

D₂O Isotope Effects on Chemical Reactions under CANDU Operating Conditions

IAPWS Canadian National Committee Workshop

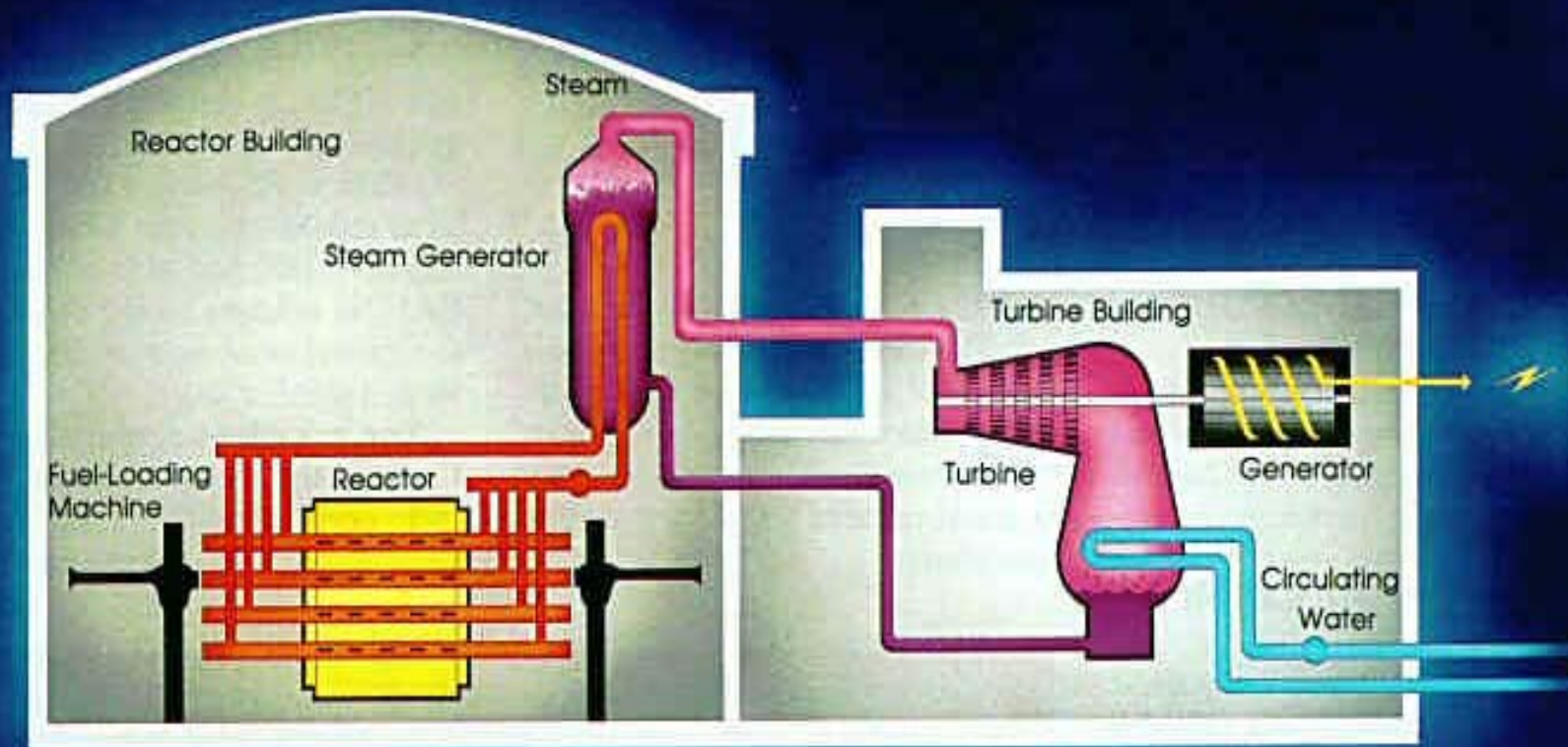
May 11 & 12, 2009

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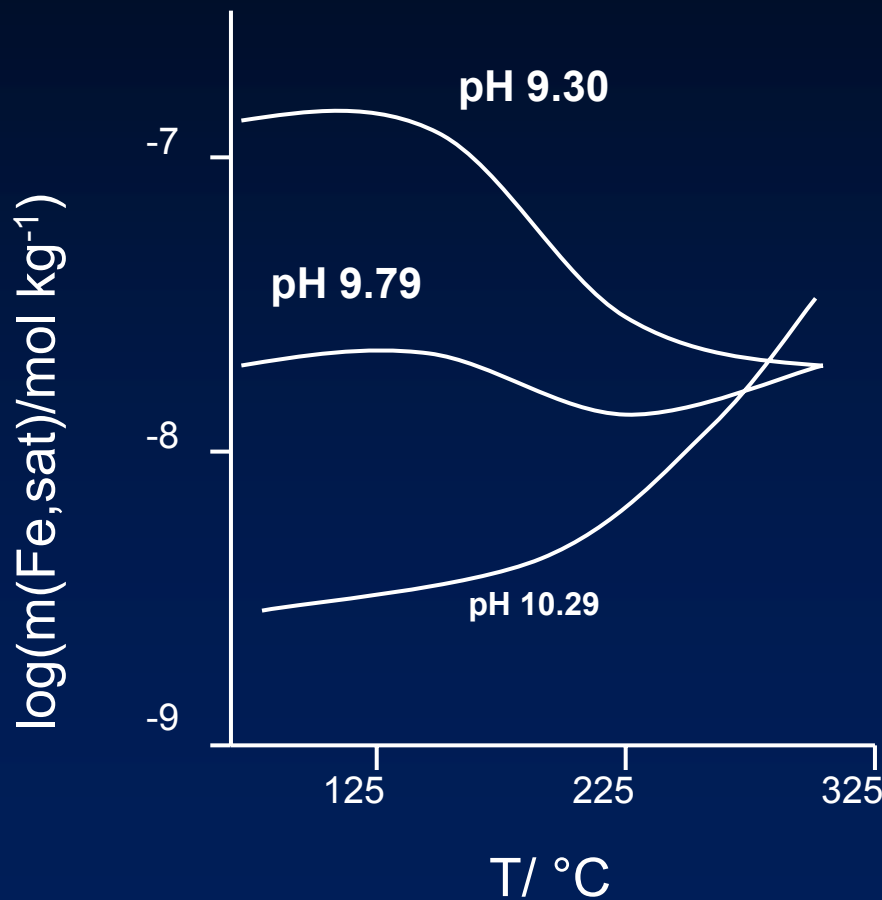


CANDU Nuclear Power Plant





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_2O ?

