

**Temperature and ionic strength influence on
U(VI/V) and U(IV/III) redox potentials
in aqueous acidic and carbonate solutions**

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Redox potentials:

$$E(\text{UO}_2^{2+}/\text{UO}_2^+) = 60 \pm 4 \text{ mV/NHE},$$

$$E(\text{U}^{4+}/\text{U}^{3+}) = -630 \pm 4 \text{ mV/NHE}$$

measured at 25°C in acidic medium (HClO_4 1M) using cyclic voltametry are in accordance with the published data. From 5°C to 55°C the variations of the potentials of these systems (measured against Ag/AgCl electrode) are linear. The entropies are then constant:

$$[\Delta S(\text{UO}_2^{2+}/\text{UO}_2^+) - \Delta S(\text{Ag}/\text{AgCl})]/F = 0 \pm 0.3 \text{ mV/}^\circ\text{C},$$

$$[\Delta S(\text{U}^{4+}/\text{U}^{3+}) - \Delta S(\text{Ag}/\text{AgCl})]/F = 1.5 \pm 0.3 \text{ mV/}^\circ\text{C}.$$

From 5°C to 55°C, in carbonate medium ($\text{Na}_2\text{CO}_3=0.2\text{M}$), the Specific Ionic Interaction Theory can model the experimental results up to $I=2\text{M}$ (Na^+ , ClO_4^- , CO_3^{2-}):

$$E(\text{UO}_2(\text{CO}_3)_3^{4-}/\text{UO}_2(\text{CO}_3)_3^{5-}) = -778 \pm 5 \text{ mv/NHE} (I=0, T=25^\circ\text{C}),$$

$$\Delta\varepsilon(25^\circ\text{C}) = \varepsilon(\text{UO}_2(\text{CO}_3)_3^{4-}, \text{Na}^+) - \varepsilon(\text{UO}_2(\text{CO}_3)_3^{5-}, \text{Na}^+) = 0.92 \text{ kg/mole},$$

$$\Delta S(\text{UO}_2(\text{CO}_3)_3^{4-}/\text{UO}_2(\text{CO}_3)_3^{5-}) = -1.8 \pm 0.5 \text{ mV/}^\circ\text{C} (I=0),$$

$$\Delta\varepsilon = \varepsilon(\text{Cl}^-, \text{Na}^+) = (1.14 - 0.007T) \text{ kg/mole}.$$

The U(VI/V) potential shift, between carbonate and acidic media, is used to calculate (at $I=0, 25^\circ\text{C}$):

$$\lg \frac{\beta_3 U(V)}{\beta_3 U(VI)} = -14,7 \pm 0,5$$

and then

$$\lg \beta_3 U(V) = 6.6 \pm 0,5$$