D$_2$O Isotope Effects on Chemical Reactions under CANDU Operating Conditions

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Magnetite Solubility in Nuclear Reactor Primary Coolant Circuits

- An increase of 1 pH unit avoids in-core deposits
- Minimizes $^{60}$Co activity transport
- Impact on long-term feeder thinning?
- Behaviour in D$_2$O?
Magnetite Solubility

Aqueous Solution

\[ \text{Fe}^{2+} \rightleftharpoons \text{FeOH}^{+} \rightleftharpoons \text{Fe(OH)}_{2}^{0} \rightleftharpoons \text{Fe(OH)}_{3}^{-} \]

Metal Oxide

\[ \text{Fe}_3\text{O}_4 \]

Deuterium Isotope Effects at 25 °C

\[ \Delta pK = \{ pK_a(D_2O) - pK_a(H_2O) \} \approx 0.45 \]

Laughton and Robertson in Cotzee and Ritchie, *Solute-Solvent Interactions* (Marcel Dekker, NY, 1969)
Equilibrium Constant as a Function of Temperature
The Relation to Standard Partial Molar Properties

\[ \ln K_T = \ln K_{298} - \frac{1}{R} \left[ \frac{1}{T} - \frac{1}{298} \right] \Delta H^o_{298} + \frac{1}{R} \left[ \frac{\Delta C^o_p}{T} \right]_T + \frac{1}{RT} \left[ \Delta C^o_p \right]_T - \frac{1}{RT} \left[ \Delta V^o \right]_T - \frac{1}{RT} \int_1^p \Delta V^o \, dP \]

\[ \left( \frac{\partial \Delta H^o}{\partial T} \right)_p = \Delta C^o_{p,R} \]

\[ \left( \frac{\partial \ln K}{\partial P} \right)_T = -\frac{\Delta V^o_R}{RT} \]
Objectives

- Determine deuterium isotope effect for acids, bases
  - \( \Delta pK = \{ pK_a(D_2O) - pK_a(H_2O) \} \) at 250 & 300°C
  - Conductance
  - Colorimetric pH indicators
- \( D_2O \) isotope effect on \( V^\circ \) at 250 & 300°C
- Correlation for estimating \( \Delta pK \)
- Estimate \( \Delta pK \) for transition metal hydrolysis
- Correlate with glass electrode measurements at 25°C
Challenges with D$_2$O

- Define standard states:
  - “Aquamolal”: same mol faction as molality in H$_2$O
  - Molarity: same volume per solute as in H$_2$O
- PVT properties, viscosity known
- Debye-Huckel constants, dielectric constant
- Only known equilibrium constants at $t > 100^\circ$C:
  - Ionization constant $K_D$
  - Phosphate ionization constant D$_2$PO$_4^-$
Deuterium Isotope Effects on Ionization Constants From AC Conductance

Measuring *Differences* in the Degree of Ionization in \( \text{H}_2\text{O} \) and \( \text{D}_2\text{O} \) above 250 °C
Molar Conductance for Weak Acids

- HA ⇌ H⁺ + A⁻
  \((1 - \alpha)c\)  \(\alpha c\)  \(\alpha c\)

- \(\Lambda^{\text{exp}} = \alpha \lambda_{H^+} + \alpha \lambda_{A^-}\)

\[ K_a = \frac{\alpha^2 \gamma \pm \sqrt{\alpha^2 \gamma^2 + 4 \alpha^2 c}}{1 - \alpha} \]

Experimental Design

\[ \begin{align*}
\text{NaCl/H}_2\text{O} & \sim 10^{-4}\text{m} \\
\text{NaCl/D}_2\text{O} & \sim 10^{-4}\text{aqm} \\
\text{HA/H}_2\text{O} & \sim 10^{-4}\text{m} \\
\text{DA/D}_2\text{O} & \sim 10^{-4}\text{aqm}
\end{align*} \]
Acetic Acid Ionization

