TRIUMF Summer Institute 2011

Lecture 10

Chemical Kinetics

Paul Percival

Muonium Kinetics

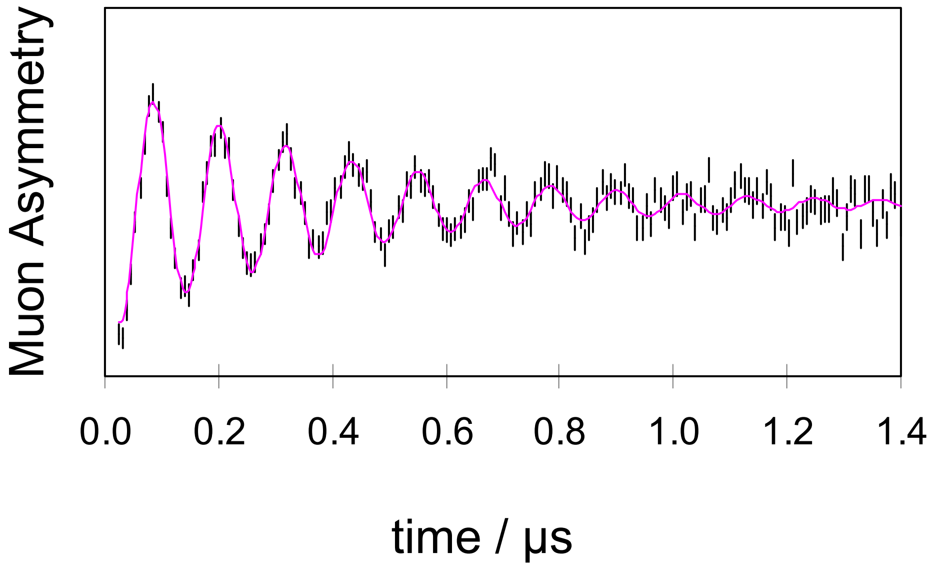
Muonium reactions are pseudo-first order because…

only a few million Mu atoms are needed for an experiment.

