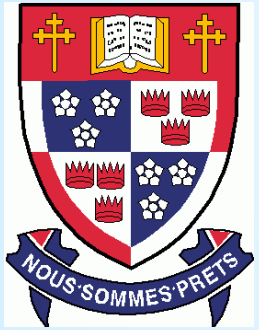
# Reaction kinetics in supercritical water as probed with muonium

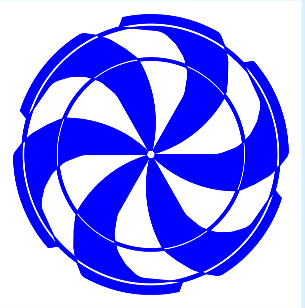



Paul Percival

Department of Chemistry

Simon Fraser University

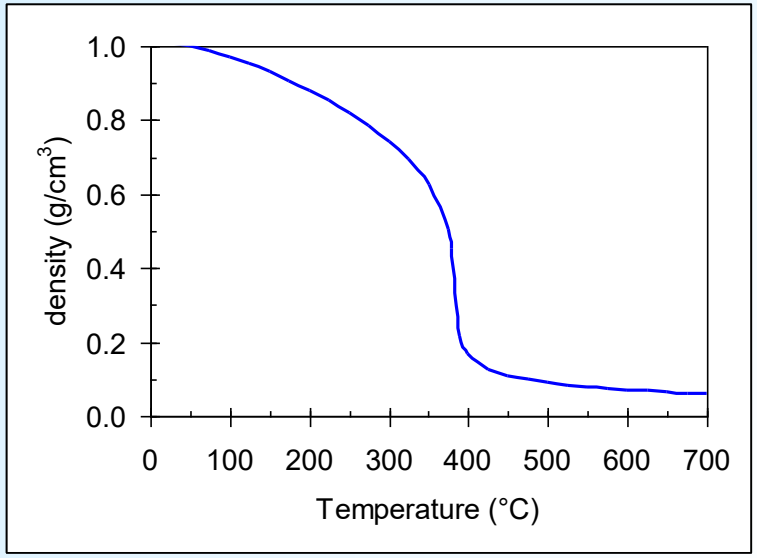
and TRIUMF



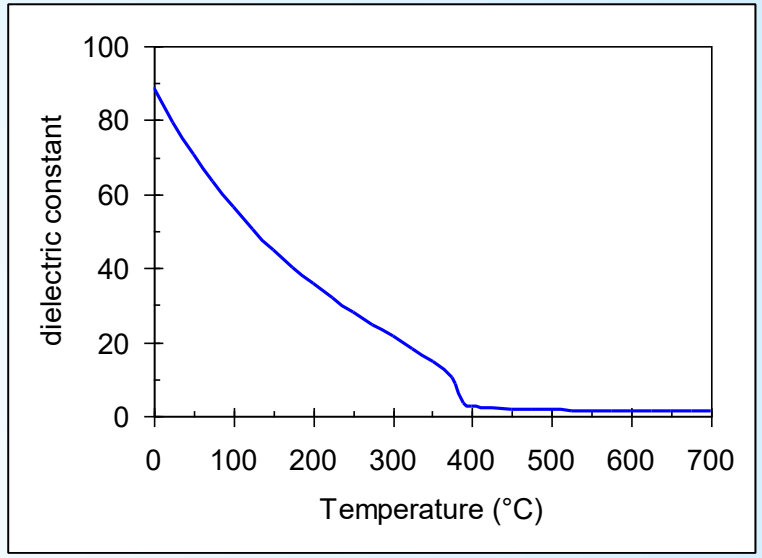
Beam-based Probes of Condensed Matter Physics, Chemistry and Related Fields in Canada, June 2021

# Properties of Water at 250 bar

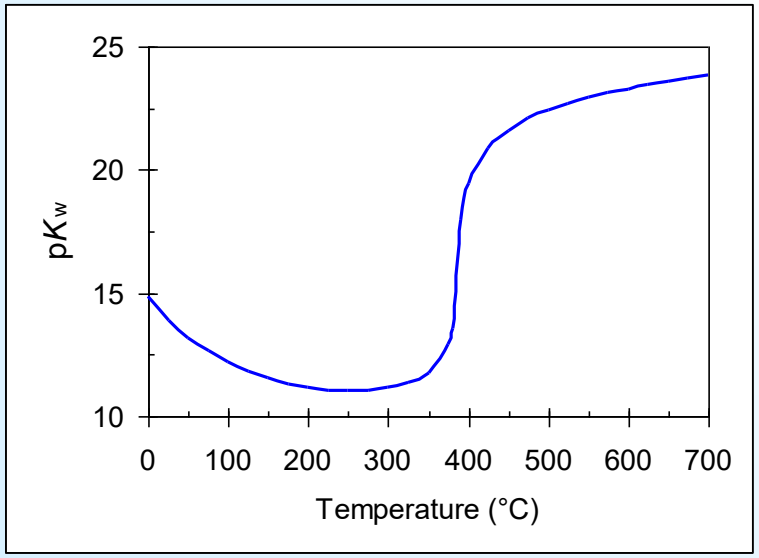
Density



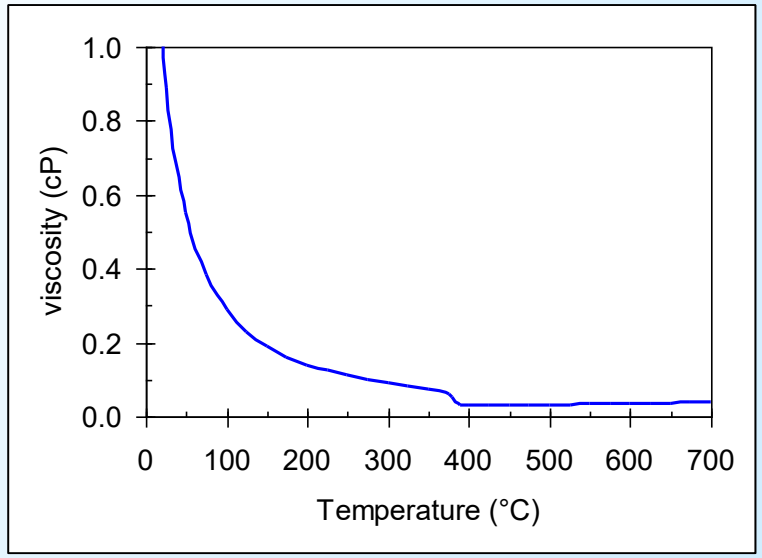

Dielectric Constant




Acid Dissociation Constant

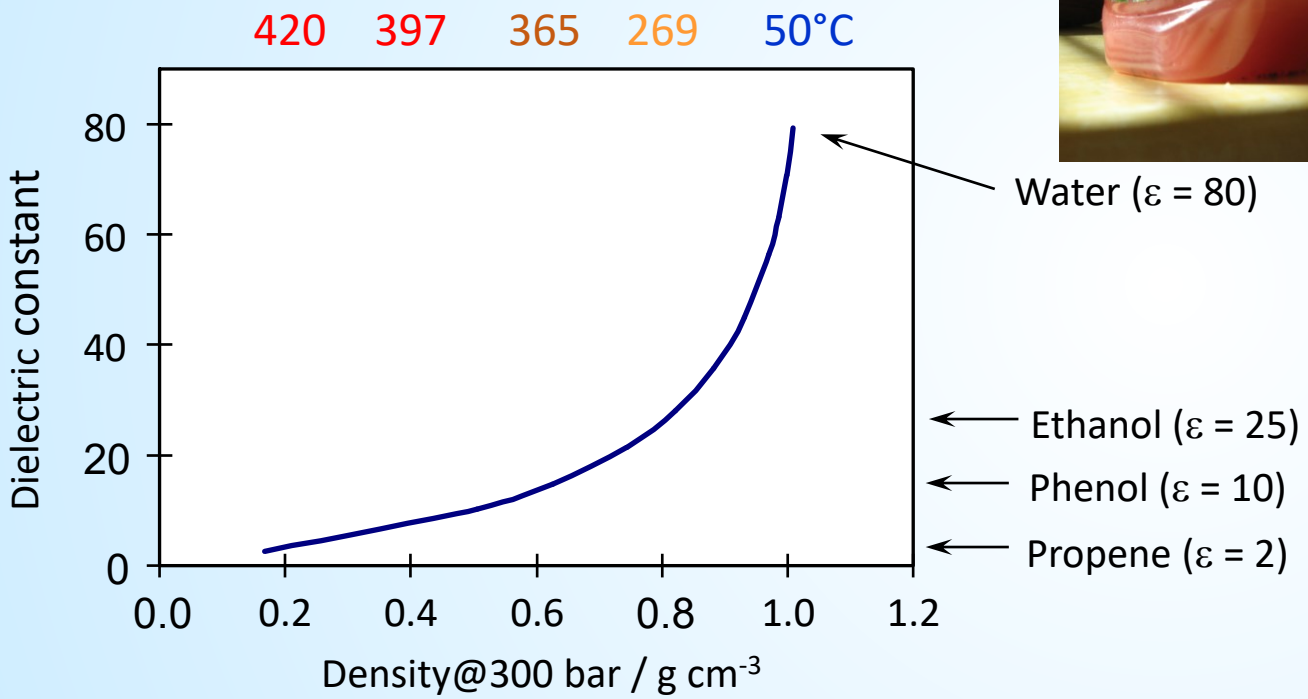



Viscosity

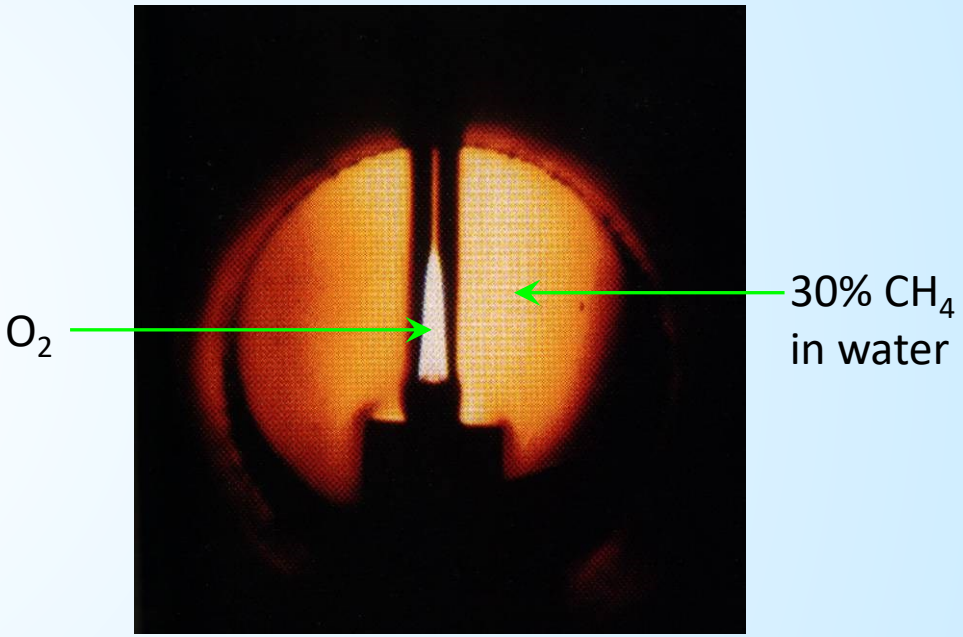


# Remarkable Chemistry in Supercritical Water

There are drastic changes in the physical properties of water close to the critical point ($T_c$ = 374°C, $P_c$ = 221 bar) and organic compounds become miscible with water.