At 250 °C

HAc ⇌ H⁺ + Ac⁻  \[ K_a (H_2O) = 1.42 \times 10^{-6} \]

\[ \Delta pK_a = pK_{a_{D_2O}} - pK_{a_{H_2O}} = 6.26 - 5.85 = 0.41 \pm 0.13 \]

At 275 °C

HAc ⇌ H⁺ + Ac⁻  \[ K_a (H_2O) = 8.02 \times 10^{-7} \]

\[ \Delta pK_a = pK_{a_{D_2O}} - pK_{a_{H_2O}} = 6.45 - 6.09 = 0.36 \pm 0.12 \]

Ionization of D₂PO₄⁻: \[ \Delta pK_a (250 °C) = 0.482; \quad \Delta pK_a (275 °C) = 0.477 \]

Mesmer and Herting J.Sol.Chem. 7,12,901-913 (1978)
Ionization Constants From Thermally Stable Colorimetric pH Indicators

Calibrating a pD Indicator for use in H₂O and D₂O above 250 °C
UV-Visible Spectroscopy
350 °C, 30 MPa

Hydrothermal Cell
- Sapphire windows
- Platinum body
- HPLC injection

Colorimetric pH Indicators
- Thermally stable
- 350 °C, 30 MPa

Acridine
β-Naphthol
β-Naphthoic Acid
Colorimetric pD Measurements

• Why β-Naphthol?
  Overlaps with the only known accurate buffer for D₂O at high temperatures

• pD Buffer System
  $\text{D}_2\text{PO}_4^- \rightleftharpoons \text{DPO}_4^{2-} + \text{D}^+$

• Targets for study:
  $\text{NapOD} \rightleftharpoons \text{NapO}^- + \text{D}^+$
  $\text{B(OD)}_3 + \text{D}_2\text{O} \rightleftharpoons \text{B(OD)}_4^- + \text{D}^+$
**β-Naphthol Spectra in Phosphate pD Buffers**

- Measurements in weak acid and base
  - Yield spectra of species NapOD and NapO⁻
- Buffer spectra
  - Yield equilibrium mixture of NapOD and NapO⁻ at known pD

\[
A_{\text{NapOD,buffer}} = f_1 A_{\text{NapOH,Acid}} + f_2 A_{\text{NapO-,Base}}
\]
Equilibrium Constants of $\beta$-Naphthol in a $D_2PO_4^-/DPO_4^{2-}$ Buffer

$\text{NapOD} \rightleftharpoons \text{NapO}^- + D^+$

$$A(\lambda) = (\varepsilon_{\text{NapOD}}(\lambda) b m_{\text{NapOD}}^* + \varepsilon_{\text{NapO}^-}(\lambda) b m_{\text{NapO}^-}^*) \rho_{\text{solution}}$$

$$Q_{\text{NapOD}} = \left(\frac{m_{\text{NapO}^-}}{m_{\text{NapOD}}}\right) m_{D^+}$$

$$m_{D^+} = Q_2 \left(\frac{m_{D_2PO_4}^-}{m_{DPO_4^{2-}}}\right)$$

$$K_{\beta-\text{Naphthol}} = \left(\frac{m_{\text{NapO}^-} m_{D^+}}{m_{\text{NapOD}}}\right) \left(\frac{\gamma_{\text{NapO}^-} \gamma_{D^+}}{\gamma_{\text{NapOD}}}\right) = \left(\frac{m_{\text{NapO}^-}}{m_{\text{NapOD}}}\right) \left(\frac{m_{D^+}}{m_{D_2PO_4}^-}\right)^2$$
Ionization Constants of $\beta$-Naphthol in D$_2$O and H$_2$O

- Obtained at different buffer ratios
  \[ \text{NapOD} \rightleftharpoons \text{NapO}^- + \text{D}^+ \]
- Comparison with literature in H$_2$O
  - Xiang and Johnston (1994)
- Low temperature data from literature
  - Wehry and Rogers (1966)

