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Redox potentials of M(VI)/M(V) limiting carbonate complexes (M = U or Pu) at different ionic strengths and temperatures. Entropy and heat capacity. .

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For waste disposal programs, actinide aqua ions and limiting complexes had been studied by cyclic voltametry. Measured redox potentials in non complexing media were modelled by using SIT and Taylor's series expansions to the second order for ionic strength I, and temperature T, influences. These data treatments give standard values for redox potential E degrees, corresponding Delta S degrees, Delta H degrees and Delta C(p)degrees of reactions, and excess values (variations of E'degrees, Delta S, Delta H and Delta C-p with I) that can be deduced by using T influence on fitted SIT coefficients Delta epsilon. This methodology is used here at 5 to 70 ℃ in 0.3 to 1.5 M Na_2CO_3 media (I = 0.9 to 4.5 M).

$$E^\circ = 0.191 \pm 0.015 \ (-0.779 \pm 0.010) \text{ V/SHE},$$
$$\Delta S^\circ = -178 \pm 37 \ (-174 \pm 5) \text{ J.K}^{-1}\text{.mol}^{-1}$$
$$\Delta Cp^\circ = -516 \pm 744 \ (-414 \pm 176) \text{ J. K}^{-1}\text{.mol}^{-1}$$

and

$$\Delta\varepsilon = -0.17_5 \pm 0.04 + (2.1 \pm 2.0)10^{-3}\,\Delta T - (2.4 \pm 7.7)10^{-5}\,(\Delta T)^2/2$$
$$(-0.91 \pm 0.10 + (7.0 \pm 1.9)10^{-3}\,\Delta T - (5.8 \pm 0.11)\,10^{-5}\,(\Delta T)^2/2) \text{ kg.mol}^{-1}$$

are obtained at 25℃ and I = 0 for the

$$MO_2(CO_3)_3^{4-} + e^- \rightarrow MO_2(CO_3)_3^{5-}$$

reaction where M = Pu and U respectively).

$$\lg(\beta_3^{V}/\beta_3^{VI}) = -12.6 \pm 0.3 \ (-14.65 \pm 0.17)$$

is deduced.

$$\lg \text{ beta(3)(V)} = 3.1 \pm 1.4 \ (6.95 \pm 0.18)$$

is proposed using published beta(3)(VI) values.