2O^a$ at 25°

Sample wt, mg	Mol of sample × 10^5	Heat, cal	ΔH, kcal/mol
11.77	2.348	0.1233	5.251
10.62	2.119	0.1074	5.068
		Av	5.160 ± 0.130

[a] The final concentration of Np(VI) was ~2 × 10^{-3} M; there was no evidence of any Np(V) formed by radiolysis.

The Heat of the Reaction of Np(VI) with H_2O_2.—The heat of reduction of Np(VI) measurement was also carried out in the microcalorimeter. In these experiments a neptunium stock solution was prepared which was 1.380 × 10^{-2} M in Np(VI), 4.6 × 10^{-2} M in perchloric acid, and had an ionic strength of 8.8 × 10^{-2}. A 10-ml serum pipet was used to transfer 1.5 ml of this stock solution and 8.5 ml of water to the calorimeter, to give a final solution with an ionic strength of 1.3 × 10^{-2}.

$$2NpO_2^{2+}(aq) + H_2O_2(aq) = 2NpO_2^{+}(aq) + 2H^{+}(aq) + O_2(g) \quad (1)$$

The density of a 0.6566 N solution of H_2O_2 was measured in a calibrated picnometer. Disposable 50-μl "microcap" pipets were used to transfer this H_2O_2 solution into the preweighed sample bulbs. The glass bead that was weighed with each bulb was quickly placed in the neck of the bulb, and deliberately prolonged weighings showed no detectable weight loss due to evaporation. The bulbs were then sealed with

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(20) D. J. G. Ives and G. J. Janz, "Reference Electrodes," Academic Press Inc., New York, N. Y., 1961, p 189.

(21) See ref 20, p 103.

(22) R. G. Bates, "Electrometric pH Determinations," John Wiley and Sons, New York, N. Y., 1954, p 160.

(23) A. J. Zielen, J. C. Sullivan, D. Cohen, and J. C. Hindman, *J. Amer. Chem. Soc.*, **80**, 5632 (1958).

Apiezon W wax and mounted in the calorimeter. The amount of hydrogen peroxide was always adjusted so it was the limiting reagent in the calorimetric reaction by using approximately twice the stoichiometric amount of Np(VI).

A correction for the heat effect due to the change in partial pressure of oxygen over the calorimeter solution was subtracted from the observed heat. The solubilities of nitrogen and oxygen were taken as 0.0143 ml of N_2/ml of H_2O and 0.0284 ml of O_2/ml of H_2O,[24] and the heats of solution given by Latimer[25] for nitrogen and oxygen of −2140 and −2990 cal/mol, respectively, were used. The details of these calculations are given elsewhere.[2]

The results of three separate determinations of the heat of reduction of Np(VI) with H_2O_2 are summarized in Table III.

TABLE III

THE HEAT OF REDUCTION OF $NpO_2^{2+}(aq)$ BY $H_2O_2(aq)$

H_2O_2 wt, g	Mol of H_2O_2 × 10^6	Obsd heat, kcal	Heat[a] corr, kcal	Corr heat, kcal		$-\Delta H_1$, kcal/mol
0.013848	4.521	−48.202	−0.193	48.009		10.61
0.014174	4.636	−48.612	−0.198	48.414		10.44
0.017595	5.728	−61.783	−0.245	61.538		10.74
					Av	10.60 ± 0.15

[a] Corrections for heat effect of O_2 released during the reduction. The ionic strength remained essentially constant at 0.013 during the course of the reaction.

The Emf of the NpO_2^+–NpO_2^{2+} Electrode.—The cell reaction of interest is

$$NpO_2^+(aq) + H^+(aq) = NpO_2^{2+}(aq) + 0.5H_2(g) \qquad (2)$$

If the cell potentials developed are reversible, the voltage is described by the Nernst equation

$$E = E^\circ - 0.05916 \log \frac{a_{NpO_2(ClO_4)_2}}{a_{HClO_4}a_{NpO_2(ClO_4)}} \qquad (3)$$

since the hydrogen electrode potential was always corrected to unit fugacity. Letting VI = $NpO_2(ClO_4)_2$, V = $NpO_2(ClO_4)$, and H = $HClO_4$, the activity terms can be separated in the usual manner

$$E = E^\circ - 0.05916 \log \left[\frac{4(M_{VI}{}^3)}{M_H{}^2M_V{}^2} + \frac{(\gamma_{VI}{}^3)}{\gamma_H{}^2\gamma_V{}^2}\right] \qquad (4)$$

