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Redox Potentials of PuO_2^{2+}/PuO_2^{+} and Pu^{4+}/Pu^{3+} at Different Ionic Strengths and Temperatures. Entropy and Heat Capacity.

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The redox potentials of the reversible couples of plutonium are measured by using cyclic voltammetry, in perchloric media at ionic strength *I,* and temperature *T*. At each *T*, the experimental results, *E(T,I)*, are extrapolated to *I = 0* by applying the Specific Interaction Theory (S.I.T.) to get interaction coefficients $\Delta\varepsilon(T)$, and *E(0, T)* (e.g., standard potential *E°*, when *T = 25°C*). It is shown that a systematic error due to disproportionation or redox impurities could explain some discrepancies observed between numerical values already published. The experimental data are fitted to the following series expansion about *T°*:

$$E(T) = E(T°) + \frac{\Delta S(T°)}{F}(T-T°) + \frac{\Delta C_p(T°)}{2T°F}(T-T°)^2 + ...$$

The entropy changes of ΔS, and heat capacity changes ΔC_p, are then determined. A second order expansion of $\Delta\varepsilon(T)$ and of the Debye Huckel term are used to propose extended S.I.T. equations that account for both the ionic strength and the temperature influences on ΔG, ΔS, ΔC_p, ΔH, and lgK. These equations are first checked using published mean activity coefficients of HCl and NaCl and then for redox equilibria of plutonium.

For the PuO_2^{2+}/PuO_2^{+} couple

$E°$ = 968 ± 10 mV

$\Delta\varepsilon(T)$ = -0,22 ± 0.03 kg.mol^{-1}

$\left(\frac{\partial \Delta \epsilon}{\partial T}\right)_P$ = 0.001 kg(mol.K)$^{-1}$

$\frac{\Delta S°}{F}$ = 0.34 ± 0.04 mV.K^{-1}

$\frac{\Delta C_p}{F}$ = 4.04 ± 0.90 mV.K^{-1}

and for the Pu^{4+}/Pu^{3+} couple

$E°$ = 1044 ± 10 mV

$\Delta\varepsilon(T)$ = -0,33 ± 0.05 kg.mol^{-1}

$\left(\frac{\partial \Delta \epsilon}{\partial T}\right)_P$ = 0.002 kg(mol.K)$^{-1}$

$\frac{\Delta S°}{F}$ = 1.67 ± 0.14 mV.K^{-1}

$\frac{\Delta C_p}{F}$ = 1.77 ± 3.20 mV.K^{-1}

The small discrepancy between the numerical values of entropy changes deduced from electrochemical and calorimetric techniques are discussed for actinides redox couples.