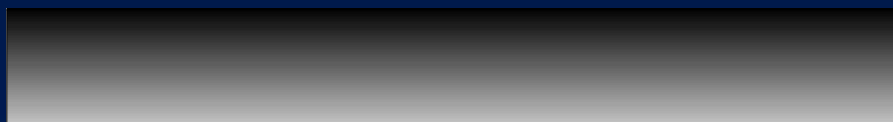


Magnetite Solubility

Aqueous Solution



Metal Oxide



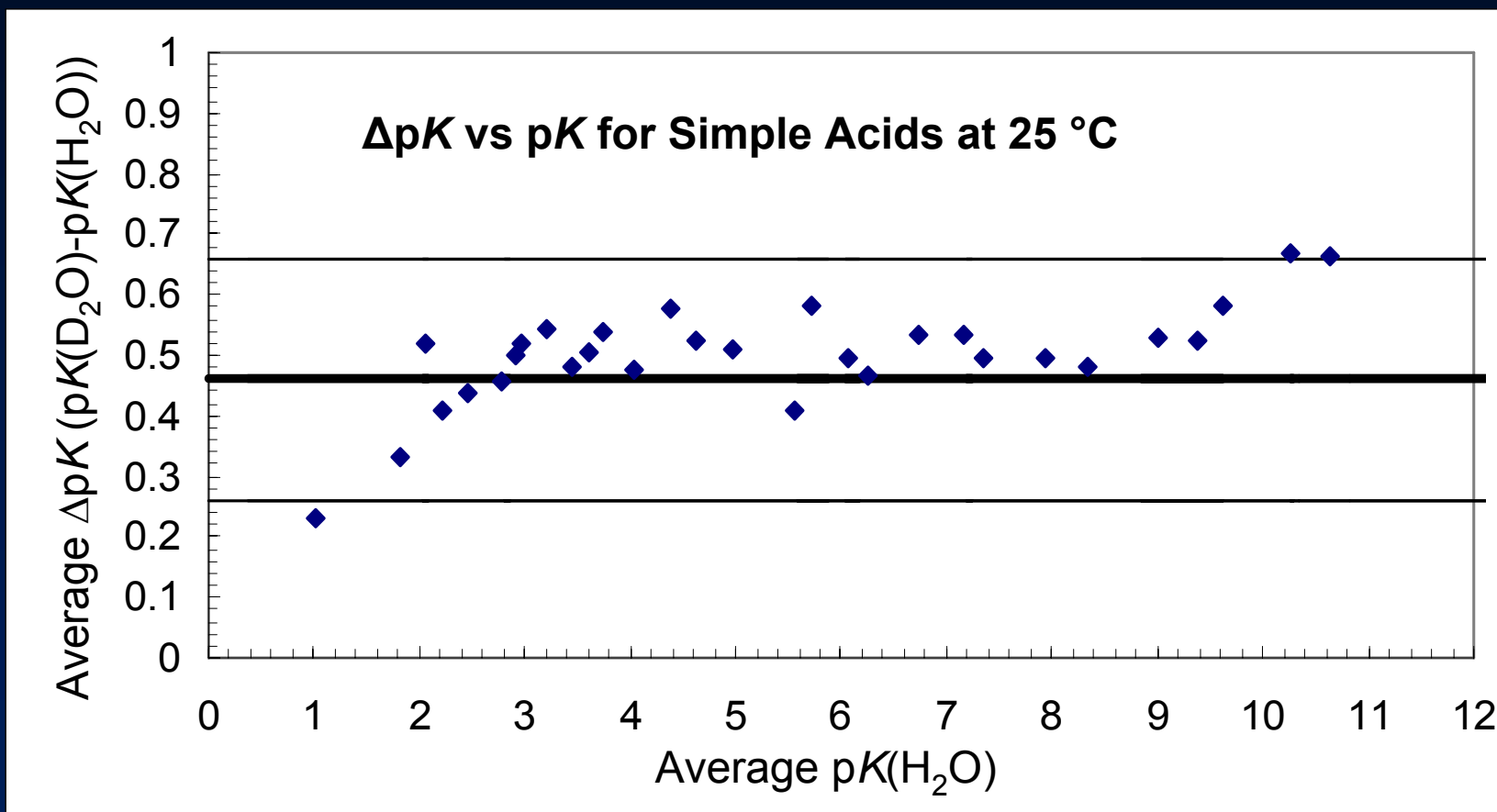
Shvedov and Tremaine, *J. Sol. Chem.* 29, 905 (2000)

Tremaine and LeBlanc, *J. Sol. Chem.* 9, 415 (1980)



Deuterium Isotope Effects at 25 °C

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





Equilibrium Constant as a Function of Temperature

The Relation to Standard Partial Molar Properties

$$\ln K_T = \ln K_{298} - \frac{1}{R} \left[\frac{1}{T} - \frac{1}{298} \right] \Delta H_{298}^{\circ} + \frac{1}{R} \int_{298}^T \frac{\Delta C_p^{\circ}}{T} dT - \frac{1}{RT} \int_{298}^T \Delta C_p^{\circ} dT - \frac{1}{RT} \int_1^p \Delta V^{\circ} dP$$

$$\left(\frac{\partial \Delta H_R^{\circ}}{\partial T} \right)_P = \Delta C_{P,R}^{\circ}$$

$$\left(\frac{\partial \ln K}{\partial P} \right)_T = \frac{-\Delta V_R^{\circ}}{RT}$$



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
- **D₂O isotope effect on V° at 250 & 300°C**
- **Correlation for estimating ΔpK**
- **Estimate ΔpK for transition metal hydrolysis**
- **Correlate with glass electrode measurements at 25°C**