Using one extended form of the Debye–Hückel activity theory

$$\log \gamma = -\frac{0.511|Z_+Z_-|\mu^{1/2}}{1 + \mu^{1/2}} + B\mu \qquad (5)$$

Substituting this relation into the activity coefficient term of eq 4, the following relationship can be obtained

$$0.05916 \log \frac{\gamma_{VI}{}^3}{\gamma_H{}^2\gamma_V{}^2} = \frac{0.06046\mu^{1/2}}{1 + \mu^{1/2}} - 0.05916\bar{B}\mu \qquad (6)$$

where $\bar{B} = 3B_{VI} - 2B_H - 2B_V$. Substitution of this result into eq 4 finally yields

$$E' = E + 0.05916 \log \frac{4M_{VI}{}^3}{M_H{}^2M_V{}^2} - \frac{0.06046\mu^{1/2}}{1 + \mu^{1/2}} = E^\circ - 0.05916\bar{B}\mu \qquad (7)$$

E° can now be obtained by plotting E' as a function of μ and extrapolating to infinite dilution in a procedure suggested elsewhere.[26]

Cell solutions were prepared by mixing stock Np(V) and Np(VI) solutions to obtain the desired concentrations, followed by a series of dilutions with either standardized perchloric acid or water. The best results were obtained when Np(VI) solutions prepared with $NpO_2(NO_3)_2 \cdot xH_2O$ were used. Those prepared with neptunium(VI) hydroxide were slow to attain equilibrium, in that the observed change of potential with time was greater for the Np(V)–Np(VI) electrode than for the hydrogen electrode.

Considerable difficulty was involved in obtaining reversible potentials for this cell at these low ionic strengths. A number of various electrodes and solutions, equilibrated for various times, were tried. Consequently, the cell does not behave in an entirely reproducible and reversible manner in all cases. One series of runs appeared to work rather well, and the data from these measurements are summarized in Table IV. It should be pointed out that when more stock $NpO_2(ClO_4)_2$ solution was added to a cell solution of this series, the corrected potential fell somewhat below that expected. However, the addition of perchloric acid corrected this trend, and, while this behavior cannot be satisfactorily explained, a small hydrolysis effect may have been involved.

TABLE IV

DATA FOR THE Np(V)–Np(VI) ELECTRODE

10^2 $[H^+]$, M	10^3 [Np(VI)], M	10^3[Np(V)], M	$10^2\mu$	$-\Delta E$ × 10^2,[a] V	$-E$,[b] abs V	$-E'$, abs V	Total [Np] × 10^3, M
9.100	3.558	9.895	9.100	5.27	1.18620	1.239	13.453
5.688	2.224	6.185	5.688	3.88	1.19951	1.238	8.409
3.412	1.334	3.710	3.411	2.29	1.21399	1.237	5.044
5.853	2.094	6.748	7.156	4.99	1.19324	1.243	8.842
3.269	1.811	3.493	4.192	−0.52	1.21933	1.214	5.304
5.049	1.338	2.582	5.709	8.55	1.20657	1.292	3.920

[a] $\Delta E = 0.05916 \log (4M_{VI}{}^3/M_H{}^2M_V{}^2) - [0.06046\mu^{1/2}/(1 + \mu^{1/2})]$. [b] E°(extrapolated) = 1.236 ± 0.010 V.

The extrapolation of E' to infinite dilution gave a value for the standard potential of the NpO_2^{2+}–NpO_2^+ couple, $E^\circ = -1.236 \pm 0.01$ abs V, for the best series of measurements observed in this research.