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

[A] is constant

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



The Mu signal decays exponentially

$$[\mathrm{Mu}] = [\mathrm{Mu}]_{t=0}\, \mathrm{e}^{-\lambda t}$$

with $\lambda = k_{\mathrm{M}}[\mathrm{A}]$

second-order rate constant

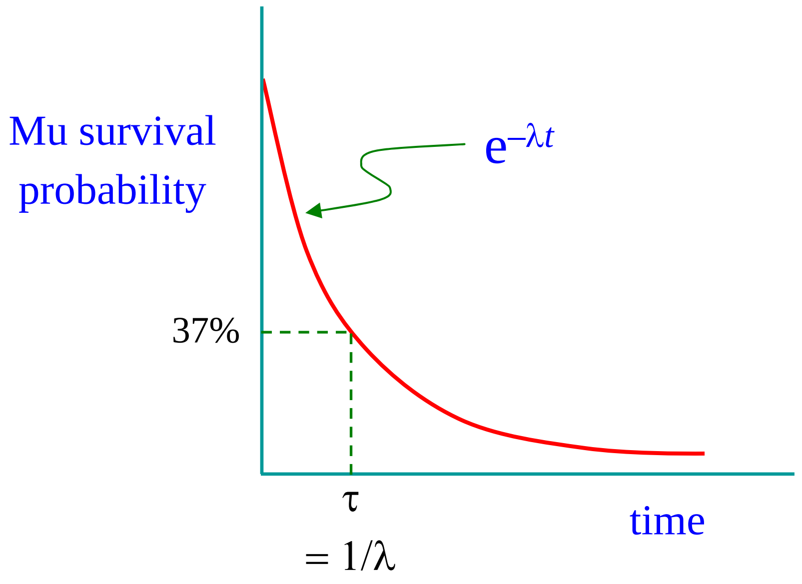
units: $\mathrm{M}^{-1}\mathrm{s}^{-1}$

The Ergodic Principle

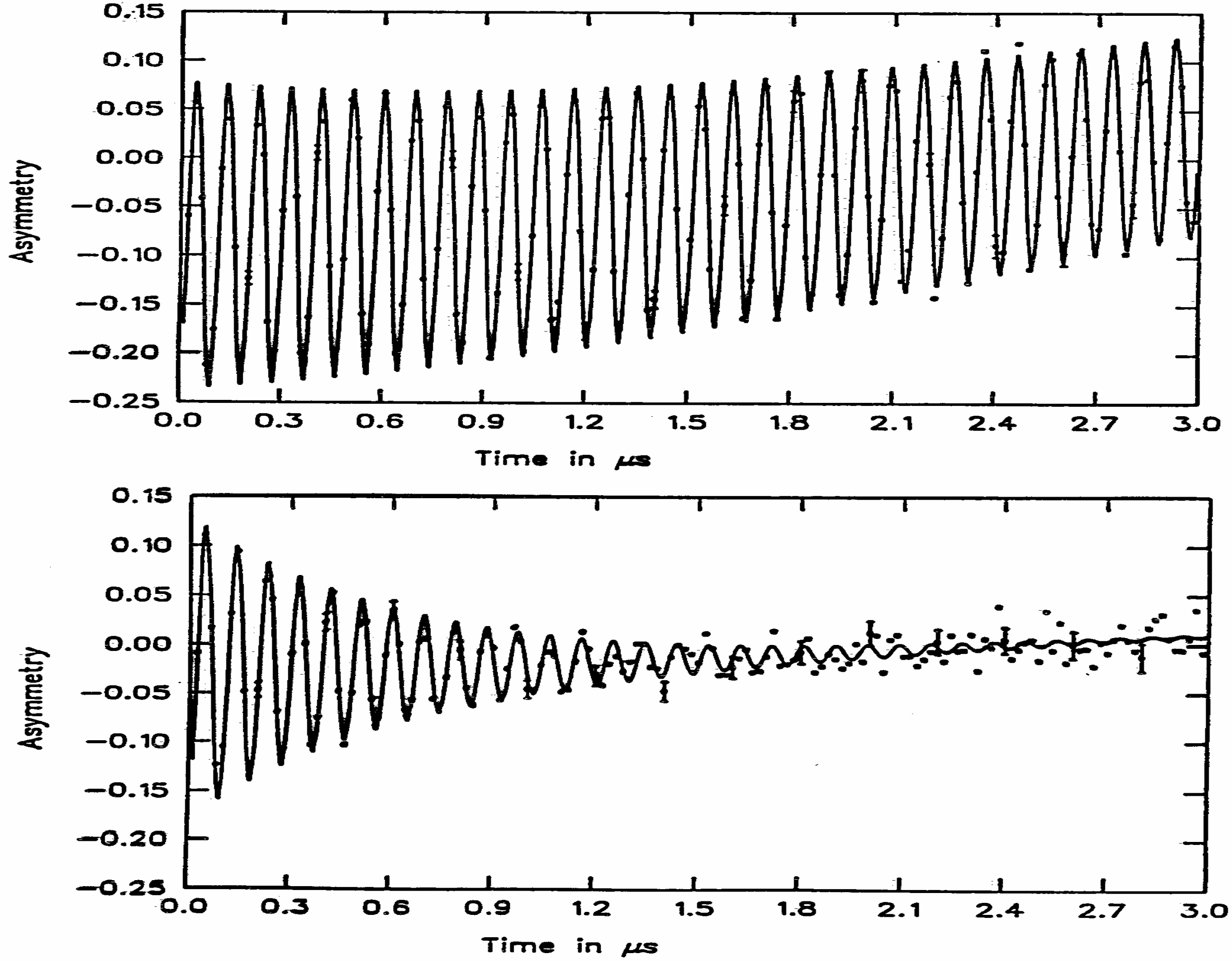
Complaint: What does [Mu] mean when we only have one Mu atom at a time?

Answer: It doesn't matter if the atoms are present at the same time or spread over an interval.

The average of a parameter over time and the average over the statistical ensemble are the same



Chemical Decay of Muonium



7.7 G TF

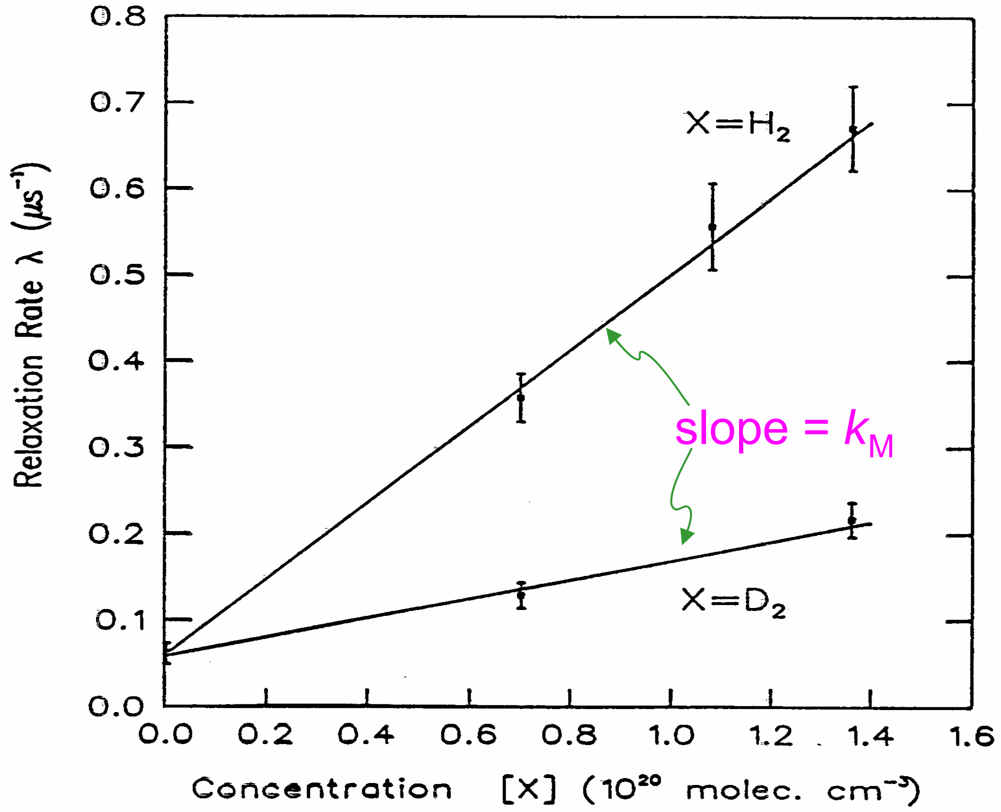
pure
nitrogen
gas

N_2 +
1% C_2D_2

Garner, Fleming, Arseneau, Senba, Reid and Mikula (1990)

