

Interpretation of temperature influence on sorption

The slope of $R \ln K_d$ vs $1/T = -\Delta H_{\text{measured}}$

For the following sorption equilibrium:



the equilibrium constant is:

$$K = \frac{[\text{HCO}_3^-] [\text{CO}_3^{2-}]^2 [\text{NpO}_{2(\text{f})}]}{([\text{NpO}_2(\text{CO}_3)_3^{5-}] [\text{H}_{(\text{f})}])}$$

$$K \approx \frac{[\text{HCO}_3^-] [\text{CO}_3^{2-}]^2}{[\text{H}_{(\text{f})}]} K_d$$

derivating this equation we obtain

$$(d \log_{10} K)_T \approx 0 + 0 + (d \log_{10} K_d)_T - 0$$

since in our experimental conditions

$[\text{HCO}_3^-]$, $[\text{CO}_3^{2-}]$ and $[\text{H}_{(\text{f})}]$ did not vary with T.

Finally: $(d \log_{10} K)_T \approx (d \log_{10} K_d)_T$

hence

the slope of $R \ln K_d$ vs $1/T$

\approx the slope of $R \ln K$ vs $1/T$

using Van't Hoff equation

$$= -\Delta H_{\text{measured}}$$

Thermodynamic cycle to interpret Np sorption

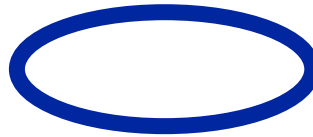
$$\Delta H_{\text{measured}} = 0.4 \pm 1.7 \text{ kJ.mol.}^{-1}$$



$$\Delta H(\beta_3) \approx$$

$$-16 \pm 3$$

$$\text{kJ.mol.}^{-1}$$



$$\Delta H(K_1) =$$

$$15.4 \pm 4$$

$$\text{kJ.mol.}^{-1}$$



$$\Delta H_{\text{H/Np}} \approx -1 \pm 6 \text{ kJ.mol.}^{-1}$$

$$\Delta H_{\text{H/Np}} = \Delta H(\beta_3) + \Delta H_{\text{measured}} + \Delta H(K_1)$$

Another presentation of the above thermodynamic cycle:

$$\begin{aligned}
 \Delta H_{\text{measured}} & : \quad \text{NpO}_{2(f)} + \text{HCO}_3^- + 2 \text{CO}_3^{2-} - \text{H}_{(f)} - \text{NpO}_2(\text{CO}_3)_3^{5-} \\
 & = \text{NpO}_{2(f)} - \text{H}_{(f)} - \text{NpO}_2(\text{CO}_3)_3^{5-} + 2 \text{CO}_3^{2-} + \text{HCO}_3^- \\
 = \Delta H_{\text{H/Np}} & : = \text{NpO}_{2(f)} - \text{H}_{(f)} & - \text{NpO}_2^+ + \text{H}^+ \\
 - \Delta H(\beta_3) & : \quad - \text{NpO}_2(\text{CO}_3)_3^{5-} + 2 \text{CO}_3^{2-} & + \text{NpO}_2^+ & + \text{CO}_3^{2-} \\
 - \Delta H(K_1) & : \quad + \text{HCO}_3^- & & - \text{H}^+ - \text{CO}_3^{2-}
 \end{aligned}$$