Thermodynamic Calculations

The Entropy of $NpO_2^{2+}(aq)$.—The reaction involved for the solubility and heat of solution measurements is

$$NpO_2(NO_3)_2 \cdot 6H_2O(c) = NpO_2^{2+}(aq) + 2NO_3^-(aq) + 6H_2O \qquad (8)$$

The free energy of solution may be calculated from the relationship

$$\Delta F_8^\circ = -RT \ln [4(m\gamma)^3a_{H_2O}{}^6] \qquad (9)$$

The activity coefficients for $NpO_2(NO_3)_2$ and water were estimated by plotting the activity coefficients of Robinson and Lim[27] for closely similar $UO_2(NO_3)_2$

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[24] W. F. Linke, "Solubilities, Inorganic and Metal-Organic Compounds," Vol. 1 and 2, American Chemical Society, Washington, D. C., 1958.

[25] W. M. Latimer, "Oxidation Potentials," 2nd ed, Prentice-Hall Inc., Englewood Cliffs, N. J., 1952, p 367.

[26] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd ed, Reinhold Publishing Corp., New York, N. Y., 1958, p 430 ff.

[27] R. A. Robinson and C. K. Lim., *J. Chem. Soc.*, 1840 (1951).

solutions as a function of molality. The γ values at 2.95 m were estimated to be 1.97 and 0.7535, respectively. With these estimates, $\Delta F_8^\circ = -2940 \pm 260$ cal/mol.

The average value for the heat of solution obtained in this research is $\Delta H_8 = 5160 \pm 130$ cal/mol. The Np(VI) concentration in the calorimeter was about 2×10^{-3} M. An extended form of the Debye–Hückel theory can be used to make the small correction to infinite dilution. The heat of dilution of the electrolyte ϕ_L can be approximated at these concentrations as[28]

$$\phi_L = \frac{\nu}{2} A_H |Z_+Z_-| \mu^{1/2} \alpha - 2.303RT^2 \nu_+\nu_- \left(\frac{dB}{dT}\right) M \quad (10)$$

where

$$\alpha = (1 + \mu^{1/2})^{-1} - \sigma(\mu^{1/2})/3 \quad (11)$$

The function $\sigma(\mu^{1/2})$ has been tabulated elsewhere.[29] Thus, it follows that

$$\Delta H_s^\circ = \Delta H_s - \frac{\nu}{2} A_H |Z_+Z_-| \mu^{1/2} \alpha - 2.303RT^2 \nu_+\nu_- \left(\frac{dB}{dT}\right) M \quad (12)$$

Using values tabulated elsewhere[30] for other 2:1 electrolytes, $\nu = 3$, $A_H = 688$, $\mu^{1/2}\alpha = 0.0487$, $dB/dT = 1.6 \times 10^{-3}$, and $M = 2 \times 10^{-3}$, then $\Delta H_s^\circ = \Delta H_s - 103$ and $\Delta H_s^\circ = 5060 \pm 100$ cal/mol. Assuming that the first hydrolysis constant for Np(VI) can be taken to be the same as that suggested by Baes and Meyer[31] for U(VI), $K \approx 2 \times 10^{-6}$, any small corrections due to this effect can be estimated. Under the conditions in the calorimeter, Np(VI) was 0.3% hydrolyzed. Using the reported value[31] for the heat of hydrolysis of U(VI) at 25° of 10.5 kcal/mol, the hydrolysis contribution amounts to only 6×10^{-2} cal, a negligible amount.

ΔS_8° can now be obtained from the ΔF_8° and ΔH_8° values yielding $\Delta S_8^\circ = 26.8$ gibbs mol^{-1}.

It should be possible to reliably estimate the entropy of crystalline $NpO_2(NO_3)_2 \cdot 6H_2O$ from the experimentally known value for $UO_2(NO_3)_2 \cdot 6H_2O$ of 120.9 gibbs mol^{-1}. The U(VI) ion has no unpaired electrons while the Np(VI) ion has one, and there will be a magnetic contribution to the entropy of the Np(VI) ion. If it is assumed that there is no spin–orbit coupling for this electron, then the magnetic entropy would be due only to the magnetic moment of the electron from its own spin, so that S_{mag}(spin only) $= R \ln (2S + 1) = 1.4$ gibbs mol^{-1}. If spin–orbit coupling does occur, however, the Russell–Saunders treatment gives a magnetic entropy contribution $S_{mag} = R \ln (2J + 1) = 3.6$ gibbs mol^{-1}. Because the presence of spin–orbit coupling is not known for certain, an average value will be taken so that $S_{mag} = 2.5 \pm 1.1$ gibbs mol^{-1}. This conclusion is similar to the one reached by Figgis.[32] The entropy of $NpO_2(NO_3)_2 \cdot 6H_2O$ can now be estimated to be 123.4 ± 1.1 gibbs mol^{-1}, and the entropy of the Np(VI) ion is obtained from ΔS_8° to be -20.3 gibbs mol^{-1}. Giving due consideration to the reliability of some of the estimates used in obtaining this number, the value -20 ± 2 gibbs mol^{-1} will be adopted for the partial molal entropy of NpO_2^{2+}(aq). Auxiliary values for other species in eq 8 were from the Bureau of Standards compilation.[33]

