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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Data Treatment

$E_{T,I}$ Experimental Data

Data at I = 0

I Regression

T Regression

Modelling

$E_{(T,I)}\ F/(R\ T\ \ln 10) - 9\ D_{T,I} = E_{(T,0)}\ F/(R\ T\ \ln 10) - \Delta\varepsilon_T\ m_{Na^+}$

$E_{T,I} \approx E_{T°,I} + \Delta S_{T°,I} / F\ \Delta T + \Delta Cp_{T°,I} / (2\ F\ T°)\ \Delta T^2$

$E_{T,I} \approx E_{T°,0} + \Delta S_{T°,0} / F\ \Delta T + \Delta Cp_{T°,0} / (2\ F\ T°)\ \Delta T^2$

$\Delta\varepsilon_T \approx \Delta\varepsilon_{T°} + \Delta\varepsilon'_{T°}\ \Delta T + (\Delta\varepsilon''_{T°} / 2)\ \Delta T^2$

SIT formula for I corrections on E, ΔS, ΔCp and ΔH

$$E_{(T,I)} = E_{(T,0)} + (9\ D_{T,I} - \Delta\varepsilon_T\ m_{Na^+})\ R\ T\ \ln 10 / F$$

$$\Delta S_{T°,I} = \Delta S_{T°,0} + [9\ (D_{T°,I} + T°\ D'_{T°,I}) - (\Delta\varepsilon_{T°} + T°\ \Delta\varepsilon'_{T°})\ m_{Na^+}]\ R\ \ln 10$$

$$\Delta Cp_{T°,I} = \Delta Cp_{T°,0} + [9\ (2\ D'_{T°,I} + T°\ D''_{T°,I}) - (2\ \Delta\varepsilon'_{T°} + T°\ \Delta\varepsilon''_{T°})\ m_{Na^+}]\ R T°\ \ln 10$$

$$\Delta H_{T°,I} = \Delta H_{T°,0} + [9\ D'_{T°,I} - \Delta\varepsilon'_{T°}\ m_{Na^+}]\ R\ T°^2\ \ln 10$$