A Flame in Water!




2000 bar, 450°C

W. Schilling and E.U. Franck,
*Ber. Bunsenges. Phys. Chem*. 1988

SCWO can be used for the destruction of hazardous waste.
sewage sludge, chemical weapons, water recycling on spacecraft

# Remarkable Biology in Superheated Water

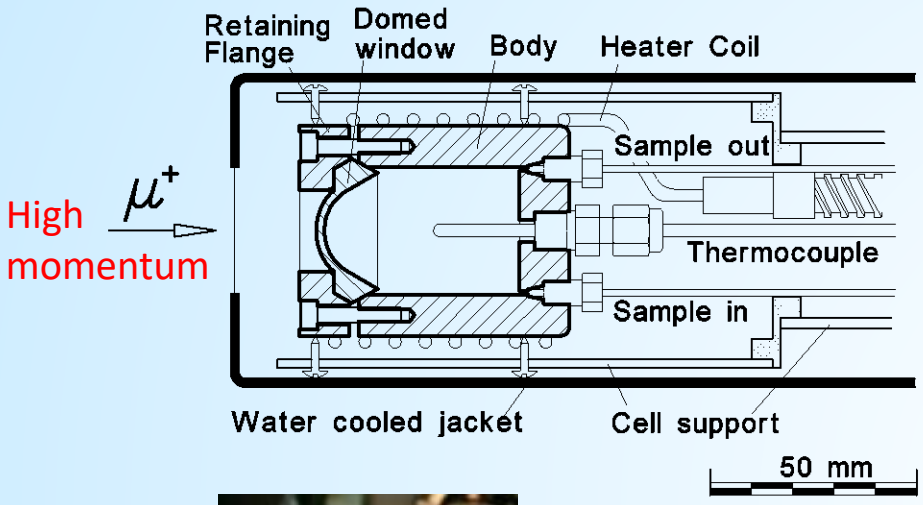
V. Tunnicliffe, U. Victoria

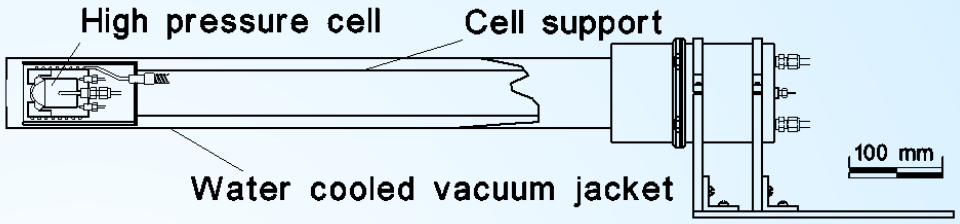
"Black smoker" hydrothermal vent on the floor of the Pacific Ocean (Juan da Fuca Ridge), West of Vancouver Island at a depth of about 1.5 km.

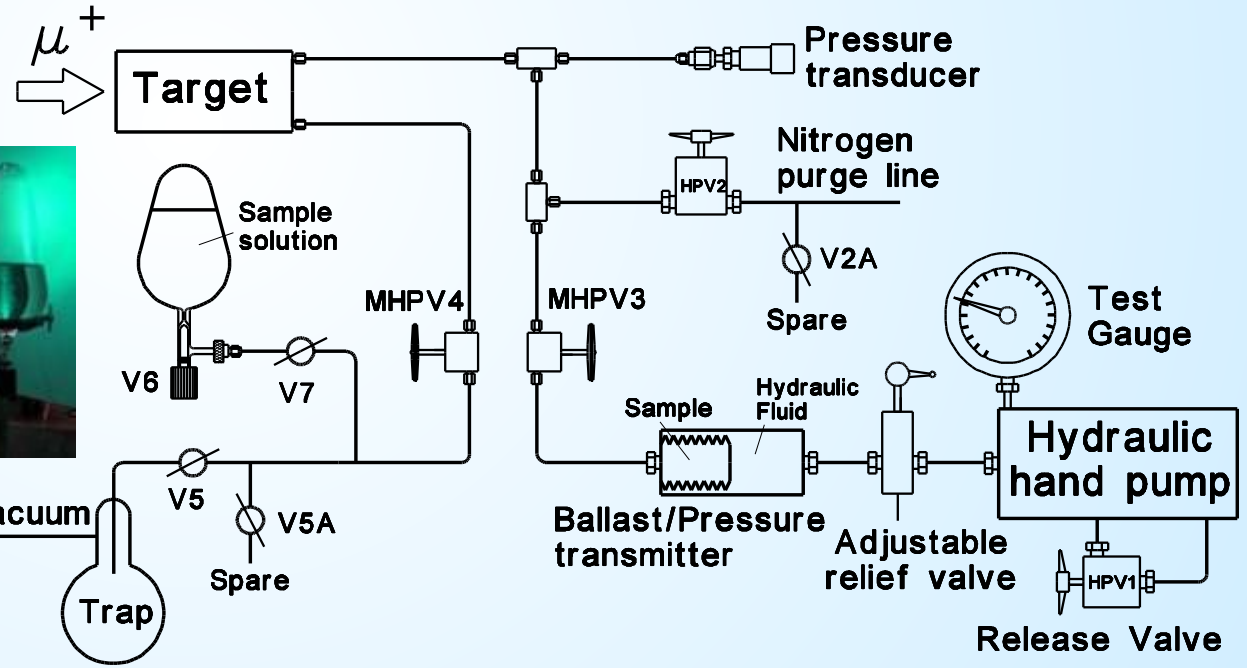
The temperature of the hot water jet is 320°C. The surrounding sea water is at 2°C.

Bacteria and Archaea live around these vents, in temperatures up to 100°C.

# High-Temperature, High-Pressure Target Cell and Sample-Handling System



# My Principal Collaborators

Dr. Jean-Claude Brodovitch

Prof. Khashayar Ghandi

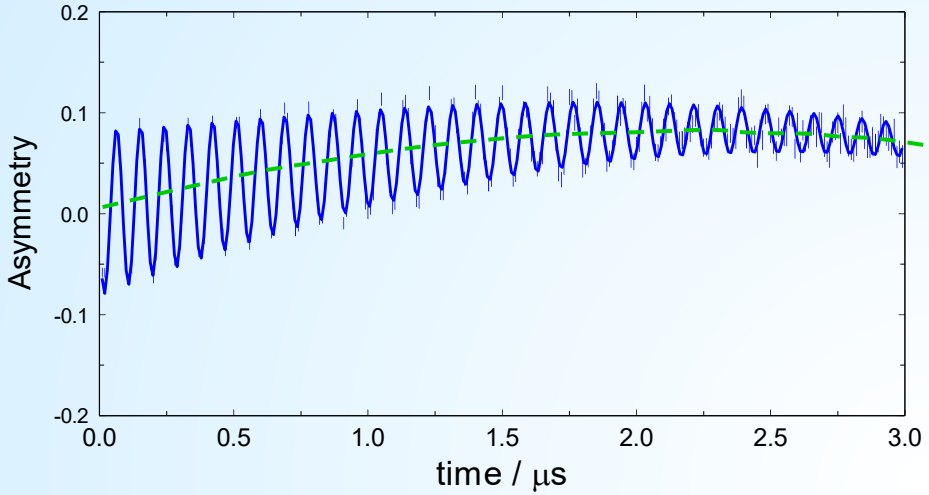
Ph.D. Thesis, Simon Fraser University (2002):
"Muonium Chemistry in Sub and Supercritical Water"

currently professor at University of Guelph

# Muonium is long-lived in Supercritical Water

400°C, 245 bar

8 G

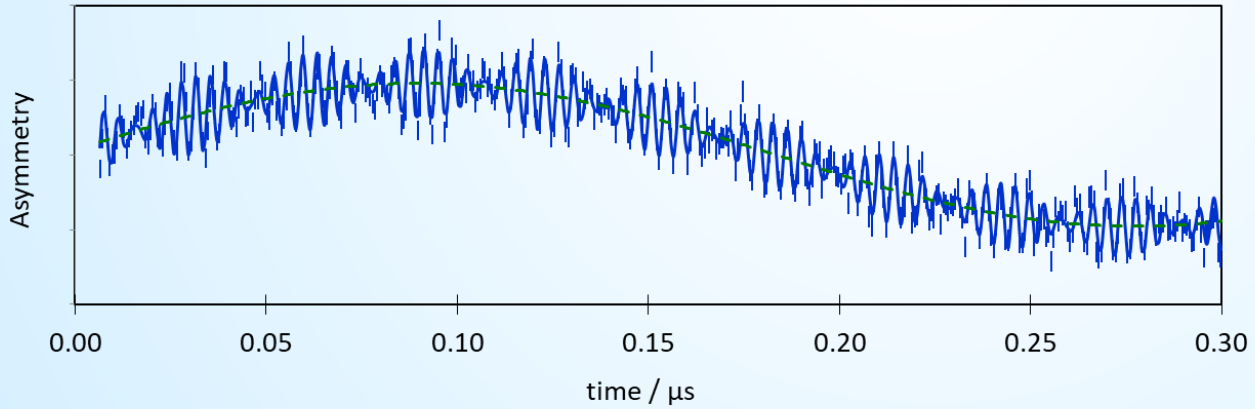


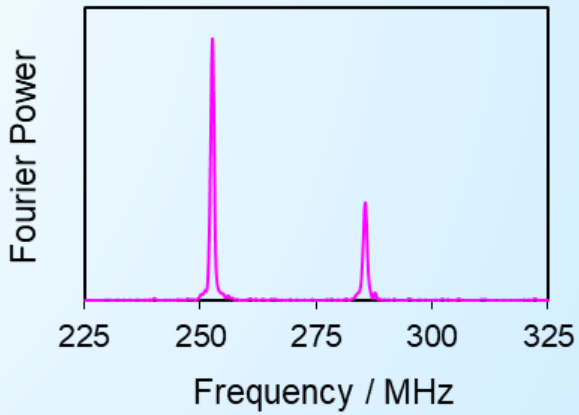

Diamagnetic signal

Muonium precession

Percival, Brodovitch, Ghandi et al., Phys. Chem. Chem. Phys. (1999)