The Entropy of Np(V).—The entropy of Np(V) can be obtained from the heat of reduction of Np(VI) by H_2O_2 (eq 1). Making corrections for dilution as before to the observed heat of reduction, $\Delta H_1 = -10{,}601$ cal mol^{-1}, ΔH_1° is reliably estimated to be $-10{,}454$ cal mol^{-1}. In this calculation it should be noted that the heat of formation of 0.33 M H_2O_2 (as used in the calorimeter) is essentially the same as the value at infinite dilution;[33] thus, the corrected value $\Delta H_2^\circ = 28.07 \pm 0.14$ kcal mol^{-1}, can be combined with the free energy, $\Delta F_3^\circ = 28.51$ kcal mol^{-1}, for the NpO_2^{2+}–NpO_2^+ electrode to obtain $\Delta S_3^\circ = -1.5$ gibbs mol^{-1}. Using auxiliary data as before,[32] and the experimental value for the entropy of NpO_2^{2+}(aq) as given earlier, the partial molal entropy of NpO_2^+(aq) becomes -6.2 ± 2 gibbs mol^{-1}.

Other Actinide Thermodynamic Functions

It is possible to make more reliable estimates of thermodynamic functions for other actinide element ions than has been possible using the experimentally determined values for NpO_2^{2+} and NpO_2^+ from this research. A few of these are summarized below.

Table V

Estimated E° Values for Actinide(V)–Actinide(VI) Electrode Potentials

Couple	E_{formal}, abs V	Ref	E°, abs V
NpO_2^+–NpO_2^{2+}	−1.136	*a*	−1.236
UO_2^+–UO_2^{2+}	−0.063	*b*	−0.163
PuO_2^+–PuO_2^{2+}	−0.913	*c*	−1.013
AmO_2^+–AmO_2^{2+}	−1.60	*d*	−1.70

[a] J. C. Sullivan, J. C. Hindman, and A. J. Zielen, *J. Amer. Chem. Soc.*, **83,** 3373 (1961). [b] E. S. Kritchevsky and J. C. Hindman, *ibid.*, **71,** 2096 (1949). [c] S. W. Rabideau, *ibid.*, **78,** 2705 (1956). [d] R. A. Penneman and L. B. Asprey, U. S. Atomic Energy Commission Document AECU-936 (1950).

E° Estimates.—The difference between the standard potential of the NpO_2^{2+}–NpO_2^+ electrode, −1.236 V, and the value of the "formal" potential reported elsewhere[34] of −1.136 V is 0.1 V. Therefore it will be assumed that the difference is a constant correction that can be made to the other actinide "formal" potentials. In Table V such corrections are indicated and perhaps

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TABLE VI

ESTIMATED ENTROPIES (IN GIBBS MOL^{-1}) FOR ACTINIDE MO_2^+(aq) IONS AT 25°

		S_{mag}		$\bar{S}°_{MO_2^+(aq)}$		
Element	Ground state	Spin only[a]	Spin–orbit[b]	Spin only[c]		Spin–orbit[d]
U	$^2F_{5/2}$	1.4	3.6	−7.0		−7.0
Np	$^2H_4$	2.2	4.4		−6.2	
Pu	$^4I_{9/2}$	2.8	4.6	−5.6		−6.0
Am	$^5I_4$	3.2	4.4	−5.2		−6.2

[a] $S_{mag} = R \ln (2S + 1)$. [b] $S_{mag} = R \ln (2J + 1)$. [c] $\bar{S}°_{NpO_2^+}$(exptl) − S_{mag,NpO_2^+}(spin only) + S_{mag,MO_2^+} (spin only). [d] $\bar{S}°_{NpO_2^+}$ (exptl) − S_{mag,NpO_2^+}(spin–orbit) + S_{mag,MO_2^+}(spin–orbit).