Extracting the Second-order Rate Constant

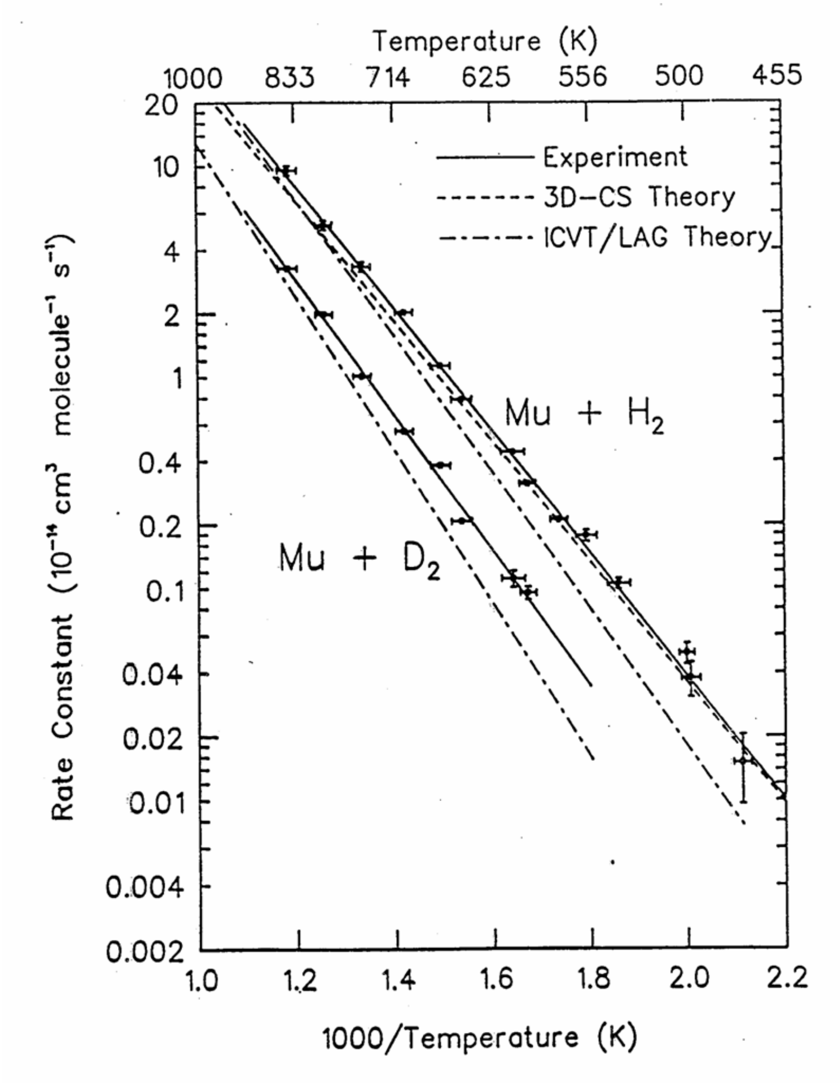
Muonium decay rate $\lambda = \lambda_0 + k_M[X]$



slope = k_M

Reid, Garner, Lee, Senba, Arseneau and Fleming (1987)