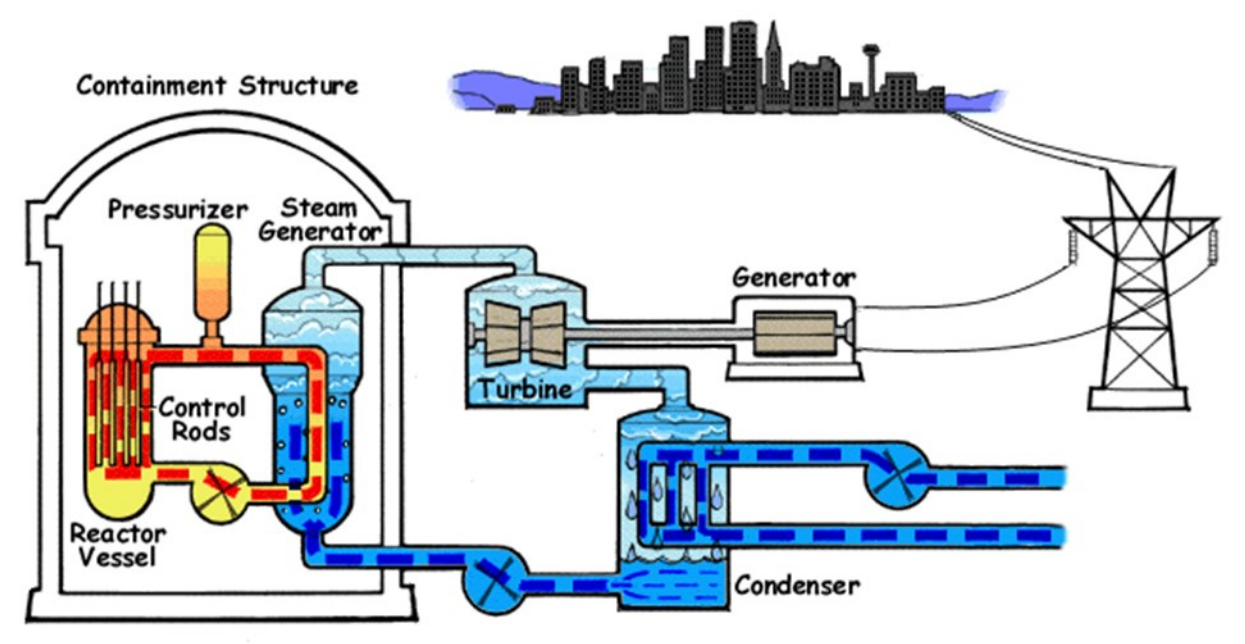
194 G



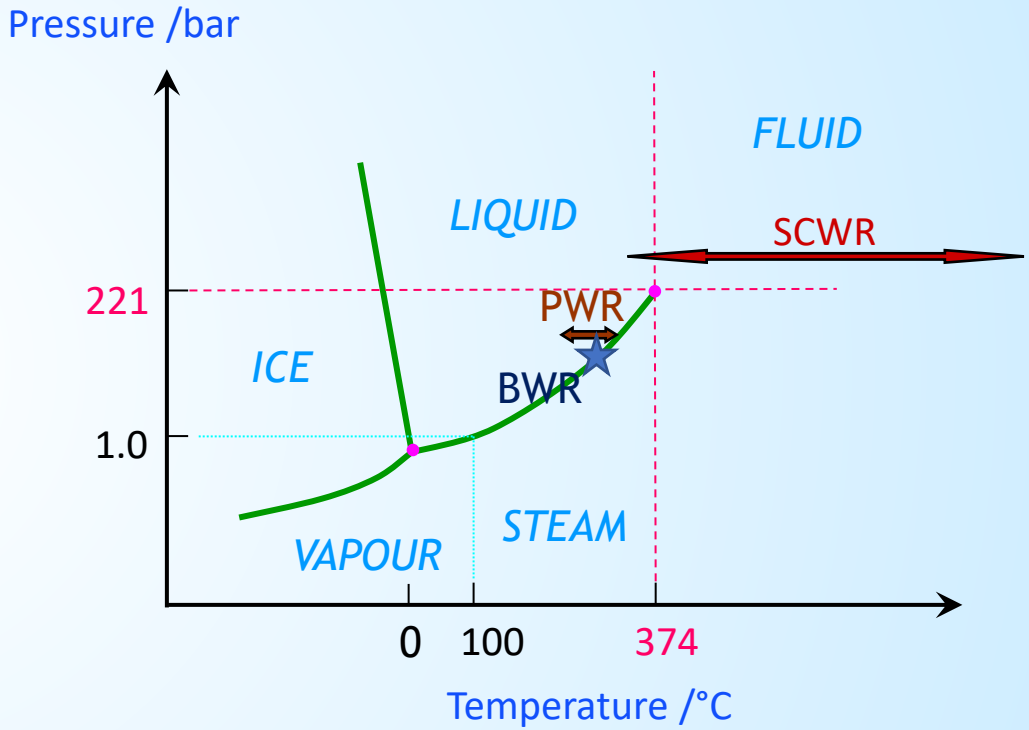



# Superheated Water in the Nuclear Power Industry

## Water-cooled Nuclear Reactors




## Phase Diagram of Water




Nuclear reactor heat source + Supercritical steam turbine technology = Supercritical Water Reactor

There are 22 nuclear power reactors in Canada, producing ~15% of Canada's electricity. All are CANDU reactors.

# Muonium Decay Through Chemical Reaction

$$\mathrm{Mu} + \mathrm{A} \longrightarrow \text{products}$$

$$-\frac{d[\mathrm{Mu}]}{dt} = k_{\mathrm{M}}[\mathrm{A}][\mathrm{Mu}] = \lambda_{\mathrm{M}}[\mathrm{Mu}]$$

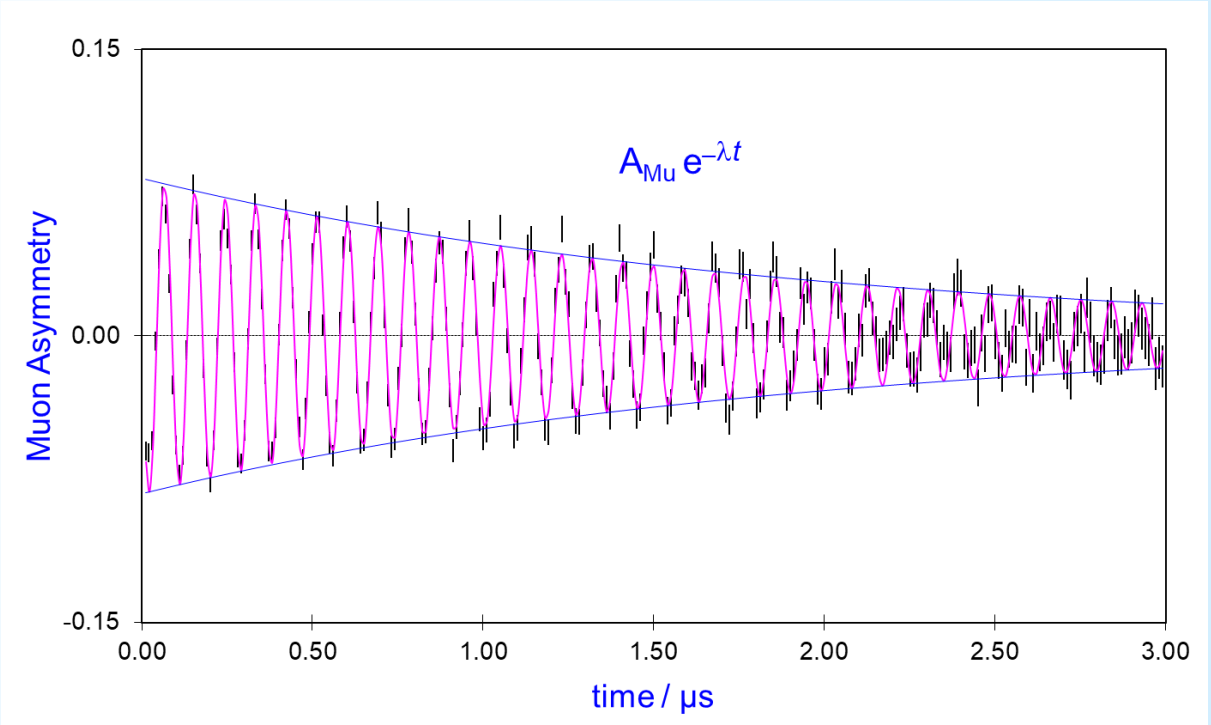
The Mu signal decays exponentially with decay rate

$$\lambda = \lambda_0 + \lambda_{\mathrm{M}} = \lambda_0 + k_{\mathrm{M}}[\mathrm{A}]$$

