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ELECTROCHEMICAL DETERMINATION OF THE OXIDATION POTENTIALS AND THE THERMODYNAMIC STABILITY OF THE VALENCE STATES OF THE TRANSURANIUM ELEMENTS IN AQUEOUS ALKALINE MEDIA

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At the end of the 1960s only rough assessments based on thermodynamic data were available of the oxidation potentials of neptunium, plutonium, and americium, as well as data based on solubility products of the hydroxides, ionic radii of the ions, and other factors [1, 2]. The direct electrochemical measurements did not attract the interest of radiation chemists, evidently due to the anticipated poor solubility of the hydroxides of the transuranium elements in aqueous alkaline media. The situation changed after the discovery of the heptavalent state of these elements [3], in which they possess a relatively high solubility in alkaline solutions, which exceeds 0.1 g-ion/liter of the element [4]. Several approaches were made to determine electrochemically the potentials of all valence pairs of neptunium, plutonium, and americium in alkaline solutions, and new data were obtained on the thermodynamic stability of the different valence forms of the elements in these media.

Determination of the Oxidation Potentials of Np, Pu, and Am in Alkaline Solutions. The formal potentials of the pairs, generally accepted in the chemistry of the transuranium elements, were determined in 0.1-0.15 M NaOH and 0.1-4.0 M LiOH. They differ from the standard ones in that they have been measured at equal concentrations and not at the activities of the oxidized and reduced forms of the element (Table 1). It can be seen from the table that data for the potentials of the pairs (VII)-(VI) of plutonium and americium were not available in the literature and that the potential of this pair of neptunium was determined in 1-10 M NaOH without taking into account the diffusion potential between the saturated KCl solution of the calomel reference electrode and the alkaline solutions [5]. In order to determine the potential of the pair (VII)-(VI) of neptunium and plutonium by the compensation method, we have measured [6, 7] the emf of the chain

Pt | C₁ (M) NaOH, [Np (VII)], [Np (VI)] | C₂ (M) NaOH, HgO | Hg

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TABLE 1. Formal Pair Potentials of Neptunium, Plutonium, and Americium in 1 M and 10 M NaOH at 25°C (against the normal hydrogen electrode)

Ele-	1	Pair potentials, V (n. h. e)				
ment	Source of data		(VII)—(VI)	(VI)-(V)	(V) - (IV)	(IV) (III
Np	Lit. data 1 M NaOH Our data	Calculated* Experimental 1M NaOH 10M NaOH	0,588 0,589 0,247	$ \begin{array}{c c} 0,48 \\ 0,30 \\ 0.14 \\ 0,05 \end{array} $	0,39 -0,95 -1,0	-1,76 -1,8 -2,0
Pu	Lit. data 1 M NaOH Our data	Calculated Experimental 1M NaOH 10M NaOH	0.849 0,552	$\begin{array}{c} 0,26\\ 0,24\\ 0,21\\ 0,17\end{array}$	$ \begin{array}{c} 0,76 \\ -0,72 \\ -0,78 \end{array} $	-0,95 -0,96 -1,18
Am	Lit. data 1 M NaOH Our data	Calculated Experimental 1M NaOH 10M NaOII	- 1,05 0,78	$ \begin{array}{c} 1,1\\ 0,65\\ 0,68\\ 0.62 \end{array} $	0,7 - 0,40 0,37	$ \begin{array}{c} -0,4 \\ 0,5 \\ 0.27 \\ 0.25 \end{array} $

* The calculated values of the potentials were obtained according to [1].



Fig. 1. Formal potentials E_0 of the pairs M(VII) - M(VI) of the transuranium elements as function of the logarithm of alkali concentration at 25°: 1) Np(VII) - Np(VI); 2) Pu(VII) - Pu(VI); 3) Am-(VII) - Am(VI).

Fig. 2. Potentials E_0 of the pairs M(VII) - M(VI) of the transuranium elements in aqueous alkali solutions: 1) Np(VII) - Np(VI); 2) Pu(VII) - Pu(VI); 3) Am(VII) - Am(VI); 4) Np(VI) - Np(V); 5) Pu(VI) - Pu(V); 6) Am(VI) - Am(V); 7) equilibrium potential of the oxidation of water with oxygen evolution.