Fundamental Kinetic Studies: H + H_2



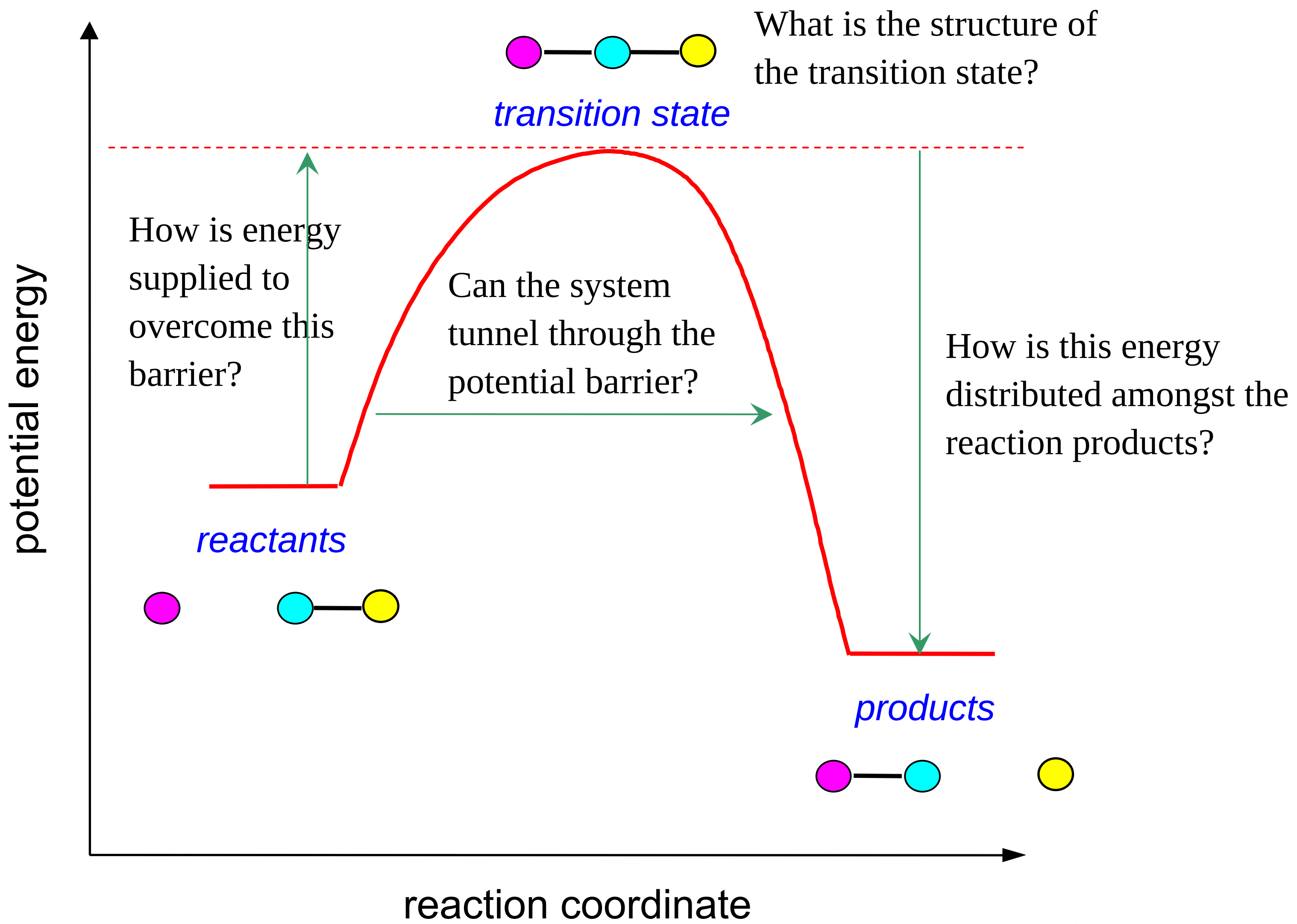
Experimental tests of reaction rate theory: Mu+H_2 and Mu+D_2

Fleming et al,

J. Chem. Phys. 1987

Reaction Dynamics

What is the probability that the system will move from reactants to products?



What is the structure of the transition state?

How is energy supplied to overcome this barrier?

Can the system tunnel through the potential barrier?

How is this energy distributed amongst the reaction products?

1-D Reaction Coordinate

The potential energy *V* is the internal energy *U* from thermodynamics.

In the Born-Oppenheimer Approximation the nuclear and electronic parameters are separable: product of wavefunctions, sum of energies.

The potential energy surface then corresponds to a plot of the energy of the system as a function of nuclear coordinates.

The simplest reaction “surface” has 1 dimension, such as the interatomic distance in the dissociation of a diatomic. e.g. AB → A + B

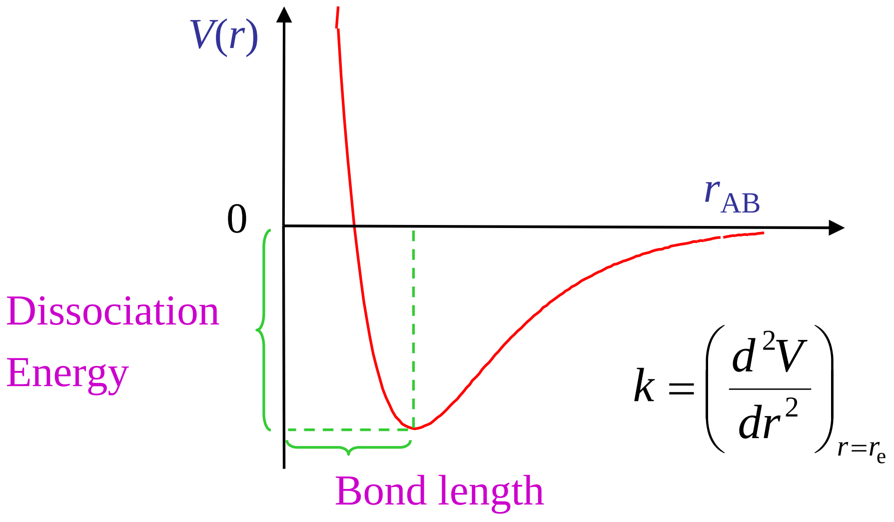
For $r \approx r_e$ the potential can be modelled by the simple harmonic oscillator.