The second-order rate constant is

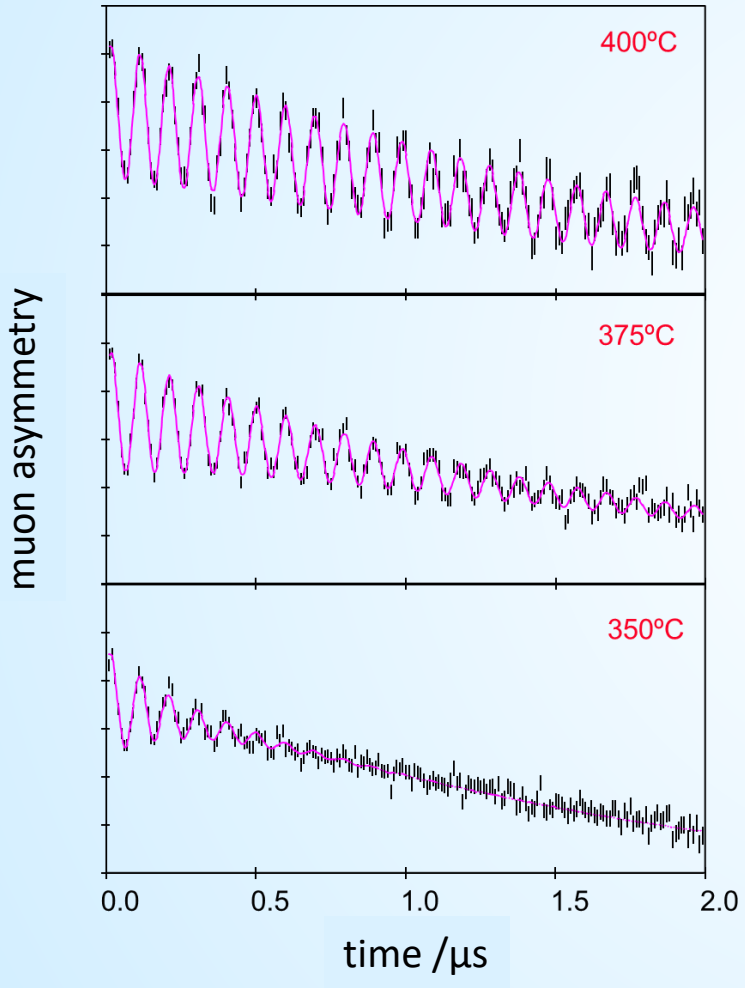
$$k_{\mathrm{M}} = \frac{\lambda - \lambda_0}{[\mathrm{A}]}$$

Muonium reactions are pseudo-first order because only a few million Mu atoms are needed for an experiment.



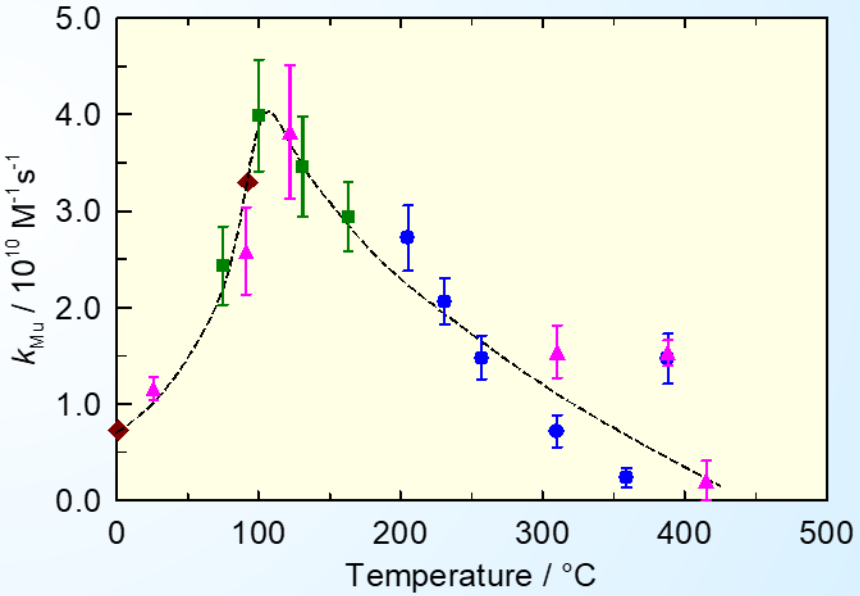
# Non-Arrhenius Kinetics

Mu in $1.4 \times 10^{-4}$ M $(Ni^{2+})_{aq}$ at 250 atm




Ghandi, Percival, Brodovitch, et al., Phys. Chem. Chem. Phys. (2002)

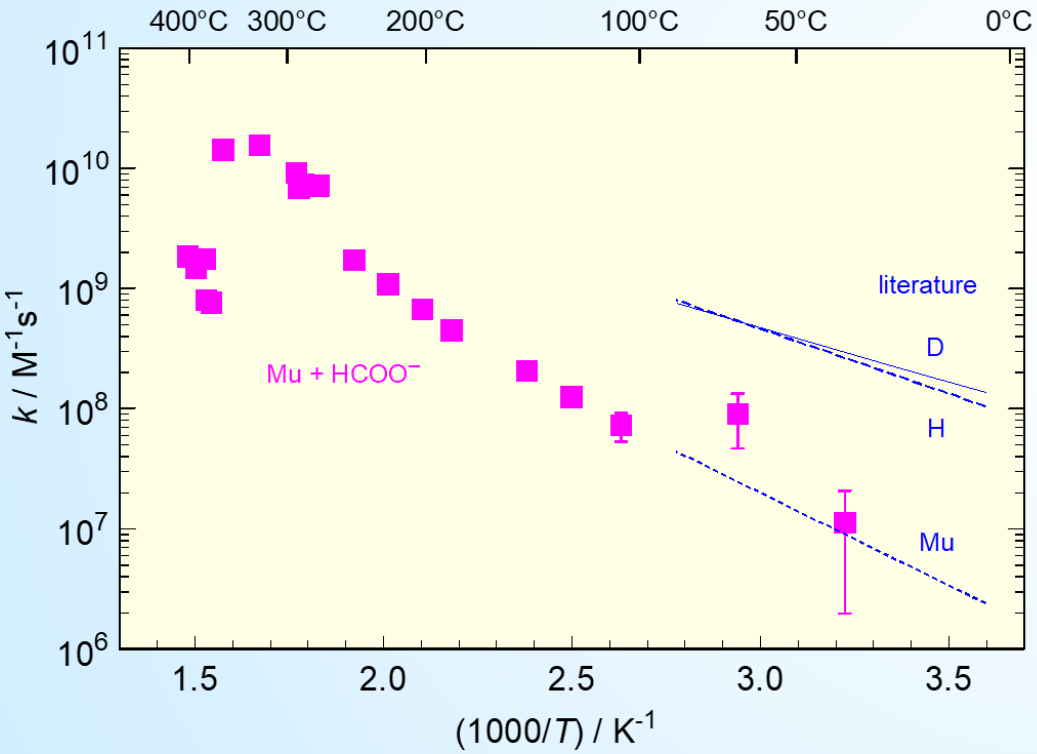
Mu + $Ni^{2+}$ spin exchange



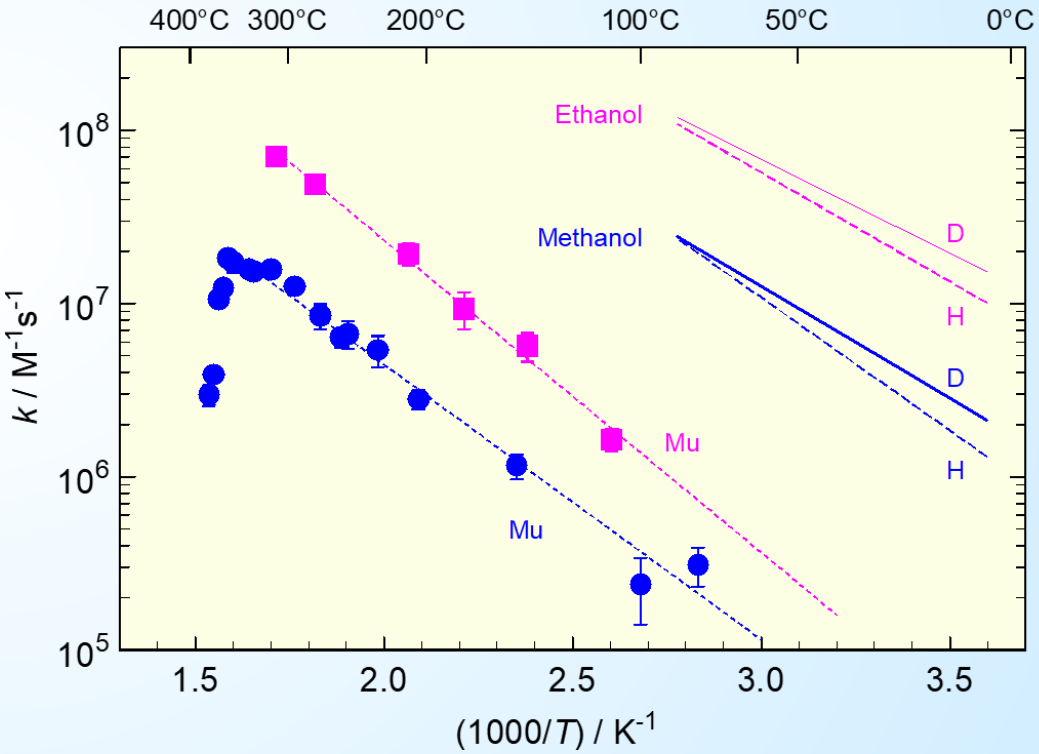
# Non-Arrhenius Kinetics — Chemical Reactions

Ghandi, Brodovitch, Percival, et al., Physica B (2003)