Challenges with D₂O

- Define standard states:
 - “Aquamolal”: same mol fraction as molality in H₂O
 - Molarity: same volume per solute as in H₂O
- PVT properties, viscosity known
- Debye-Huckel constants, dielectric constant
- Only known equilibrium constants at $t > 100^{\circ}\text{C}$:
 - Ionization constant K_D
 - Phosphate ionization constant D_2PO_4^-



Deuterium Isotope Effects on Ionization Constants From AC Conductance

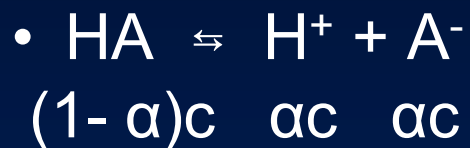
Measuring *Differences* in the Degree of Ionization
in H_2O and D_2O above $250\text{ }^\circ\text{C}$



Supercritical AC Conductance Cell

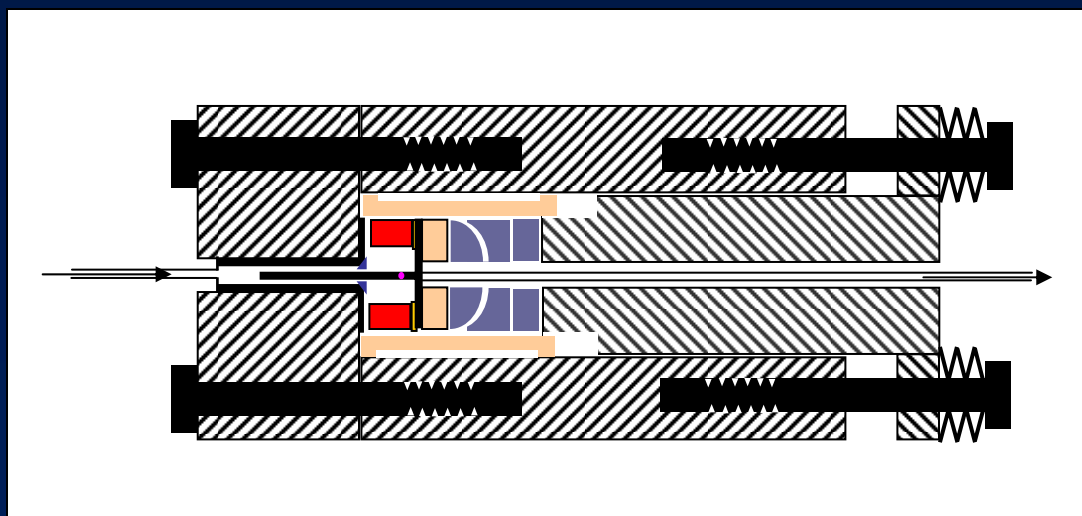
400 °C, 30 MPa

Molar Conductance for Weak Acids



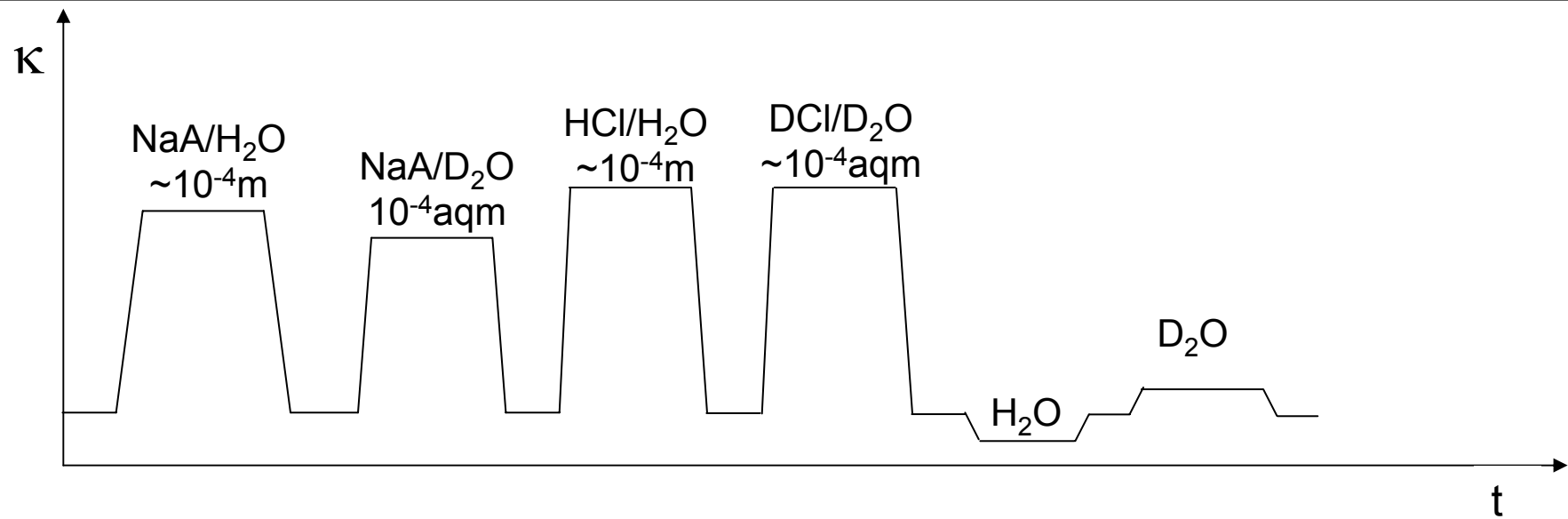
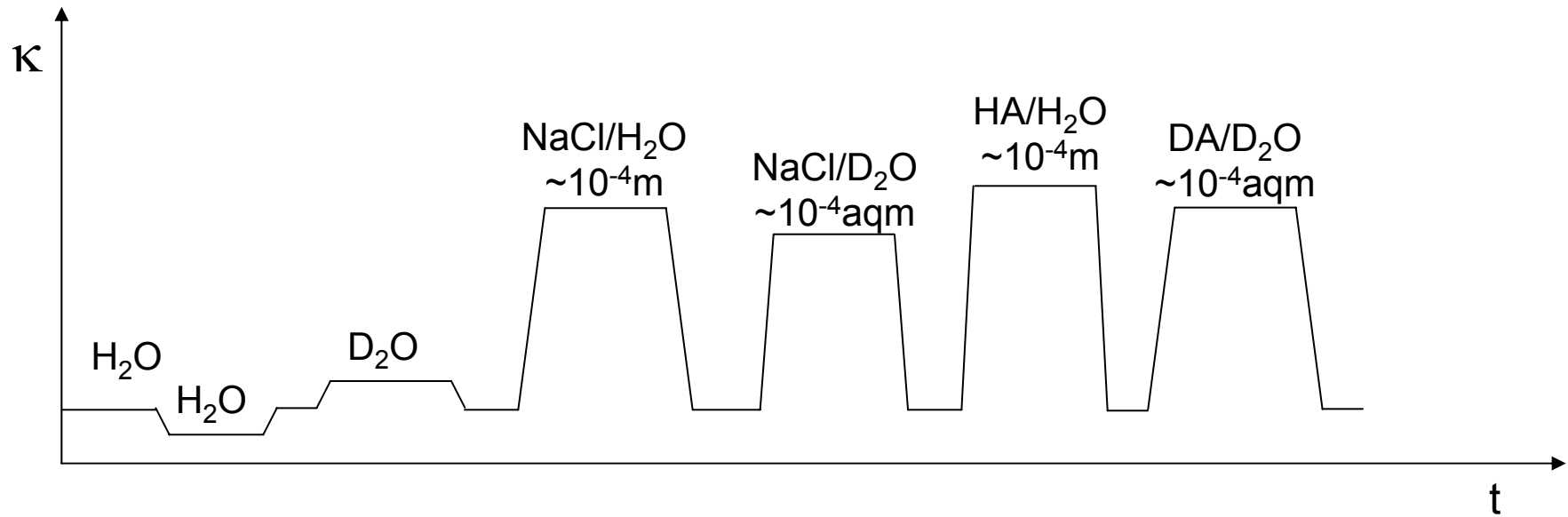
$$\Lambda^{\text{exp}} = \alpha \lambda_{\text{H}^+} + \alpha \lambda_{\text{A}^-}$$