$$V(r) = V(r_e) + \tfrac{1}{2}k(r - r_e)^2$$

But extreme anharmonicity is needed to model dissociation:

The Morse Potential

$$V(r) = D_e\left[1 - e^{-\alpha(r-r_e)}\right]^2 - D_e$$



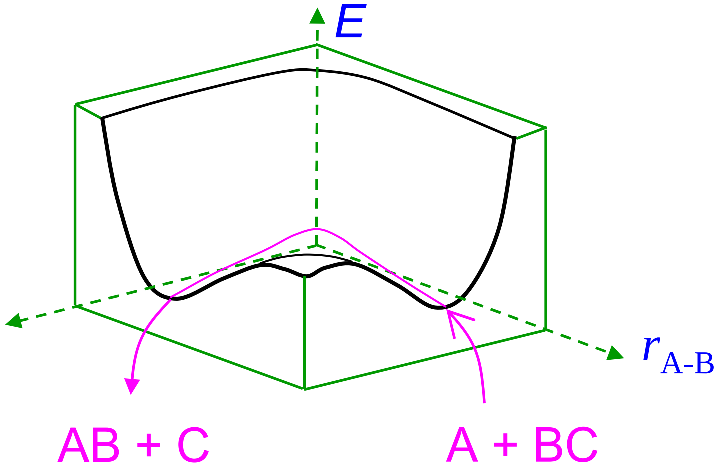
$$k = \left(\frac{d^2V}{dr^2}\right)_{r=r_e}$$

2-D Potential Energy Surface

A collinear triatomic reaction such as

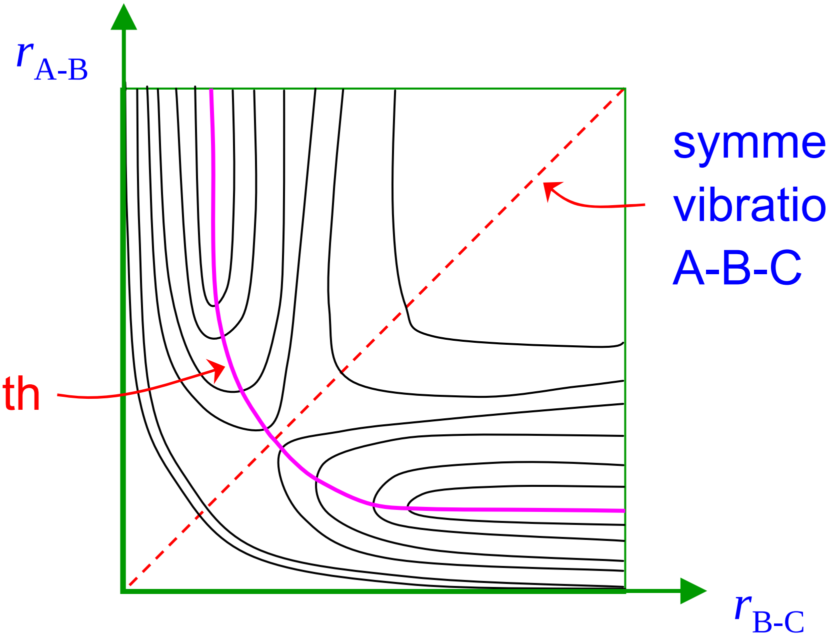
A + BC → AB + C

needs a 3-D plot:



"collinear"
= angle fixed

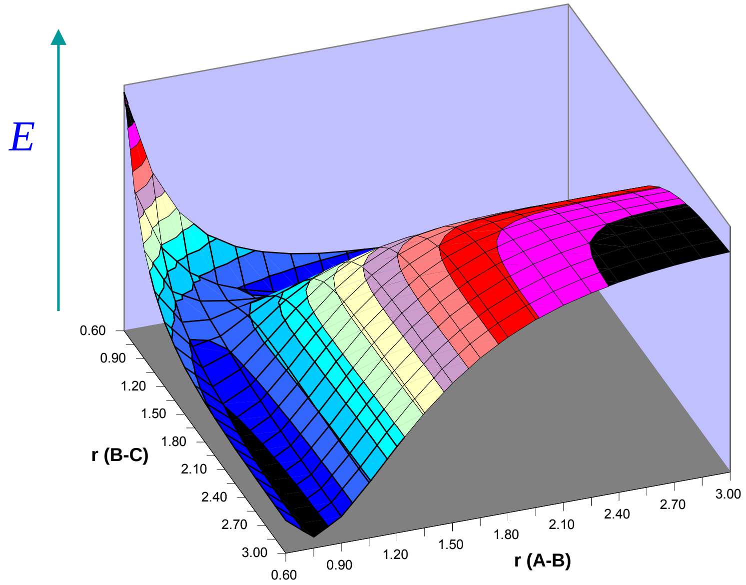
or a contour plot:

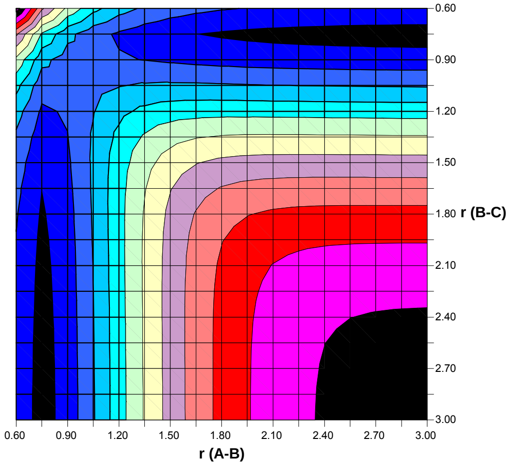


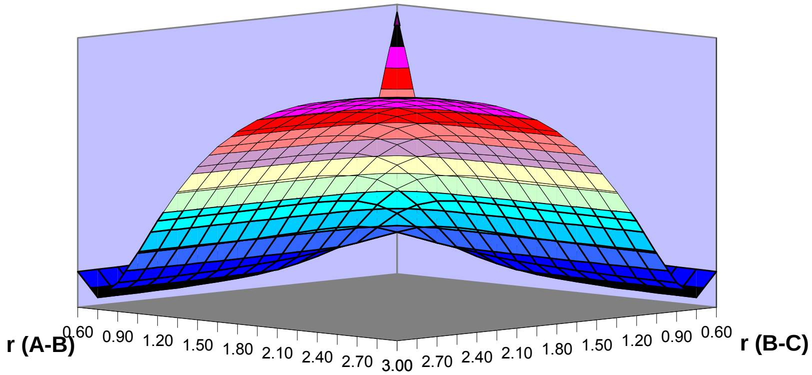
symmetric vibration of A-B-C

minimum energy path

Views of a Potential Energy Surface







Skewed Coordinate System

PE surfaces can be used for classical trajectory calculations as long as the effective mass of the reacting system (modelled by rolling ball) is constant.

A mass-weighted coordinate system diagonalizes the kinetic energy of the system.

$$X = \alpha r_{ab} + \beta r_{bc}\cos\theta$$

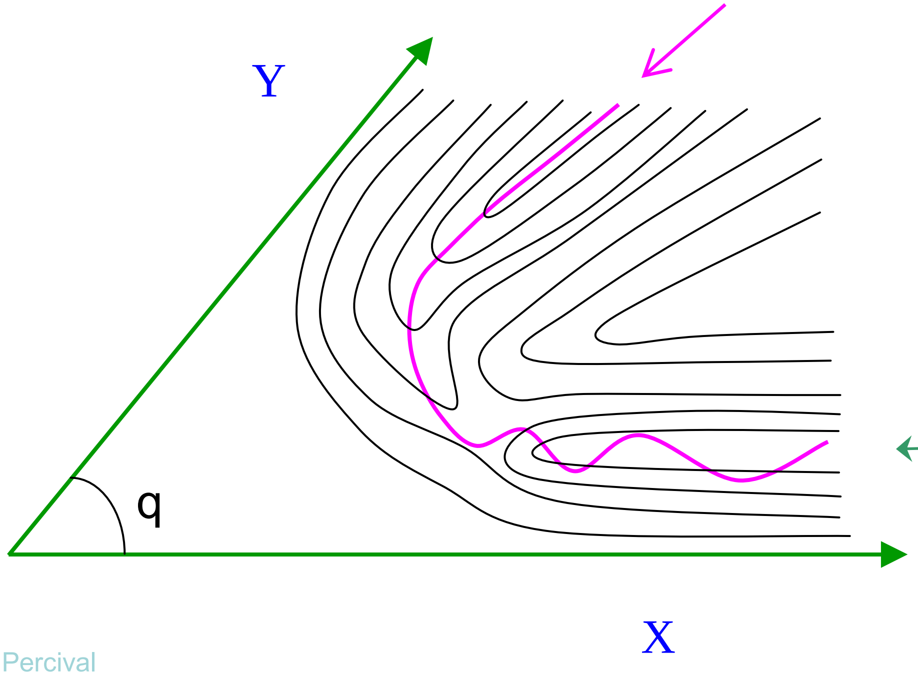
$$Y = \beta r_{bc}\sin\theta$$

$$\alpha = \left[\frac{m_a(m_b + m_c)}{M}\right]^{\frac{1}{2}}$$

$$\beta = \left[\frac{m_c(m_b + m_a)}{M}\right]^{\frac{1}{2}}$$

$$M = m_a + m_b + m_c$$

$$\cos^2\theta = \frac{m_a m_c}{(m_a + m_b)(m_b + m_c)}$$



vibrational
excitation
of product

The LEPS Surface

An analytic function is often more practical than a table of points – it is continuous and can have adjustable parameters.