## H abstraction from formate



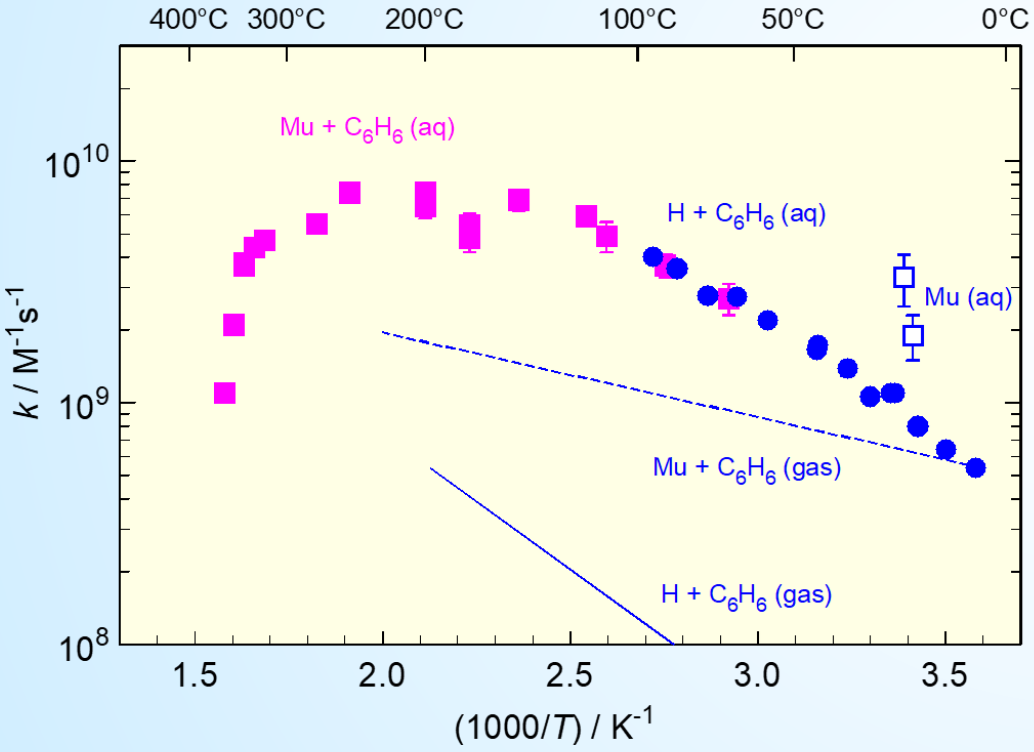

## H abstraction from alcohols



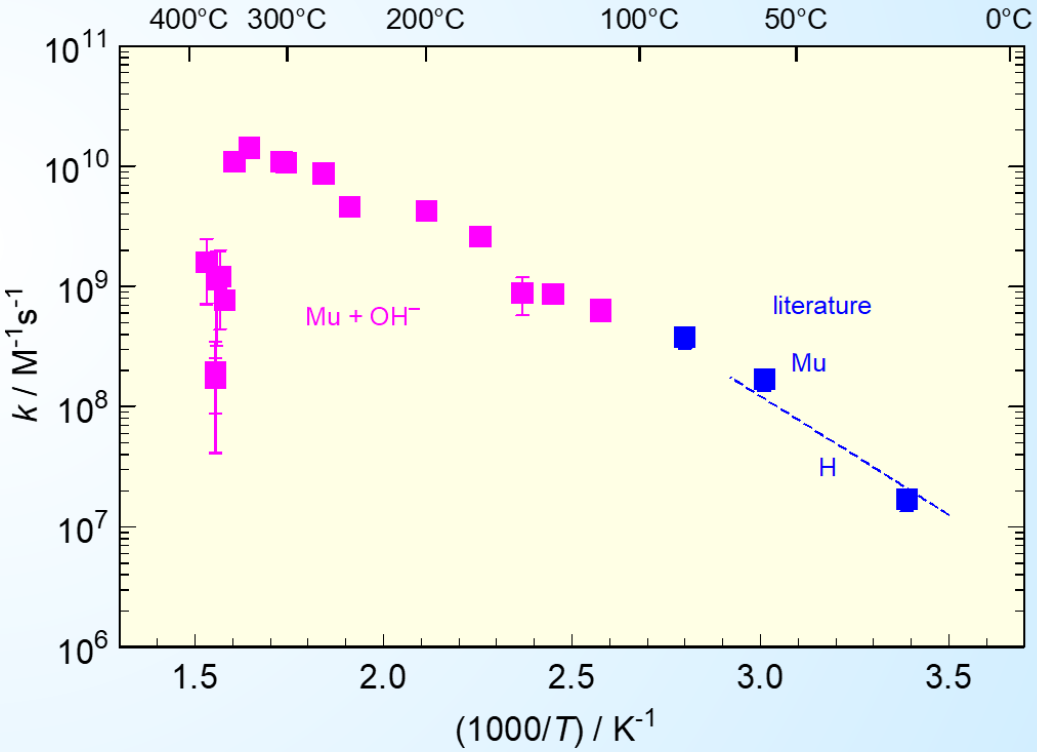
# Non-Arrhenius Kinetics — Chemical Reactions

Ghandi, Brodovitch, Percival, et al., Physica B (2003)

## Mu + benzene




## Mu + $OH^- \rightarrow MuOH + e^-_{aq}$



# A Model for collision-controlled kinetics

Reaction rates in liquids depend on diffusion of the reactants to form the encounter pair, as well as the activated chemical reaction.

$$\mathrm{Mu} + \mathrm{A} \leftrightarrows \{\mathrm{MuA}\} \rightarrow \mathrm{products}$$

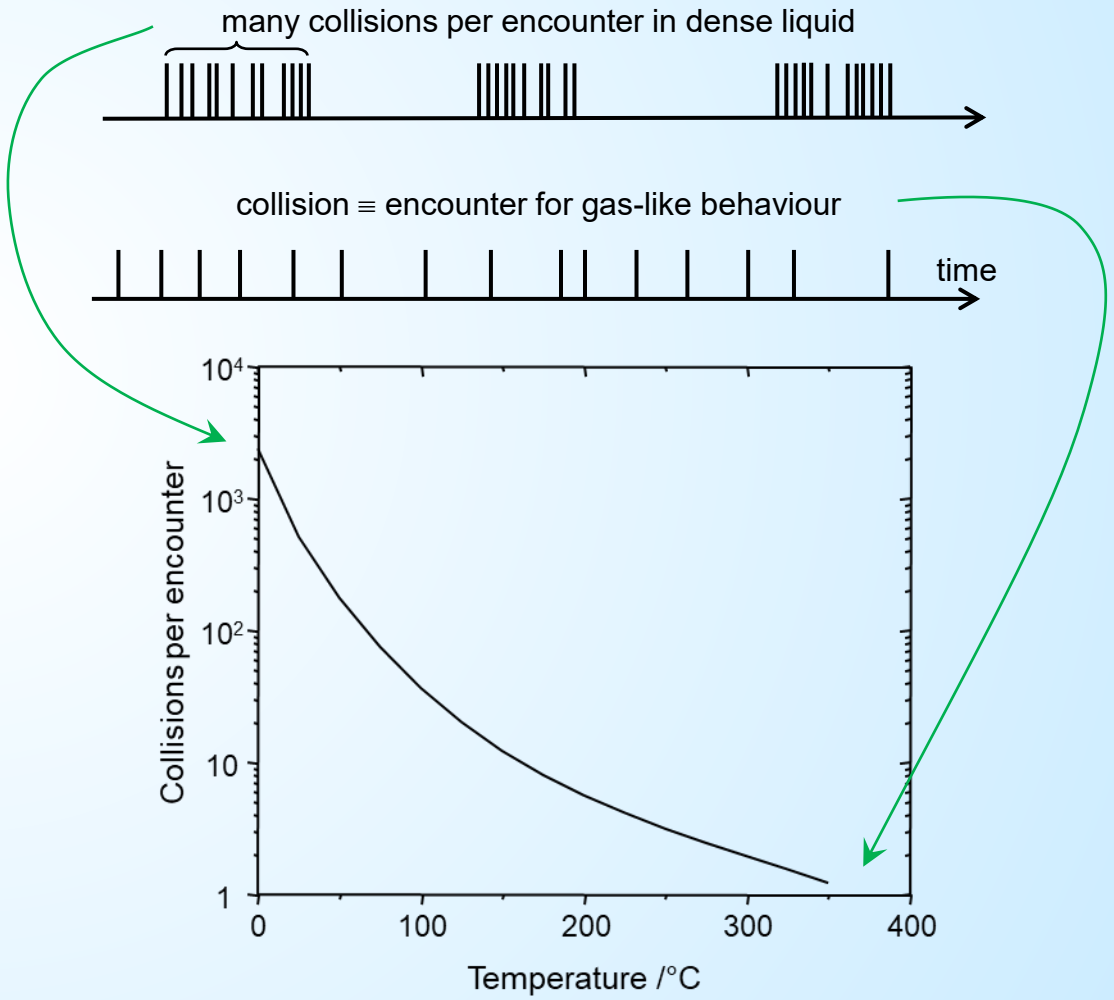
$$\frac{1}{k_{\mathrm{obs}}} = \frac{1}{k_{\mathrm{diff}}} + \frac{1}{k_{\mathrm{act}}}$$

$$k_{\mathrm{diff}} = 4\pi\left(R_{\mathrm{Mu}} + R_{\mathrm{A}}\right)\left(D_{\mathrm{Mu}} + D_{\mathrm{A}}\right)$$

$$k_{\mathrm{act}} = f_{\mathrm{R}} A \exp\left(-E_a / RT\right) \qquad f_{\mathrm{R}} = \frac{PZ_{\mathrm{coll}}}{\tau_{\mathrm{enc}}^{-1} + PZ_{\mathrm{coll}}}$$

The key factor in the fall-off with temperature seems to be the drop in the number of collisions between a pair of reactants over the duration of their encounter.

Ghandi, Brodovitch, Percival, et al., Phys. Chem. Chem. Phys. (2002)



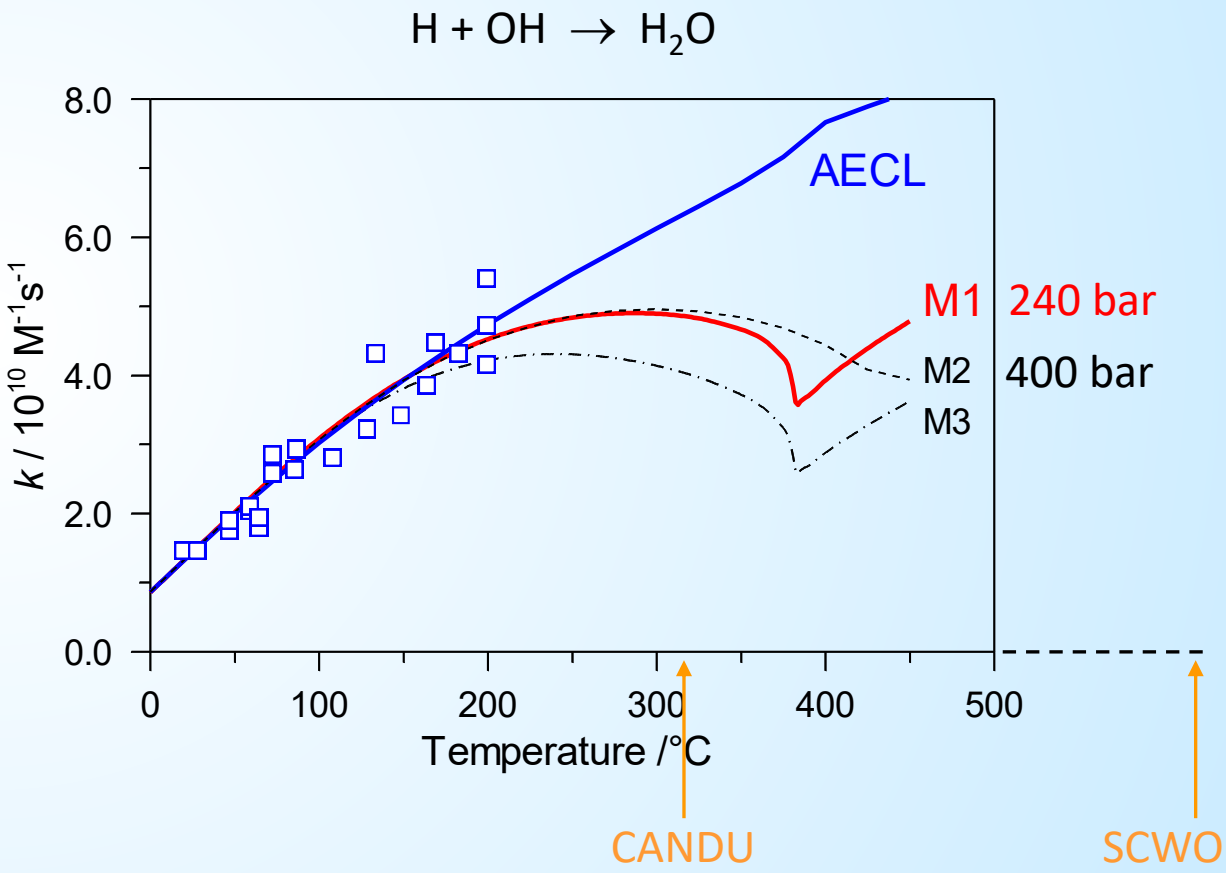
# AECL Water Radiolysis Models were based on Extrapolations