$$K_a = \frac{\alpha^2 \gamma_{\pm}^2 c}{1 - \alpha}$$



Zimmerman, Gruskiewicz and Wood, *J. Phys. Chem.* 99, 11612 (1995)

Experimental Design





Acetic Acid Ionization

At 250 °C



$$K_a (\text{H}_2\text{O}) = 1.42 \times 10^{-6}$$



$$K_a (\text{D}_2\text{O}) = 5.53 \times 10^{-7}$$

$$\Delta pK_a = pK_{a_{\text{D}_2\text{O}}} - pK_{a_{\text{H}_2\text{O}}} = 6.26 - 5.85 = 0.41 \pm 0.13$$

At 275 °C



$$K_a (\text{H}_2\text{O}) = 8.02 \times 10^{-7}$$



$$K_a (\text{D}_2\text{O}) = 3.66 \times 10^{-7}$$

$$\Delta pK_a = pK_{a_{\text{D}_2\text{O}}} - pK_{a_{\text{H}_2\text{O}}} = 6.45 - 6.09 = 0.36 \pm 0.12$$

Ionization of D_2PO_4^- : ΔpK_a (250 °C) = 0.482; ΔpK_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

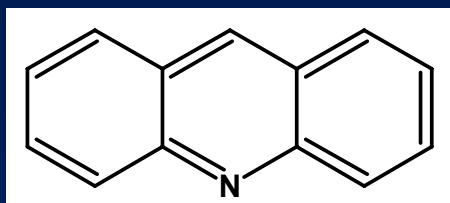


Hydrothermal Cell

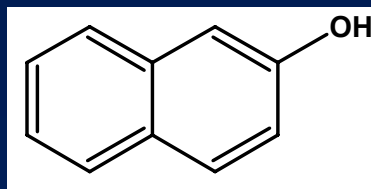
- Sapphire windows
- Platinum body
- HPLC injection