where $C_1 \simeq C_2$. The concentrations of the hexa- and heptavalent Np and Pu were varied in the range from $1 \cdot 10^{-4}$ to $8 \cdot 10^{-3}$ g-ion/liter. At a constant alkali concentration the potential of the pairs Np(VII) - Np(VI) and Pu(VII) - Pu(VI) follows the Nernst equation. With increasing concentration of alkali the formal potentials of the pairs Np(VII) - Np(VI) and Pu(VII) - Pu(VI) decrease symbatically. The relationship between these potentials and the logarithm of alkali concentration is nonlinear (Fig. 1) since the formal potentials have been calculated without account of the unknown activity coefficients of the ions of the transuranium elements and of hydroxyl. The potential of the pair Am(VII) - Am(VII) in alkaline solutions could not be measured by the direct potentiometric method, because its large value significantly exceeded the potential of O₂ evolution from aqueous solutions at the Pt electrode. Thus, the potential of Am(VII) - Am(VI) in 1 M NaOH was determined by correlation from the optical absorption spectra of Np(VII), Pu(VII), and Am(VII), and from our measured potentials of the pairs Np(VII) - Np(VI) and Pu(VII) - Pu(VI). This was based on the linear relationship which exists between the frequency of bands with charge transfer in the spectra of the alkaline solutions of U(VI), Np(VI), Pu(VI), and Am(VI) and the potentials of the pairs (VI) - (V) of these elements. A similar relationship was constructed for the heptavalent elements and a value of 1.05 V [8] obtained for the potential of the pair Am(VII) - Am(VI) in 1 M NaOH. The values of this potential in solutions with a higher alkali content were obtained by extrapolation, by assuming that the character of change of the potential of the pair (VII) - (VI) with increasing alkali concentration was symbatic not only for Np and Pu, but also for

[NaOH],		AgO	[NaOH],	K7[Cu (IO8)2]		
mole/ liter	calc.,%	found,%	mole/ liter	calc.,%	found, %	
1,2 3,7 5,6 7,8 11,0 14,7	0,5 2 9 41 100 100	$ \begin{array}{c} >5 \\ >5 \\ 8 \\ 37 \\ 97 \\ 99 \end{array} $	6,8 8,4 9,6 11,1 14,0 15,9	0 7 46 59 74 99,9	0 5 43 57 72 97	

TABLE 2. Calculated and Experimental Yields of Pu(VII)in the Reactions of Pu(VI) with Ag(II) and Cu(III) in Solutions with Different Alkali Concentrations



Fig. 3. Calculated and experimental degrees of disproportionation of Am(VI) in alkaline solutions: 1) calculated; 2) determined.

Am. A comparison of the potentials of the pairs M(VII) - M(VI) of plutonium (0.849 V) and americium (1.05 V) in 1 M NaOH with the standard potentials of known oxidants in an alkaline medium shows that Pu(VII) and particularly Am(VII) can be considered as strong oxidants. If we take into account only the potential-forming oxidants which in distinction from ozone and persulfate possess high exchange currents, and which are capable of creating high electrode potentials by polarization, Pu(VII) and Am(VII) in 1 M NaOH must be considered as the strongest potential-forming oxidants. With increasing alkali concentration the formal potentials of the (VII) - (VI) pairs of Np, Pu, and Am, and consequently also the oxidizing properties of the heptavalent elements decrease significantly. The difference between the formal and standard potentials is small in dilute electrolyte solutions and increases with the increasing ionic strength of the solution. It was therefore necessary to check the possibility of using our formal potentials to predict the direction and degree of completeness of chemical reactions, occurring with the participation of heptavalent transuranium elements in concentrated alkaline solutions.

The interaction of Pu(VI) in 1-14 M NaOH with KMnO_4 , silver oxide and Cu(III) periodate was studied. A comparison of the formal potentials obtained for the pair Pu(VII) – Pu(VI) at different alkali concentrations with the standard values for the pairs $\text{MnO}_4^- - \text{MnO}_4^{2^-}$ and $\text{AgO}-\text{Ag}_2\text{O}$ which depend only weakly on concentration, has shown that KMnO_4 and silver oxide must oxidize Pu(VI) at alkali concentrations > 8 moles/liter; in dilute alkaline solutions the reaction must go in the opposite direction. The predicted conditions for the reactions and the yields of Pu(VII) in solutions with different alkali concentrations have been confirmed by spectrophotometry [9]:

$$\begin{array}{l} \operatorname{Pu}(\operatorname{VI}) + \operatorname{MnO}_{4}^{2} \xleftarrow[\operatorname{NaOH}] > 8M \\ \operatorname{Pu}(\operatorname{VI}) + \operatorname{AgO} & \xleftarrow[\operatorname{NaOH}] > 8M \\ \end{array} \\ \begin{array}{l} \operatorname{Pu}(\operatorname{VI}) + \operatorname{AgO} & \xleftarrow[\operatorname{NaOH}] > 8M \\ \end{array} \\ \end{array} \\ \begin{array}{l} \operatorname{Pu}(\operatorname{VII}) + \operatorname{AgO} & \xleftarrow[\operatorname{NaOH}] > 8M \\ \end{array} \\ \end{array}$$