Ghandi & Percival,
J. Phys. Chem. A (2003)

A.J. Elliot, AECL Report 11073 (1994)
Rate Constants and G-Values for the Simulation of the Radiolysis of Light Water over the Range 0-300°C

"All the rate constants for which data are available can be expressed as reasonable fits to the Arrhenius expression … the question arises as to whether one can simply extrapolate up the Arrhenius line to estimate the rate constant for a reaction at 300°C from data measured below 200 °C."

"While the Arrhenius fit is satisfactory, the experiments could not be performed in a temperature region (i.e., > 125°C) where some hydrated electron reaction rate constants have been observed to actually decrease with temperature."



# Gen IV Energy Technologies

Canada is one of several countries working together to lay the groundwork for the fourth-generation nuclear reactor.

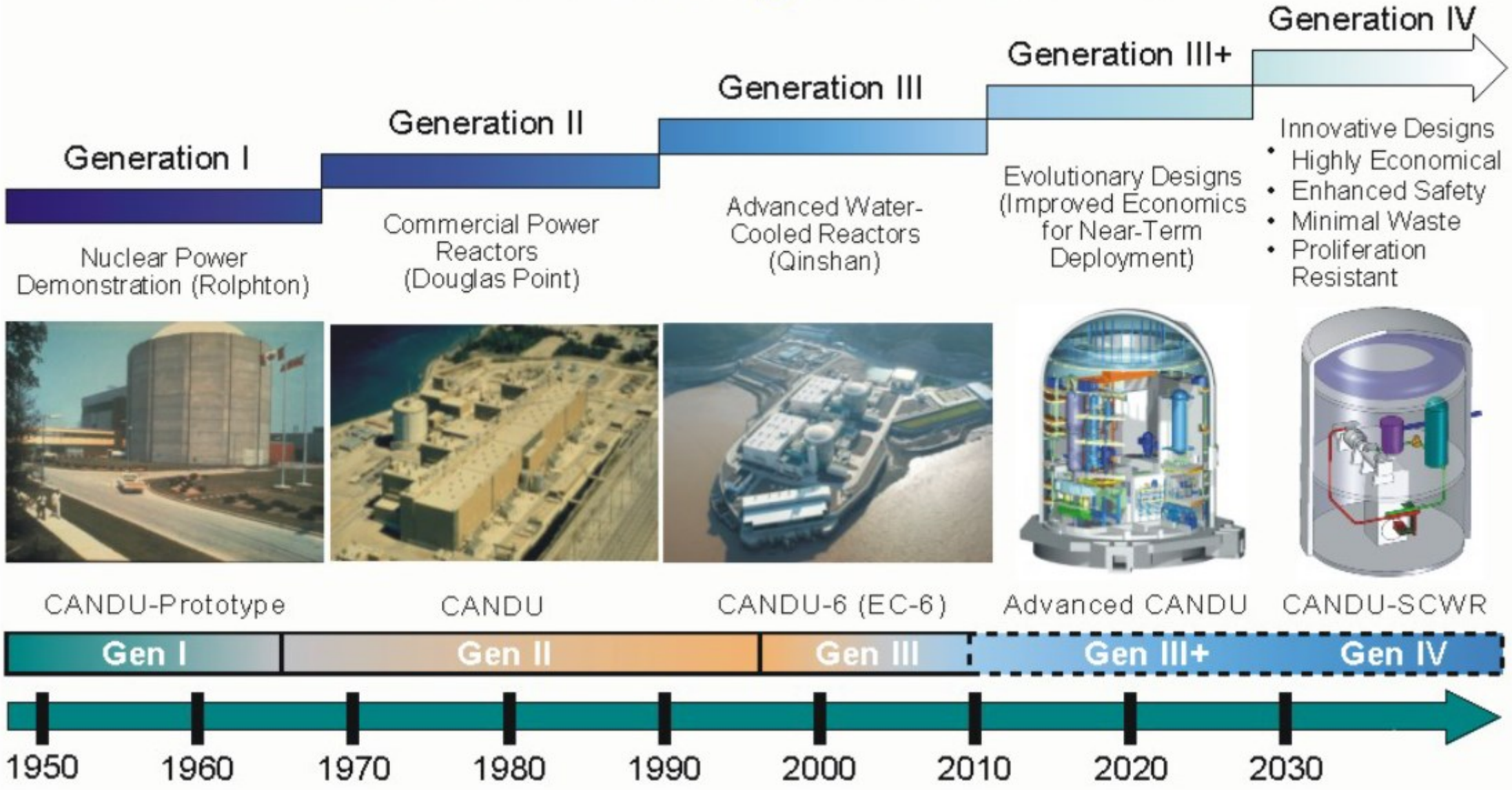

2006 The Canadian National Program on Generation IV Energy Technologies was established by Natural Resources Canada (NRCan) to support Canada's commitment to the Gen IV Forum.

Canada chose to develop the Supercritical Water Reactor (SCWR).

2008 NSERC announced the NSERC/NRCan/AECL Generation IV Energy Technologies Grant Program to encourage Canadian university researchers to contribute to two main R&D priority areas, including:

improved understanding of radiolysis under supercritical water conditions and the effect of radiolysis products on corrosion and stress corrosion cracking

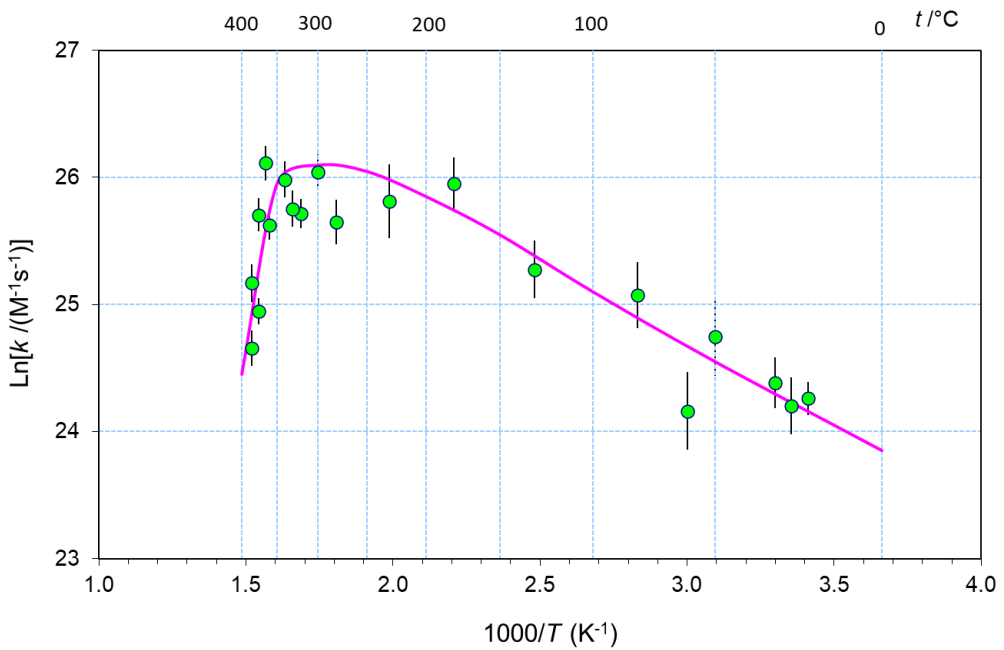
# CANDU Design Evolution



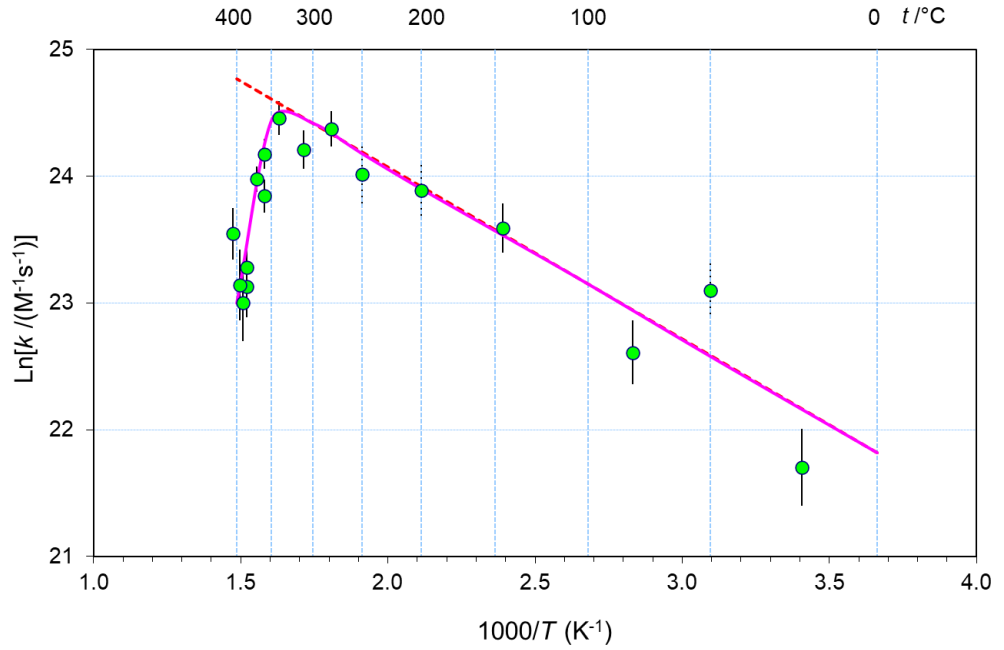

Source: Brady, Poupore and Leung, Gen IV National Program presentation to CNSC, January 2011