Colorimetric pH Indicators

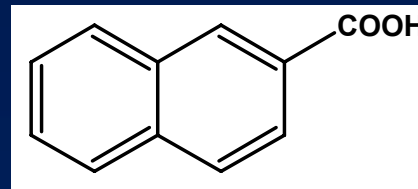
- Thermally stable
- 350 °C, 30 MPa



Acridine



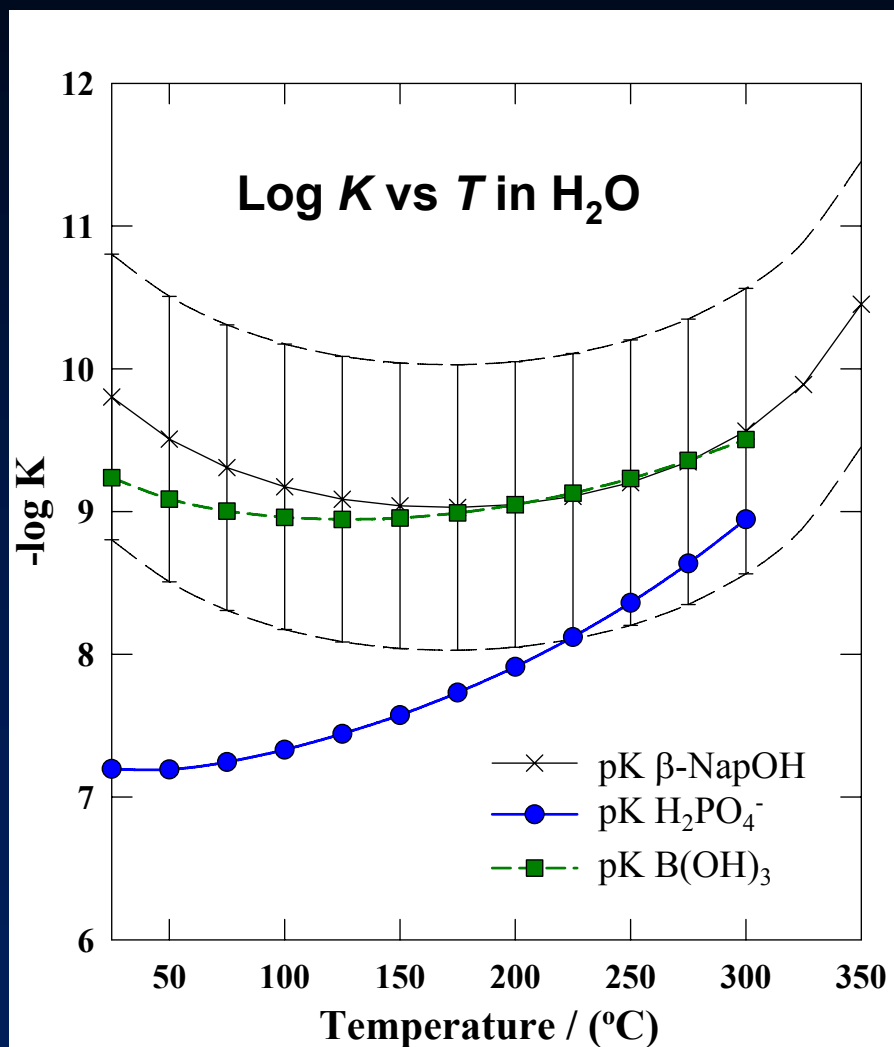
β -Naphthol



β -Naphthoic Acid



Colorimetric pD Measurements



- Why β-Naphthol?

Overlaps with the only known accurate buffer for D₂O at high temperatures

- pD Buffer System

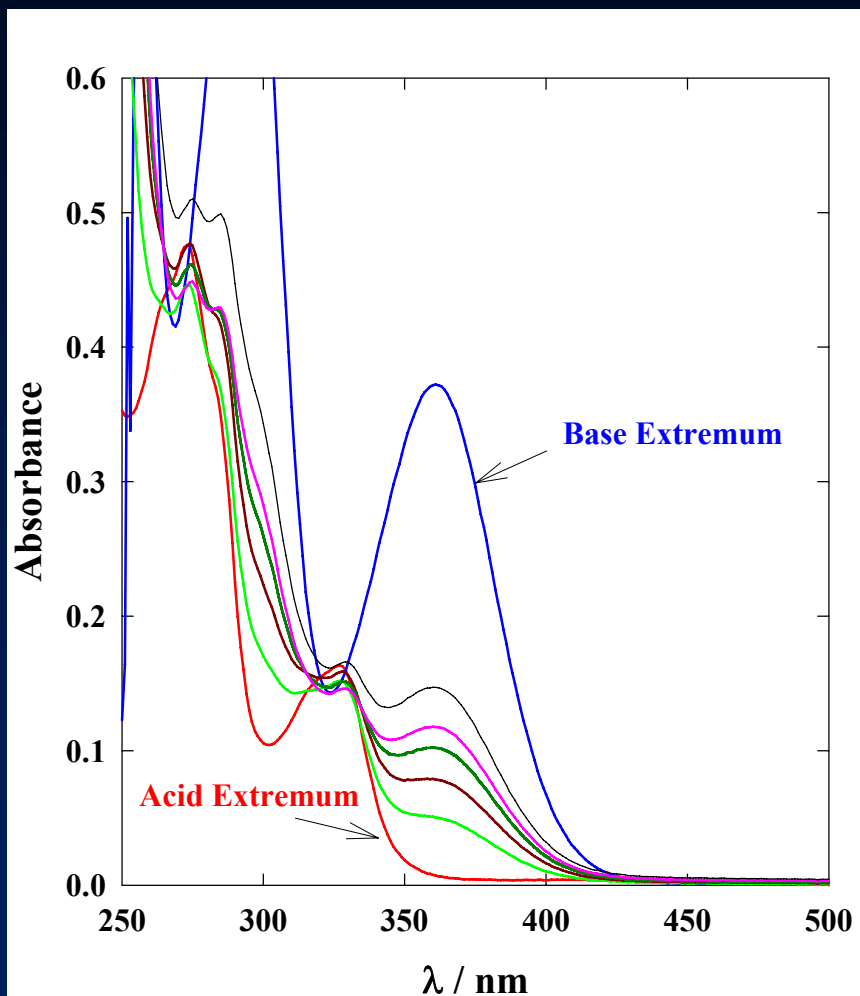


- Targets for study:





β -Naphthol Spectra in Phosphate pD Buffers



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

$$A_{\text{NapOH,buffer}} = f_1 A_{\text{NapOH,Acid}} + f_2 A_{\text{NapO-,Base}}$$



Equilibrium Constants of β -Naphthol in a $D_2PO_4^-/DPO_4^{2-}$ Buffer



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

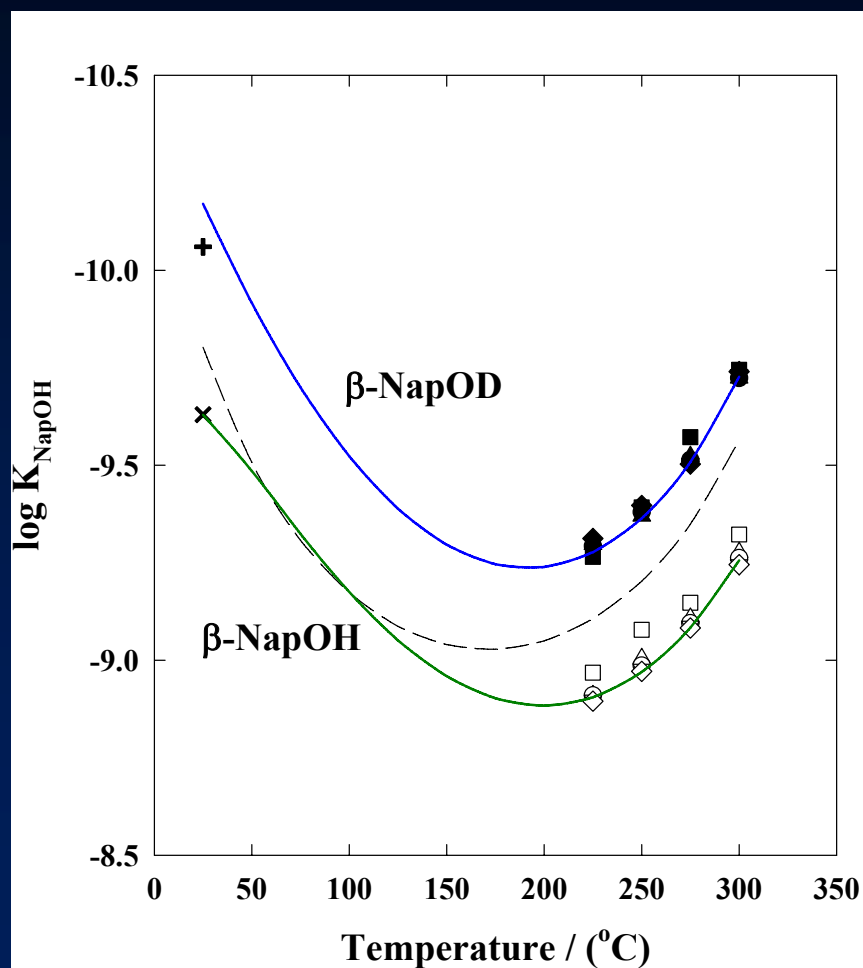
$$Q_{\text{NapOD}} = \left(\frac{m_{\text{NapO}^-}}{m_{\text{NapOD}}} \right) m_{\text{D}^+}$$