Ionization Constants of Boric Acid in D$_2$O and H$_2$O

- Boric acid ionization reaction:
  \[ \text{B(OD)$_3$} + \text{D}_2\text{O} \rightleftharpoons \text{B(OD)$_4^-$} + \text{D}^+ \]

- Measure pD of boric acid /borate buffers
  - \(\beta\)-Naphthol as colorimetric indicator

\[ K_{B(OD)_3} = \frac{m_{B(OD)_4^-}}{m_{B(OD)_3}} \gamma_{\pm \left(m_{D^+}\right)} \]

- Low temperature data
  - Edwards et al. (1962); Gold and Lowe (1968)

Bulemela et al., *J. Solution Chem.* (In Press)
Temperature Dependence of $\Delta pK$ for $D_2PO_4^-$, $\beta$-Naphtol, and Boric Acid

- $\beta$-Naphtol & boric acid consistent with $D_2PO_4^-$
- $\Delta pK$ lower at $t > 150 \, ^{\circ}C$
- Relatively independent of temperature?
Temperature Dependence of $\Delta pK$ for $D_2PO_4^-$, $\beta$-Naphthol, Boric Acid and Acetic Acid

Trends

- $\Delta pK$ is lower above 150 °C
- Magnitude of $\Delta pK$ is:
  - $D_2PO_4^-$
  - Acetic acid $\approx \beta$-Naphthol
  - $B(OD)_3$
- Can $B(OH)_3$ be used as a model for hydrolysed transition metals?
Density Measurements

Solvation Models from Partial Molar Volumes to Predict Temperature & Pressure Effects

\[
\left( \frac{\partial \ln K}{\partial P} \right)_T = -\frac{\Delta V^o_R}{RT}
\]
Apparent Molar Volume of NaCl(aq) at 300 °C and 14 MPa

High Temperature Vibrating tube Densitometer
• Relative density
  • ± 0.00002 g cm⁻³
  • to 350 °C, 30 MPa
• Yields
  • Apparent molar volume \( V_\phi \) vs molality

\[ V_\phi - A m_{aq}^{1/2} \]

\( m_{aq} \)

\( V_\phi - A m_{aq}^{1/2} \) vs molality
Towards a Predictive Model

Geochemical “Equation of State” for Aqueous Ions
Tanger and Helgeson (1988)

$$\bar{C}_p^o (ion) = a + \frac{b}{(T - 228)^2} + \Delta C_{p,Born}^o$$

$$\bar{V}^o (ion) = c + \frac{d}{T - 228} + \Delta V_{Born}^o$$

Does the Born term predict deuterium isotope effects from ~200 to 300 °C?

$$\Delta V_{2, D_2O}^o = V_{2, D_2O}^o \left\{ 1 - \left( \frac{\partial \varepsilon / \partial p}{\varepsilon_{H_2O}} \right)_{T,H_2O}^2 \right\} / \left\{ \left( \frac{\partial \varepsilon / \partial p}{\varepsilon_{D_2O}} \right)_{T,D_2O}^2 \right\}$$
Summary and Conclusions

• High precision flow instruments
  – Operate to 350 °C, 30 MPa
  – Measure differences between species in D₂O and H₂O
  – Complications from ion pairing above 300 °C

• Conductance
  – Measuring $pK_{D2O} - pK_{H2O}$ for key acids and bases

• UV-visible spectroscopy
  – Control pH with only known buffer system, DPO₄⁻ /D₂PO₄⁻
  – First thermally stable colorimetric pH indicator
  – Results for Boric Acid

• Apparent molar volumes
  – Focus on 250 to 350 °C range to define “best” theoretical model
  – NaOD, DCl and NaCl complete, LiOD in progress

• Predictive models and “equations of state”
  – Two models (Born + Corresponding States) successful
D$_2$O Project Team

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