London-Eyring-Polanyi-Sato (LEPS) surface

$$V(r_{\mathrm{ab}},r_{\mathrm{bc}},r_{\mathrm{ac}}) = \frac{Q_{\mathrm{ab}}}{1+S_{\mathrm{ab}}} + \frac{Q_{\mathrm{bc}}}{1+S_{\mathrm{bc}}} + \frac{Q_{\mathrm{ac}}}{1+S_{\mathrm{ac}}}$$

$$-\frac{1}{\sqrt{2}}\left[\left(\frac{J_{\mathrm{ab}}}{1+S_{\mathrm{ab}}} - \frac{J_{\mathrm{bc}}}{1+S_{\mathrm{bc}}}\right)^2 + \left(\frac{J_{\mathrm{bc}}}{1+S_{\mathrm{bc}}} - \frac{J_{\mathrm{ac}}}{1+S_{\mathrm{ac}}}\right)^2 + \left(\frac{J_{\mathrm{ac}}}{1+S_{\mathrm{ac}}} - \frac{J_{\mathrm{ab}}}{1+S_{\mathrm{ab}}}\right)^2\right]^{1/2}$$

$$Q(r) = \tfrac{1}{2}\left[\mathrm{M}(r)(1+S^2) + \mathrm{AM}(r)(1-S^2)\right]$$

$$J(r) = \tfrac{1}{2}\left[\mathrm{M}(r)(1+S^2) - \mathrm{AM}(r)(1-S^2)\right]$$

Q, J and S are derived from the Coulomb, exchange and overlap integrals of the Heitler-London valence-bond theory

$$\mathrm{M}(r) = D_{\mathrm{e}}\left[\mathrm{e}^{-2\alpha(r-r_{\mathrm{e}})} - 2\mathrm{e}^{-\alpha(r-r_{\mathrm{e}})}\right]$$

Morse function

$$\mathrm{AM}(r) = \tfrac{1}{2}D_{\mathrm{e}}\left[\mathrm{e}^{-2\alpha(r-r_{\mathrm{e}})} + 2\mathrm{e}^{-\alpha(r-r_{\mathrm{e}})}\right]$$

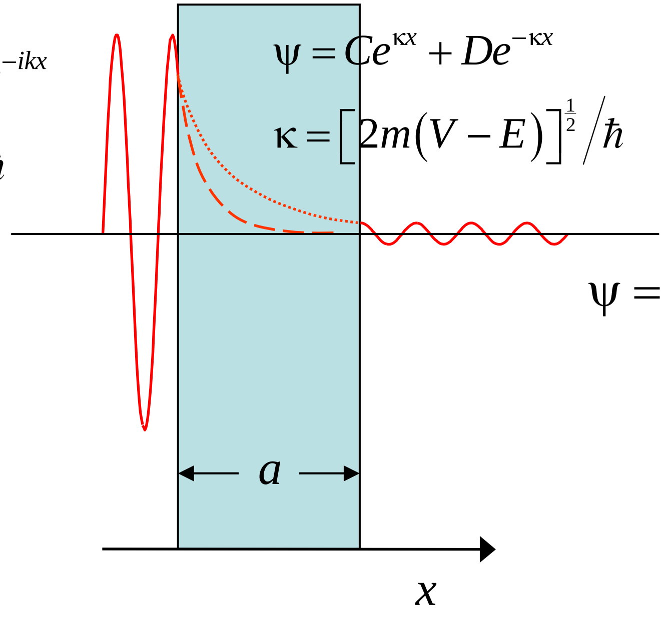
anti-Morse function

Tunnelling

Consider a particle of energy *E* striking a potential barrier of height *V*.

$$\psi = Ae^{ikx} + Be^{-ikx}$$

$$k = (2mE)^{\frac{1}{2}} / \hbar$$



$$\psi = Ce^{\kappa x} + De^{-\kappa x}$$

$$\kappa = \left[2m(V-E)\right]^{\frac{1}{2}} \big/ \hbar$$

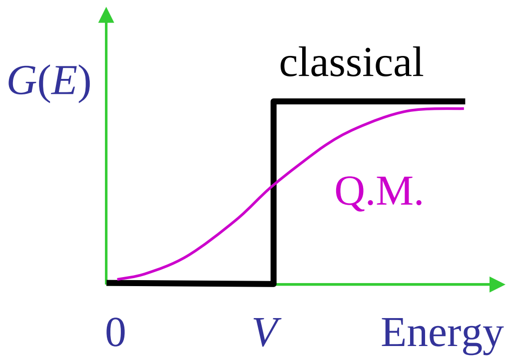
$$\psi = A'e^{ikx} + B'e^{-ikx}$$

Application of boundary conditions gives the transmission probability:

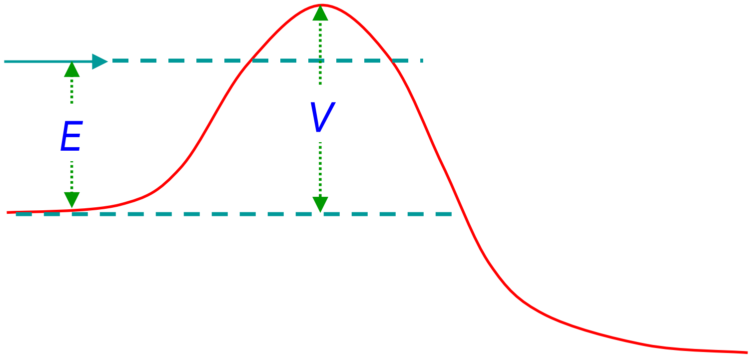
$$G = \frac{A'^2}{A^2} = \left\{ 1 + \frac{\left(e^{\kappa a} - e^{-\kappa a}\right)^2}{16\frac{E}{V}\left(1-\frac{E}{V}\right)} \right\}^{-1}$$