The reaction of Cu(III) in the complex $K_7[Cu(IO_6)_2]$ with Np(VI) and Pu(VI) gives Np(VII) at an alkali concentration > 1 M NaOH and of Pu(VII) at the concentration > 11 M NaOH. This is in agreement with the formal potentials found for the pairs Np(VII)-Np(VI) and Pu(VII)-Pu(VI) [10].

It follows from Table 2 that our values for the formal potentials of the (VII) - (VI) pairs of neptunium, plutonium, and americium can be used to predict not only the direction but also the degree of completion of redox reactions with the participation of the heptavalent transuranium elements.

The potentials of the pair (VI)-(V) (see Table 1) were determined for Np and Pu potentiometrically [11, 12], and for Am from the half-wave potential of the reversible polarographic reactions $Am(VI) + e \rightarrow Am(V)$ and $Am(V) - \bar{e} \rightarrow Am(VI)$ [13]. The potentials of the (VI)-(V) pairs of Np, Pu, and Am change only little as the concentration of the alkali increases from 0.5 to 15 M NaOH (Fig. 2) and thus, differ significantly from the potentials of the (VII)-(VI) pairs of these elements. Changing from NaOH to LiOH solutions with the same concentrations, the potentials of the pairs (VII) - (VI) and (VI) - (V) of Np and Pu increase by 7-10 mV [11, 12]. It must be pointed out that in an alkaline medium, for instance in 1 M NaOH, the potential of the pair Pu(VI) – Pu(V) (0.24 V) is higher than that of the same pair of Np (0.14 V), while the picture is opposite in an acidic medium (for instance, 1 M HClO₄): the potential of the pair (VI) - (V) for Pu, equal to 0.914 V, is lower than that of the same pair for No (1.137 V). The causes for this inversion of the potentials for the (VI) - (V) pairs of Np and Pu when changing from an acidic medium to an alkaline medium have not been established. They may be related to the form in which the ions of Np(VI) and Pu(VI) exist in an alkaline solution, however, the data available on the forms of the ions of hexa- and heptavalent transuranium elements in alkaline solutions are only qualitative. The potentials of the pairs (V) - (IV) and (IV) - (III) of Np, Pu, and Am cannot be measured potentiometrically, due to the poor solubility of the hydroxides of the tetra- and trivalent elements. These potentials were derived from the polarographic reduction of Pu(V) in alkaline solutions at the dropping Hg electrode and of Am(V) at the rotating-disc Pt electrode. In alkaline solutions (1-10 M NaOH) Np(V) is reduced at the dropping Hg cathode only at potentials which cause H_2 evolution (more negative than -1.1 V). In the same way the potentials of the pairs Np(V) - Np(IV) and Np(IV) - Np(III) in alkaline solutions have been assessed on the basis of the potentials measured in 1 M $HClO_4$ and from the potential shifts of Pu(V) - Pu(IV) and of Pu(IV) - Pu(III) in the transition from 1 M HClO₄ to 1 M NaOH. Due to the irreversibility of the reactions $M(V) + \bar{e} \rightarrow M(IV)$ and $M(IV) - \bar{e} \rightarrow M(V)$ for Pu and Am, the precision of the potentials of the pairs (V) - (IV)and (IV) - (III) in alkaline solutions is poor and amounts to ± 30 mV. However, the experimental results obtained have significantly improved the available calculated potentials of the pairs (V) - (IV) and (IV) - (III) for Np and Am, as well as the potential of (V) = (IV) for Pu (see Table 1).

Thermodynamic Stability of the Oxidation States of Np, Pu, and Am in Aqueous Alkaline Solutions. Under the thermodynamic stability of the oxidation state of an element in an aqueous solution we understand its ability to exist in this medium without entering into a redox reaction with water with the evolution of oxygen or hydrogen and without disproportionation into other valence forms. A comparison of our values for the potentials of Np(VII) – Np(VI), Pu(VII) – Pu(VI), and Am(VII) – Am(VI) with the equilibrium potential for the evolution of O_2 from alkaline solutions (0.4 V in 1 M NaOH) [14] shows that Pu(VII), Am(VII), and Am(VI) are capable of oxidizing water with the evolution of oxygen over the whole interval of alkali concentrations studied (0.1–15 M NaOH). Np(VII) is capable of oxidizing water at an alkali concentration of less than 7 moles/liter; at higher alkali concentrations it becomes thermodynamically stable in this respect, since the potential of Np(VII) – Np(VI) becomes smaller than the potential for the evolution of hydrogen from 1 M NaOH. A general characteristic of the potentials of all pairs of transuranium elements is their significant drop in the transition from acidic to allaline solutions. This increases the stability of the valence-form oxidants such as Np(VII), Pu(VII), Am(VII), and Am(IV), and Am(IV), and reduces the stability of the reducing agents such as Np(III) and Pu(III).

