CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE

Temperature influence on ionic exchanges on clayey minerals, deduced from column experiments (Summary)

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Interpretation of temperature influence on sorption

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

For the following sorption equilibrium:

$$HCO_3^- + 2\ CO_3^{2-} + \mathbf{NpO_{2(f)}} \leftarrow \mathbf{NpO_2(CO_3)_3^{5-}} + H_{(f)}$$

the equilibrium constant is:

$$K = [HCO_3^-]\,[CO_3^{2-}]^2\ \mathbf{[NpO_{2(f)}]}\ /\ (\mathbf{[NpO_2(CO_3)_3^{5-}]}\ [H_{(f)}])$$

$$K \approx [HCO_3^-]\,[CO_3^{2-}]^2\ \mathbf{K_d}\ /\ [H_{(f)}]$$

derivating this equation we obtain

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

since in our experimental conditions

$[HCO_3^-]$, $[CO_3^{2-}]$ and $[H_{(f)}]$ did not vary with T.

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

hence the slope of **R ln K_d** vs 1/T

≈ the slope of R ln K vs 1/T

using Van't Hoff equation = $-\Delta H_{measured}$

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Thermodynamic cycle to interpret Np sorption

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

$$\mathbf{H_{(f)}} + NpO_2(CO_3)_3^{5-} \rightarrow \mathbf{NpO_{2(f)}} + HCO_3^- + 2\,CO_3^{2-}$$

$\Delta H(\beta_3) \approx -16 \pm 3$ kJ.mol.$^{-1}$ ↑ — ↓ $\Delta H(K_1) = 15.4 \pm 4$ kJ.mol.$^{-1}$

$$\mathbf{H_{(f)}} + NpO_2^+ + 3\,CO_3^{2-} \rightarrow \mathbf{NpO_{2(f)}} + H^+ + CO_3^{2-} + 2\,CO_3^{2-}$$

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

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

Another presentation of the above thermodynamic cycle:

$\Delta H_{measured}$: $\mathbf{NpO_{2(f)}} + HCO_3^- + 2\,CO_3^{2-} - \mathbf{H_{(f)}} - NpO_2(CO_3)_3^{5-}$

$= \mathbf{NpO_{2(f)}} - \mathbf{H_{(f)}} - NpO_2(CO_3)_3^{5-} + 2\,CO_3^{2-} + HCO_3^-$

$= \mathbf{\Delta H_{H/Np}}$: $= \mathbf{NpO_{2(f)}} - \mathbf{H_{(f)}} - NpO_2^+ + H^+$

$-\Delta H(\beta_3)$: $-NpO_2(CO_3)_3^{5-} + 2\,CO_3^{2-} + NpO_2^+ + CO_3^{2-}$

$-\Delta H(K_1)$: $+HCO_3^- - H^+ - CO_3^{2-}$