# Non-Arrhenius Kinetics in $D_2O$

## Mu + $Ni^{2+}$ in $D_2O$



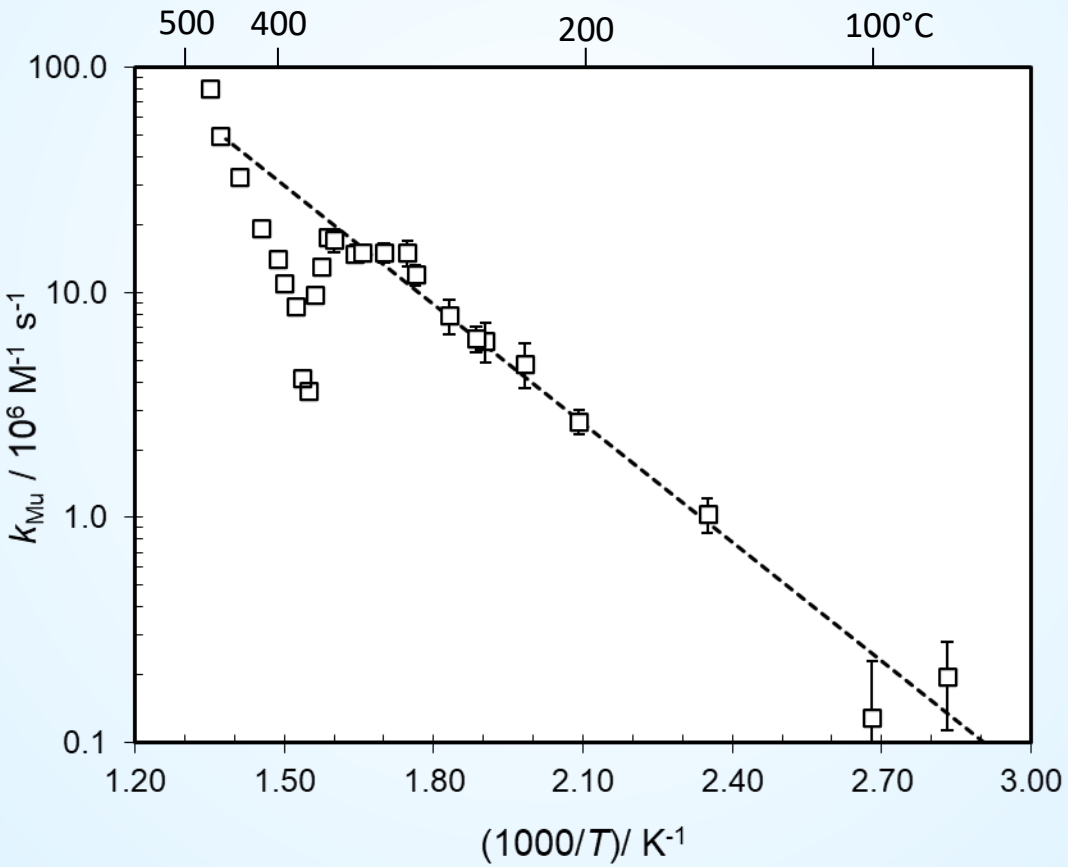

## Mu + $OD^-$ in $D_2O$



# Higher Temperature Data Confirm the Model Predictions

Percival, Brodovitch, Ghandi et al., Rad. Phys. Chem. Phys. (2007)

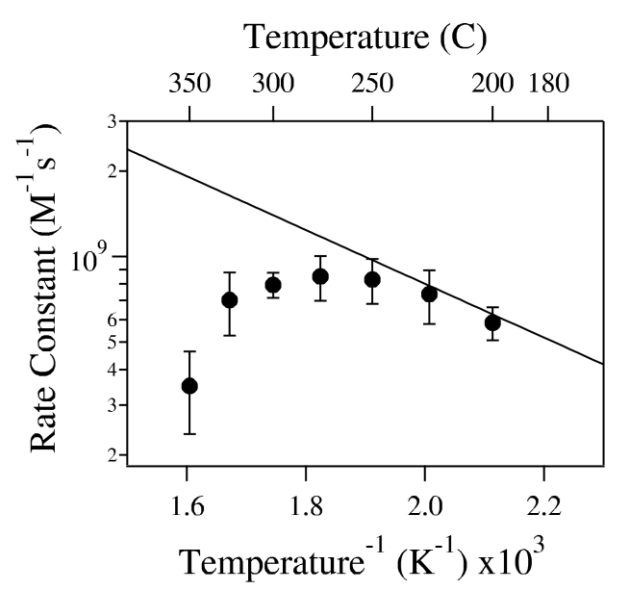
Mu + methanol



# Similar Behaviour for "Conventional" Radiolysis Transients

electron pulse radiolysis with transient UV/vis absorption spectroscopy

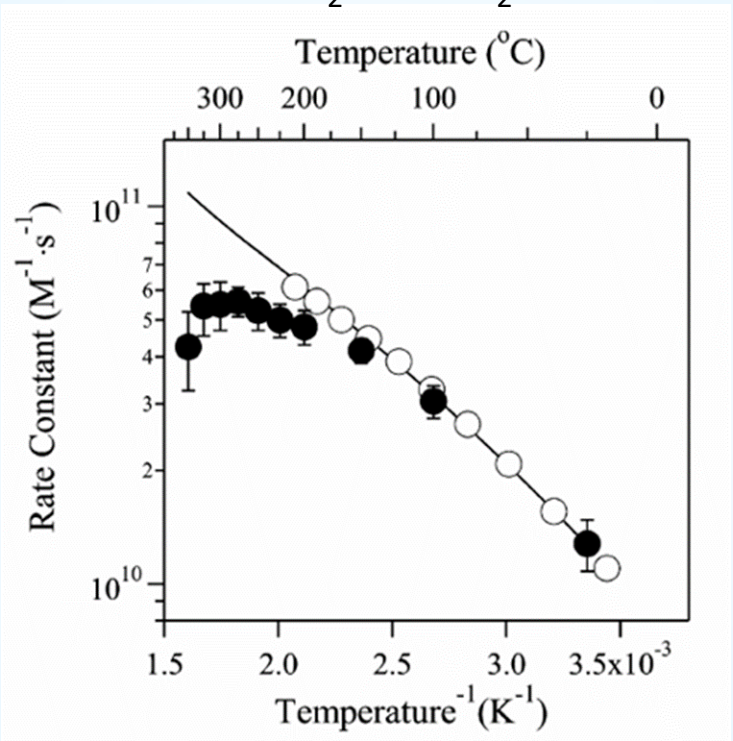
$OH + H_2 \rightarrow H + H_2O$




Argonne National Laboratory

Marin et al., Chem. Phys. Lett. A 2003

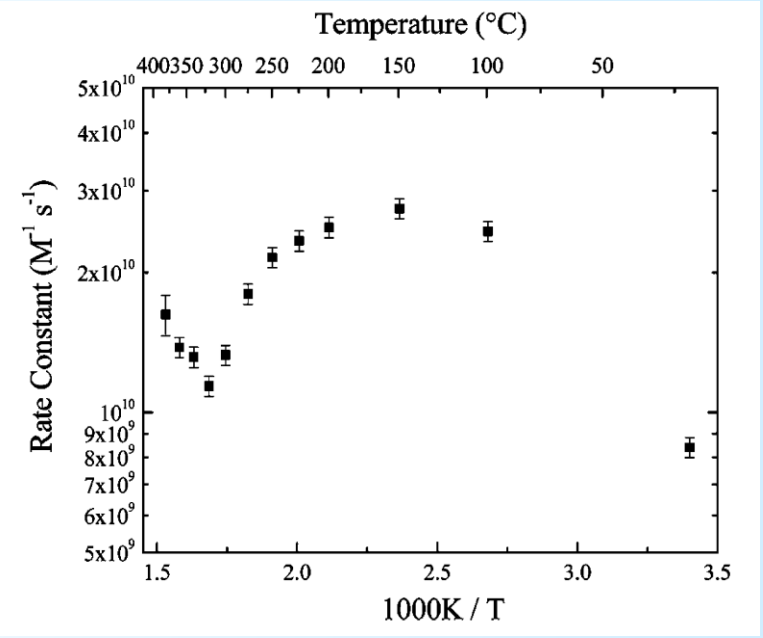
$H + O_2 \rightarrow HO_2$




Argonne National Laboratory

Janik et al., J. Phys. Chem. A 2007

OH + phenol

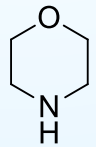



Notre Dame Radiation Laboratory

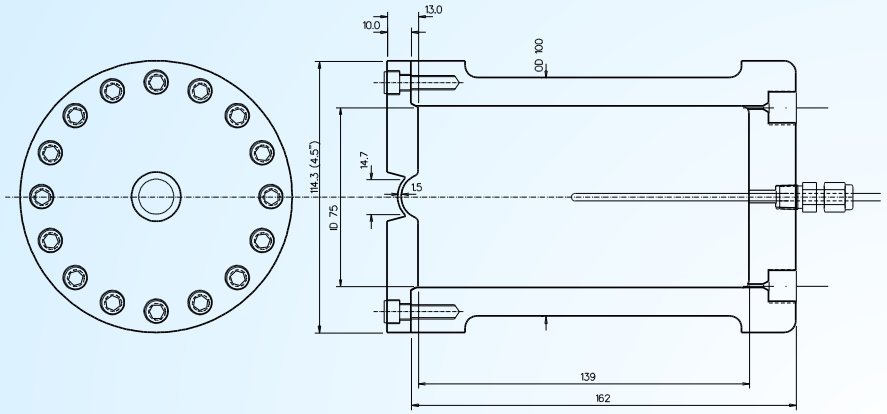
Bonin et al., J. Phys. Chem. A 2007

# Ghandi/Percival Gen IV Phase 2 Research Plan

- Commission the new high-temperature cell. ☑
- Modify the sample handing system with the addition of a high-pressure syringe pump. ☑
- Measure Mu and D fractions in pure water in $H_2O$ and $D_2O$ in the range 400–650°C.
- Measure Mu decay rates in pure water in the range 400–650°C to confirm and extend data on the Mu + $H_2O$ reaction.
- Check the isotropic muonium hyperfine frequency in supercritical water by making measurements of the frequency splitting in intermediate fields.
- Determine rate constants for fundamental reactions of Mu in water, in particular Mu + $O_2$ and Mu + $H_2$.
- Determine rate constants for reactions of Mu with various substances of a technological nature (e.g. morpholine).