The ability of the oxidizing states of Np, Pu, and Am to disproportionate also changes significantly in the transition from the acidic to the alkaline solutions. Np(V), Pu(V), Pu(IV), Am(V), and Am(IV) are capable of disproportionation in acidic solutions. In order to assess this ability in alkaline solutions, the potentials were used given in Table 1 and Fig. 2 against the normal hydrogen electrode. The values of $\Delta G - n FE_0$ were calculated for all hypothetical disproportionation reactions of the transuranium elements studied, for instance, for $2Pu(V) \rightarrow Pu(VI) + Pu(IV)$, $3Pu(V) \rightarrow Pu(VII) + 2Pu(IV)$, and others in 0.1-15 M NaOH. It was found that. in distinction from the acidic solutions, in 0.1-15 M NaOH disproportionation of all valence forms of Pu is thermodynamically not possible. Disproportionation is also impossible for all oxidation states of Np and Am in 1 M NaOH, however, by increasing the concentration of the alkali in the range 11-15 M NaOH, the potentials of the pairs (VII)-(VI) and (VI)-(V) of each element first approach each other, then they change their sign (see Fig. 2), and disproportionation $2M(VI) \rightarrow M(VII) + M(V)$ in the case of Np and Am takes place in concentrated alkaline solutions [14, 15]. Let us establish the relationship between the degree of disproportionation α , i.e., the fractions of Am(VI) or Np(VI) converted to the hepta- and pentavalent forms and the potentials E_{7-6} and E_{6-5} of the pairs (VII) – (VI) and (VI) – (V) of the element in solutions with different alkali concentrations. Let us denote with C_0 the total concentration of Am, introduced in the solution in hexavalent form. The equilibrium concentrations of the hepta- (C_7) , penta- (C_5) , and hexavalent (C_6) americium will then be, when the disproportionation reaction is completed, equal to $C_7 = C_5 = (1/2) \alpha C_0$, and $C_6 = (1 - \alpha)C_0$. By expressing the

oxidation potential of the solution after equilibrium is established by the Nernst equation, on the one hand, by the formal potential E_{7-6} and the concentrations C_7 and C_6 , and, on the other hand, by E_{6-5} and the concentrations C_6 and C_5 , we obtain the equation

$$E_{7-6} + \frac{RT}{F} \ln \frac{C_7}{C_6} = E_{6-5} + \frac{RT}{F} \ln \frac{C_6}{C_5}$$
(1)

By expressing the concentrations C_7 , C_6 , and C_5 through C_0 and α and after simple transformations, we obtain expressions which relate the degree of disproportionation α with the potentials of the pairs (VII) - (VI) and (VI) - (V)

$$E_{7-6} - E_{6-5} = \Delta E = 2 \frac{RT}{F} \ln \frac{2(1-\alpha)}{\alpha}$$
(2)

$$\alpha = \left(1 + \frac{1}{2} e^{\Delta E \frac{F}{2RT}}\right)^{-1} \tag{3}$$

The degrees of disproportionation of Am(VI) in alkaline solutions, calculated from Eq. (3) from the potentials of the pairs Am(VII)-Am(VI) and Am(VI)-Am(V) given in Fig. 2, as well as the degrees of disproportionation determined experimentally [15] are in good agreement (Fig. 3).

CONCLUSIONS

1. The oxidation potentials of neptunium, plutonium, and americium in the valence states from (III) to (VII) have been determined experimentally in 0.1-15 M NaOH.

2. Heptavalent plutonium and americium are thermodynamically able to oxidize water with the evolution of oxygen in 0.1-15 M NaOH, neptunium(VII) in 0.1-7 M NaOH.

3. All valence states of plutonium resist disproportionation in alkaline solutions; in the case of neptunium and americium only one disproportionation reaction is possible; of the hexavalent state in to penta- and heptavalent states. The degree of completion of the reaction can be calculated accurately from the oxidation potentials determined.

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