TABLE VII

ESTIMATED ENTROPIES (IN GIBBS MOL^{-1}) FOR ACTINIDE MO_2^{2+}(aq) IONS AT 25°

		S_{mag}		$\bar{S}°_{MO_2^{2+}(aq)}$		
Element	Ground state	Spin only[a]	Spin–orbit[b]	Spin only[c]		Spin–orbit[d]
U	$^1S_0$	0	0	−21.4		−23.6 (−20 (exptl)[4]
Np	$^2F_{5/2}$	1.4	3.6		−20 (exptl)	
Pu	$^3H_4$	2.2	4.4	−19.2		−19.2
Am	$^4I_{9/2}$	2.8	4.6	−18.6		−19.0

[a] $S_{mag} = R \ln (2S + 1)$. [b] $S_{mag} = R \ln (2J + 1)$. [c] $\bar{S}°_{NpO_2^{2+}(aq)}$ (exptl) − $S_{mag,NpO_2^{2+}}$(spin only) + $S_{mag,MO_2^{2+}}$(spin only). [d] $\bar{S}°_{NpO_2^{2+}(aq)}$(exptl) − $S_{mag,NpO_2^{2+}}$(spin–orbit) + $S_{mag,MO_2^{2+}}$ (spin–orbit).

provide better thermodynamic values for these interesting electrode reactions.

Entropies for Other Actinide Ions.—It is also possible to estimate the entropies for other actinide element oxycations from the value known previously for UO_2^{2+}(aq) and the experimental values determined in this research for NpO_2^+(aq) and NpO_2^{2+}(aq). The greatest uncertainty arises in estimation of the relative magnetic entropy. The effects of size and mass will be negligible only from uranium to americium. In Tables VI and VII, these estimates are summarized, using the separate methods for estimating the magnetic contribution. At the present time it is not possible to predict with certainty which of the two estimates is the more accurate.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
PURDUE UNIVERSITY, LAFAYETTE, INDIANA 47907

Standard-State Entropies for the Aqueous Trivalent Lanthanide and Yttrium Ions[1,2]

BY R. J. HINCHEY[3] AND J. W. COBBLE

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The partial molal entropies of 13 trivalent rare earth and yttrium ions at 25° have been calculated from data in the literature and from this research on the heats and free energies of solution of the hydrated trivalent chlorides. These entropies are from 10 to 15 gibbs mol^{-1} more negative than previous estimates based on the old experimental value for Gd^{3+}(aq). The entropies of the lanthanide ions correlate well with the ionic radius if the internal electronic entropy is first subtracted. Consequently the present data do not demonstrate any effects on the entropy of the postulated change in hydration number occurring near the middle of the 4f group.

I. Introduction

The present estimated and tabulated values for the partial molal ionic entropies of all of the trivalent lanthanide and actinide ions are based upon the single value for Gd^{3+} calculated by Latimer[4,5] from solubility and calorimetric data on $Gd_2(SO_4)_3 \cdot 8H_2O$. The entropy obtained, −43 gibbs mol^{-1}, is subject to considerable error because of the inability to extrapolate the measured heats of solution of gadolinium sulfate to infinite dilution; others[6,7] using the same data have obtained −47 and −48 gibbs mol^{-1}.

It was pointed out recently[7] that the requisite data exist to calculate new values for many of the trivalent lanthanides from thermal and free energy data on the hydrated rare earth chlorides. In using these values to obtain a more reliable set of entropies for all of the trivalent lanthanide ions, a good correlation of the rare earth ionic entropies with radius was observed if the internal electronic entropies were considered. To improve and extend the correlation to all of the lanthanide

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(2) Supported by the U. S. Atomic Energy Commission.

(3) Taken in part from the Ph.D. thesis of R. J. Hinchey, Purdue University, Jan 1967.

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