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

$$K_{\beta\text{-Naphthol}} = \left(\frac{m_{\text{NapO}^-} m_{\text{D}^+}}{m_{\text{NapOD}}} \right) \left(\frac{\gamma_{\text{NapO}^-} \gamma_{\text{D}^+}}{\gamma_{\text{NapOD}}} \right) = \left(\frac{m_{\text{NapO}^-}}{m_{\text{NapOD}}} \right) \left(m_{\text{D}^+} \right) \gamma_{\pm}^2$$



Ionization Constants of β -Naphthol in D_2O and H_2O



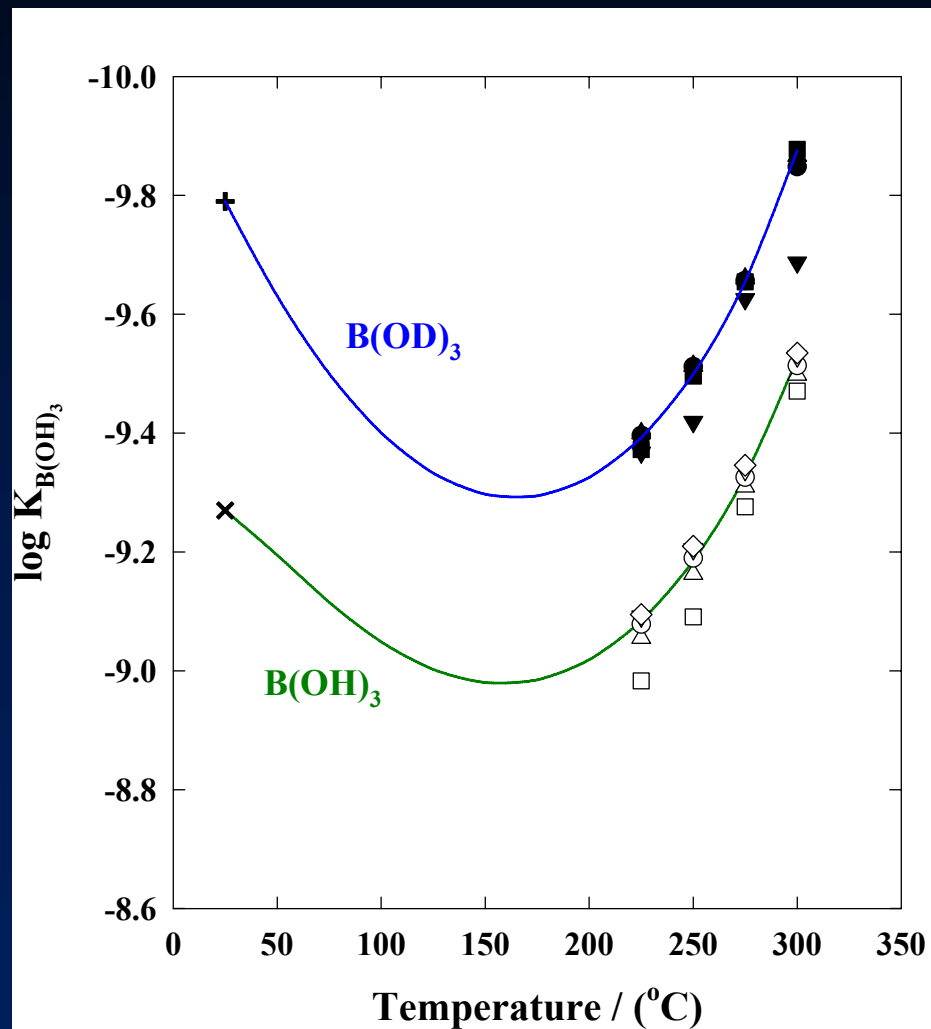
- Obtained at different buffer ratios



- Comparison with literature in H_2O
 - Xiang and Johnston (1994)
- Low temperature data from literature
 - Wehry and Rogers (1966)



Ionization Constants of Boric Acid in D₂O and H₂O



- Boric acid ionization reaction:



