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Chemical equilibria in actinide carbonate systems

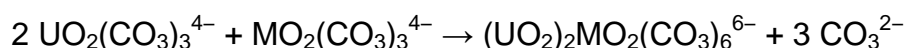
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By spectrophotometric and potentiometric methods it is shown that trimers are formed in media of high ionic strength (3 M NaClO₄) and total concentrations of hexavalent actinides higher than 10⁻³ M. The equilibrium constants for the reactions



are $\lg K(\text{U}) = -11.3 \pm 0.1$; $\lg K(\text{Np}) = -10.1 \pm 0.1$; $\lg K(\text{Pu}) = -7.4 \pm 0.2$. It is demonstrated that one of the cations of the trimer can be exchanged with another actinide cation: the equilibrium constants for the reactions



are $\lg K = -11.3 \pm 0.1, -10.0 \pm 0.2$ and -8.8 respectively for $M \equiv \text{U}, \text{Np}, \text{Pu}$. Thus, polynuclear complexes can be efficient solution "carriers" for other hexavalent actinides in waste disposal. Some properties of the solid phases $\text{MO}_2\text{CO}_3(\text{s})$ are discussed.

Experimental studies of chemical equilibria of americium (III, IV) are reviewed: in carbonate media americium(III) species are AmCO_3^+ , $\text{Am}(\text{CO}_3)_2^-$, $\text{Am}(\text{CO}_3)_3^{3-}$, $(\text{Am}_2(\text{CO}_3)_3)_\text{s}$ and $(\text{NaAm}(\text{CO}_3)_2)_\text{s}$; for americium-(IV) $\lg \beta_5 \approx 40$.

In 3 M NaClO₄ solubility measurements of neptunium(V) show that $\lg \beta_1 = 5.09$, $\lg \beta_2 = 8.15$, $\lg \beta_3 = 10.46$, $\lg K_\text{s}(\text{NaNpO}_2\text{CO}_3) = -10.56$ and $\lg K_\text{s}(\text{Na}_3\text{NpO}_2(\text{CO}_3)_2) = -12.44$; ionic strength corrections are proposed on the basis of these results.