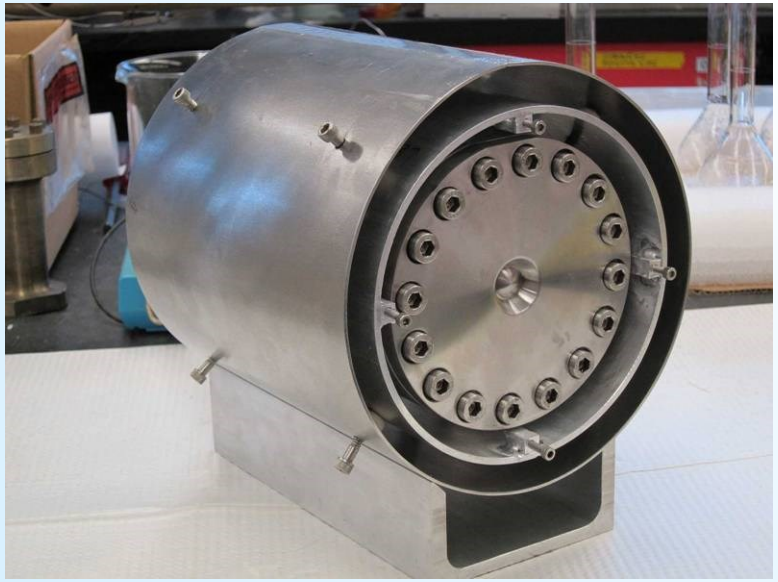


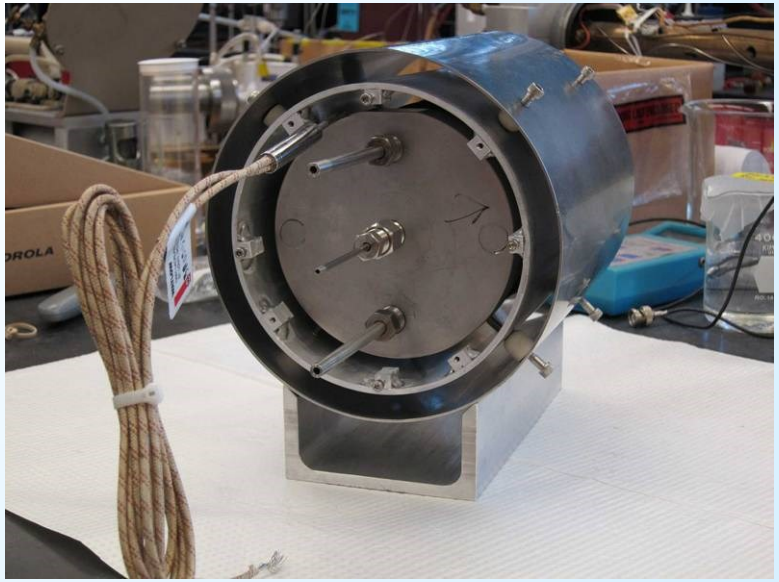
# Pressure cell for low density samples (up to ~650°C)




Tested offline to 580°C at 250 bar

Inconel 625

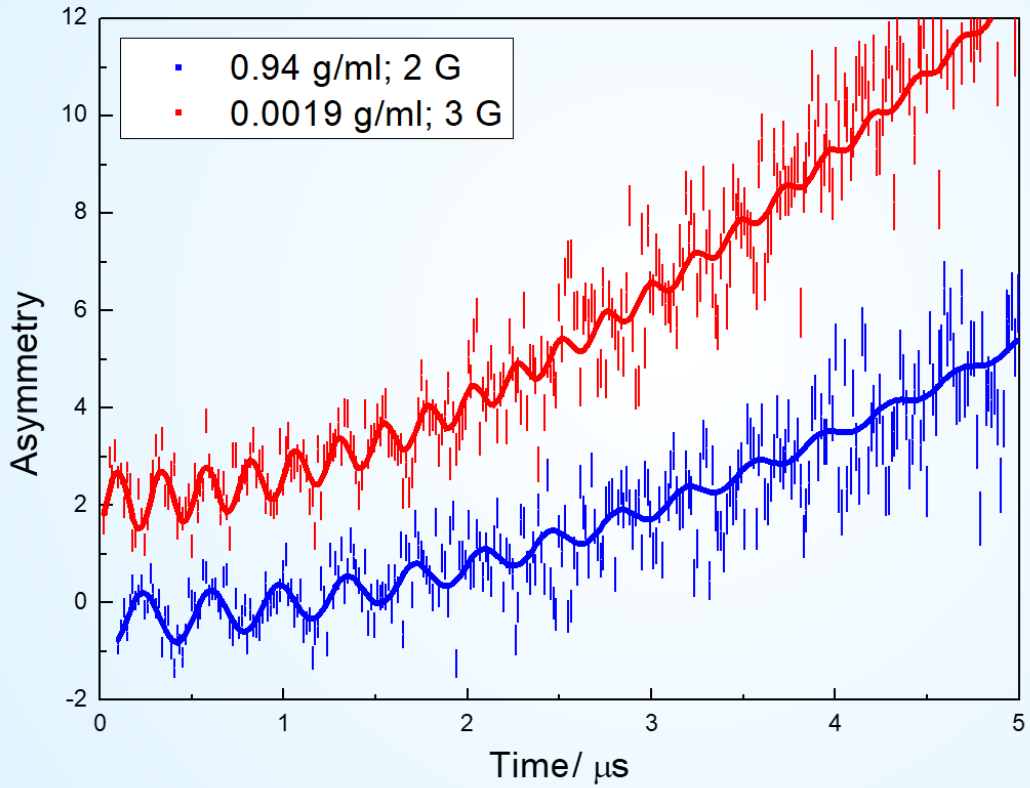




# J-PARC June 2017

Commissioning test of large cell

Liu, Percival, Ghandi, et al.,
JPS Conf. Proc. (2018)




Mu precession in dense liquid and hot gaseous water

# History of SCW Kinetics at TRIUMF

- 1994 M713 Muonium Chemistry in Supercritical Water
- 1994 M842 Muonium-substituted Free Radicals in Sub- and Supercritical Water
- 2004 M1012 Organic Free Radicals under Hydrothermal Conditions
- 2009 M1198 Reaction Kinetics in Supercritical Water as Probed with Muonium

- 2009-2012 Generation IV Energy Technologies R&D Program, phase 1 (3 years)
- 2012-2016 Generation IV Energy Technologies R&D Program, phase 2 (4 years)

! **2012** M9B failure

- 1999 Phys Chem Chem Phys Muonium in Sub- and Supercritical Water
- 2000 Physica B Hyperfine Coupling Constants of Muonium in …
- 2002 Phys Chem Chem Phys Near-diffusion-controlled reactions of muonium in …
- 2003 Physica B Muonium kinetics in sub- and supercritical water
- 2003 J Phys Chem A Prediction of Rate Constants for Reactions of the OH Radical in …
- 2007 Rad Phys Chem H atom kinetics in superheated water studied by …
- 2014 Chem Phys Kinetics of the Reaction between H• and Superheated Water …

# $H + H_2O \rightarrow H_2 + OH$

The role of the reaction $H + H_2O \rightarrow H_2 + OH$ in the radiolysis of water at high temperatures is controversial.

Swiatla-Wojcik and Buxton, Rad. Phys. Chem. 74 (2005) 210.

Comment: Bartels, Rad. Phys. Chem. 78 (2009) 191.

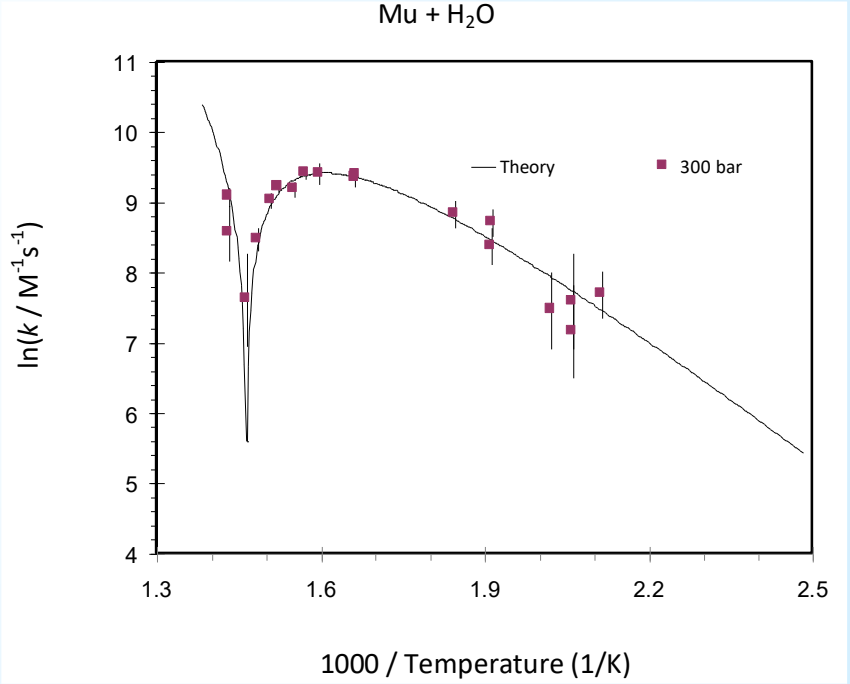
Reply: Swiatla-Wojcik and Buxton, Rad. Phys. Chem. 79 (2009) 52.

Alcorn and Ghandi modeled the temperature dependence of the overall rate constant assuming two reaction channels:

$Mu + H_2O \rightarrow MuH_2O^+ + e^-$

$Mu + H_2O \rightarrow MuH + OH$

Alcorn, Ghandi, Percival et al. Chem. Phys. (2013)



Thank you for your attention