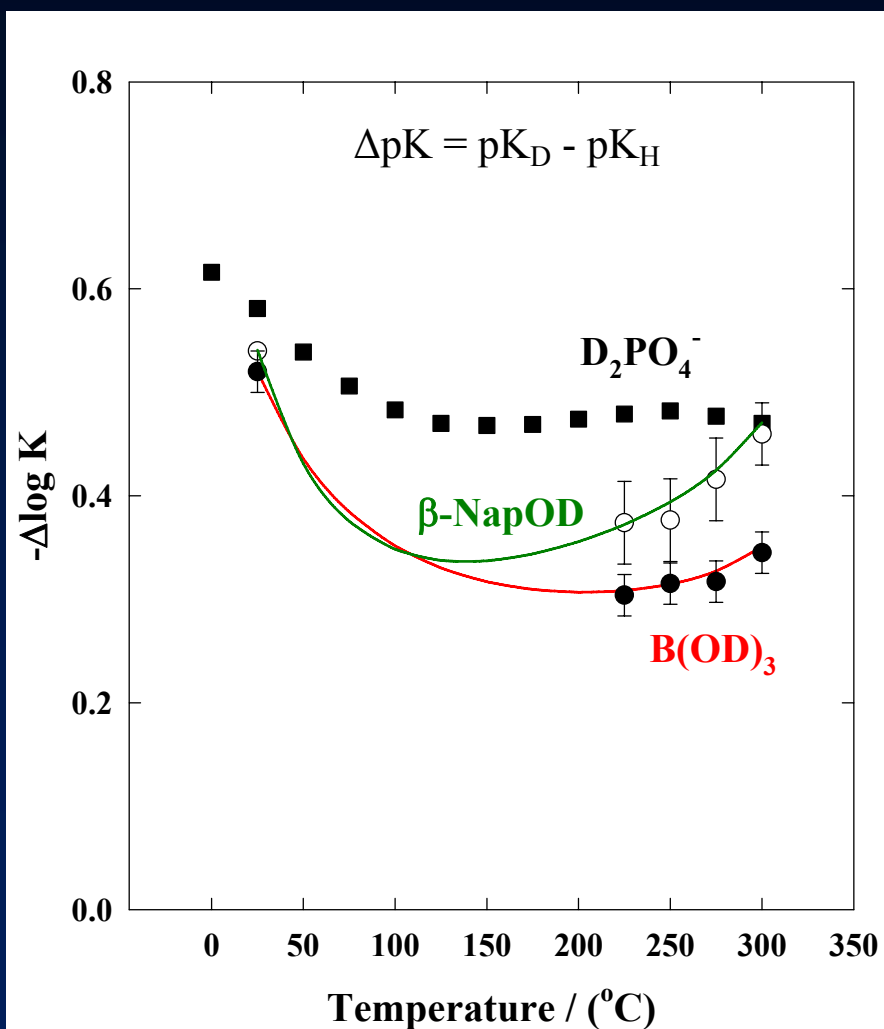
- Measure pD of boric acid /borate buffers
 - β -Naphthol as colorimetric indicator

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

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



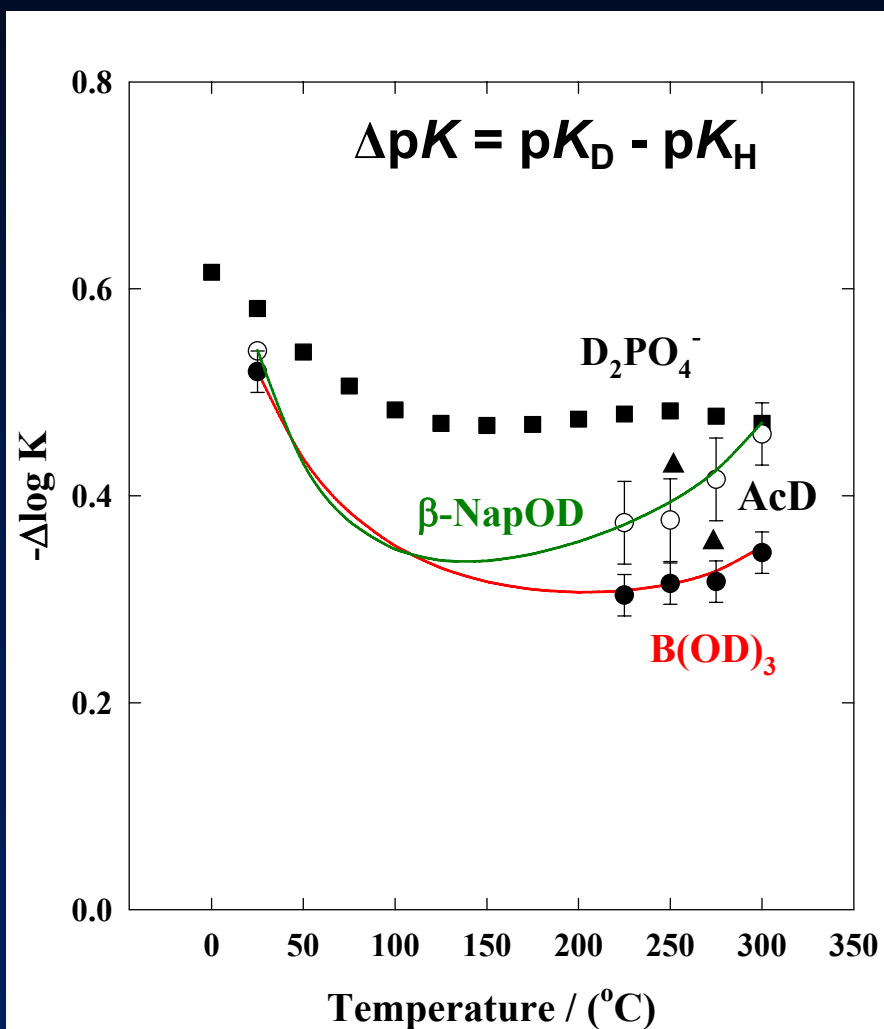
Temperature Dependence of ΔpK for $D_2PO_4^-$, β -Naphthol, and Boric Acid



- β -Naphthol & boric acid consistent with $D_2PO_4^-$
- ΔpK lower at $t > 150$ °C
- Relatively independent of temperature ?



Temperature Dependence of ΔpK for $D_2PO_4^-$, β -Naphthol, Boric Acid and Acetic Acid



Trends

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



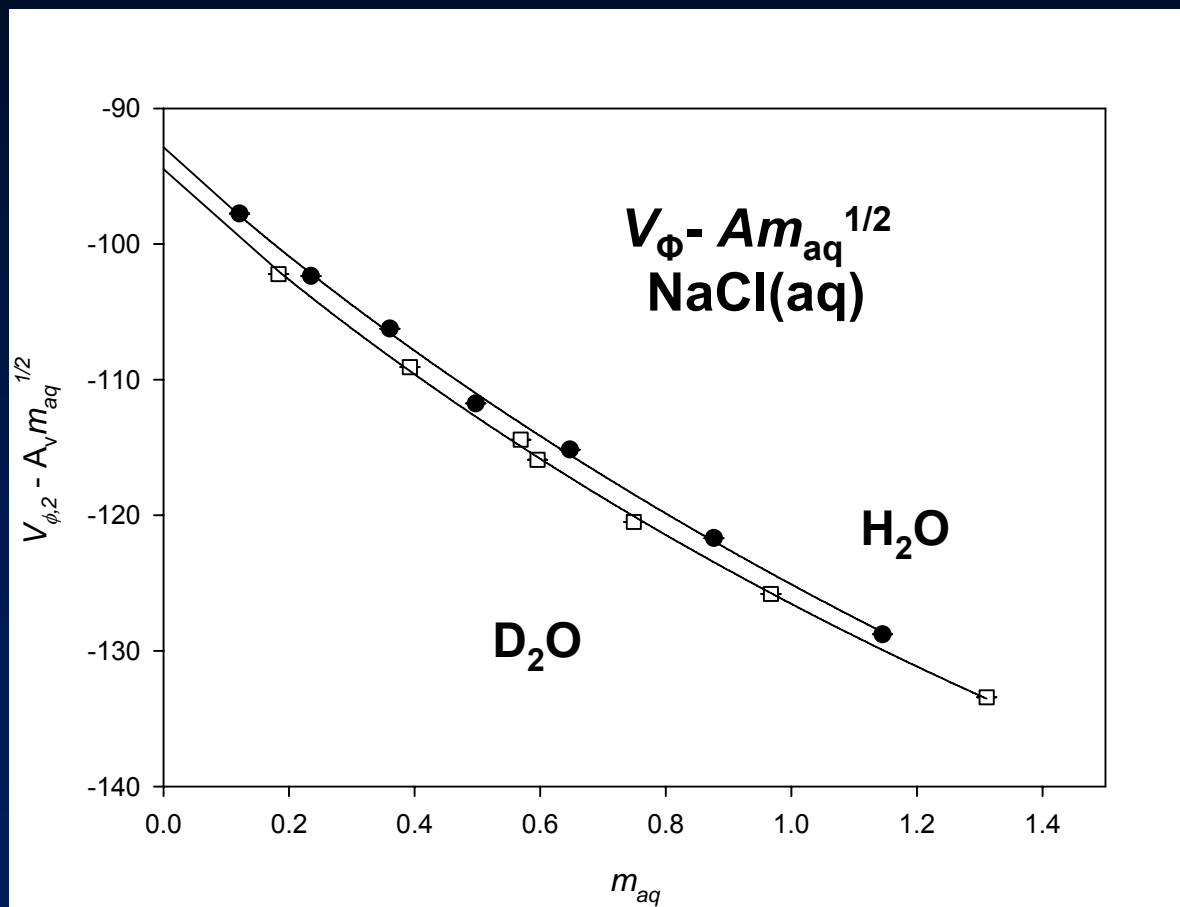
Density Measurements

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

$$\left(\frac{\partial \ln K}{\partial P} \right)_T = \frac{-\Delta V_R^o}{RT}$$

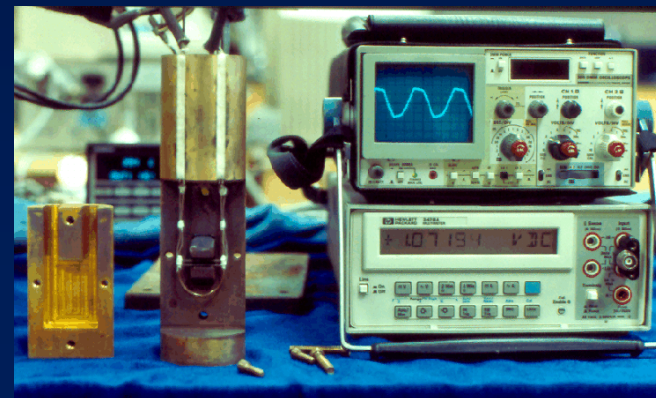


Apparent Molar Volume of NaCl(aq) at 300 °C and 14 MPa



High Temperature Vibrating tube Densitometer

- Relative density
 - $\pm 0.00002 \text{ g cm}^{-3}$
 - to 350 °C, 30 MPa
- Yields
 - Apparent molar volume V_{ϕ} vs molality

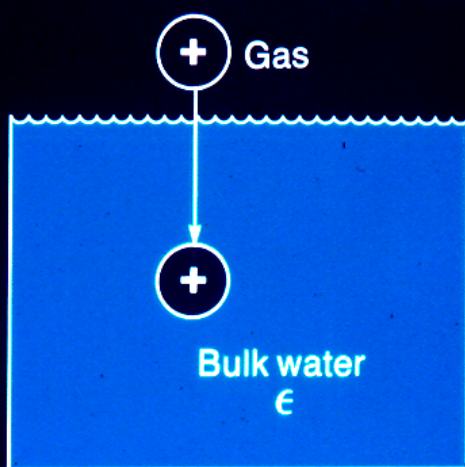




Towards a Predictive Model

Trevani et al. *J. Phys. Chem. B* 111, 2015 (2007)

Born Equation



$$\Delta G = -\frac{Z^2}{2r} \left(1 - \frac{1}{\epsilon}\right)$$

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 ?

$$\Delta V_2^o = V_{2,D_2O}^o \left\{ 1 - \frac{(\partial \epsilon / \partial p)_{T,H_2O}}{\epsilon_{H_2O}^2} \right\} / \left\{ \frac{(\partial \epsilon / \partial p)_{T,D_2O}}{\epsilon_{D_2O}^2} \right\}$$



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 $pK_{D_2O} - pK_{H_2O}$ for key acids and bases
- **UV-visible spectroscopy**
 - Control pD with only known buffer system, $DPO_4^- / D_2PO_4^-$
 - First thermally stable colorimetric pD 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



D₂O Project Team

- Dr. Liliana Trevani
- Dr. Diego Raffa
- Dr. Ephraim Bulemela
- Ms. Kristy Erikson (PhD student)
- Mr. Eric Balodis (Summer student)
- Ms. Sarah Moore (Summer student)

Funding

- NSERC
- Ontario Power Generation Ltd
- UNENE





Acknowledgments

UNENE