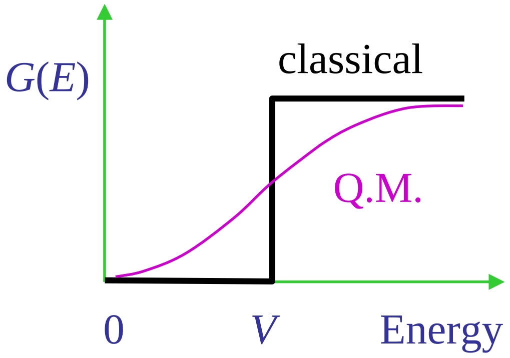
Tunnelling depends on:

- the mass of the particle
- its energy (compared to the barrier)
- the width of the barrier



Tunnelling in Chemical Reactions





The transmission probability G or permeability depends on energy.

The transmission coefficient κ is the correction factor

$$k_{\text{quantum}}(T) = \kappa(T)\, k_{\text{classical}}(T)$$

$$\kappa(T) = \frac{\int_0^\infty k_{\text{quant}}(T)\, dE}{\int_0^\infty k_{\text{class}}(T)\, dE} = \frac{\int_0^\infty G_{\text{quant}} e^{-E/RT} dE}{\int_0^\infty G_{\text{class}} e^{-E/RT} dE} = \frac{\int_0^\infty G_{\text{quant}} e^{-E/k_B T} dE}{\int_V^\infty e^{-E/k_B T} dE} = \frac{e^{V/k_B T}}{k_B T} \int_0^\infty G_{\text{quant}} e^{-E/k_B T} dE$$

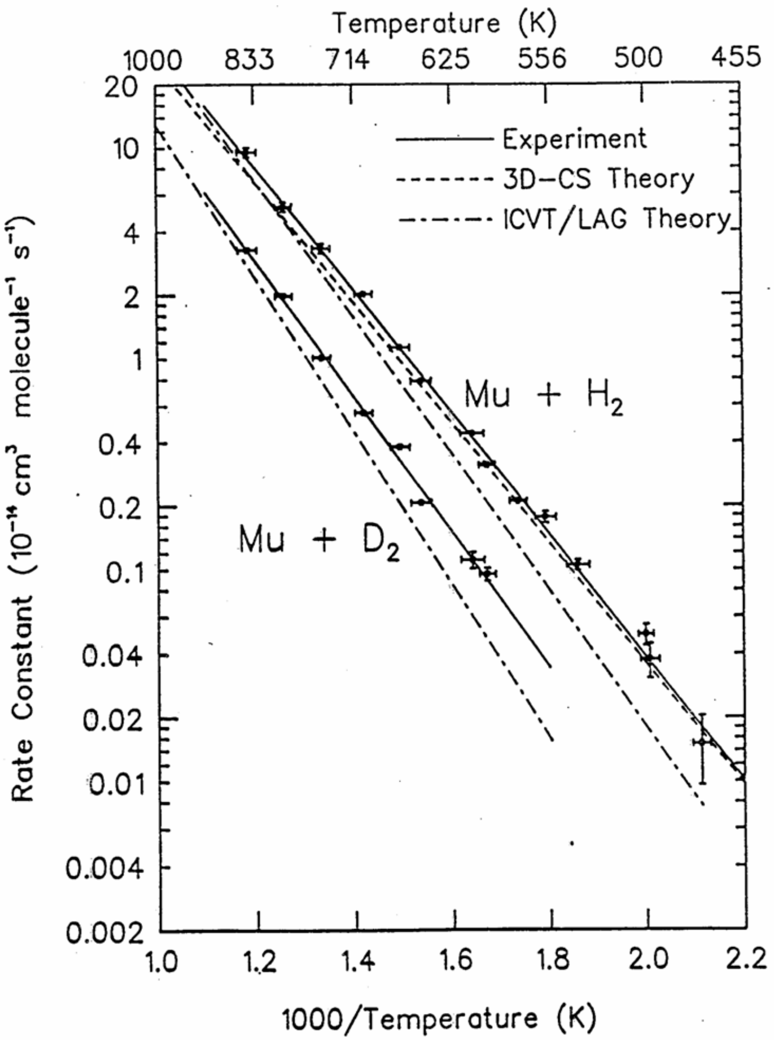
The PE curve is often approximated by a standard function to get an analytic solution.

e.g the Eckart barrier gives

$$\kappa(T) = 1 + \frac{1}{24}\left(\frac{h\nu^{\ddagger}}{k_B T}\right)^2 + \ldots$$

imaginary frequency of reaction coordinate

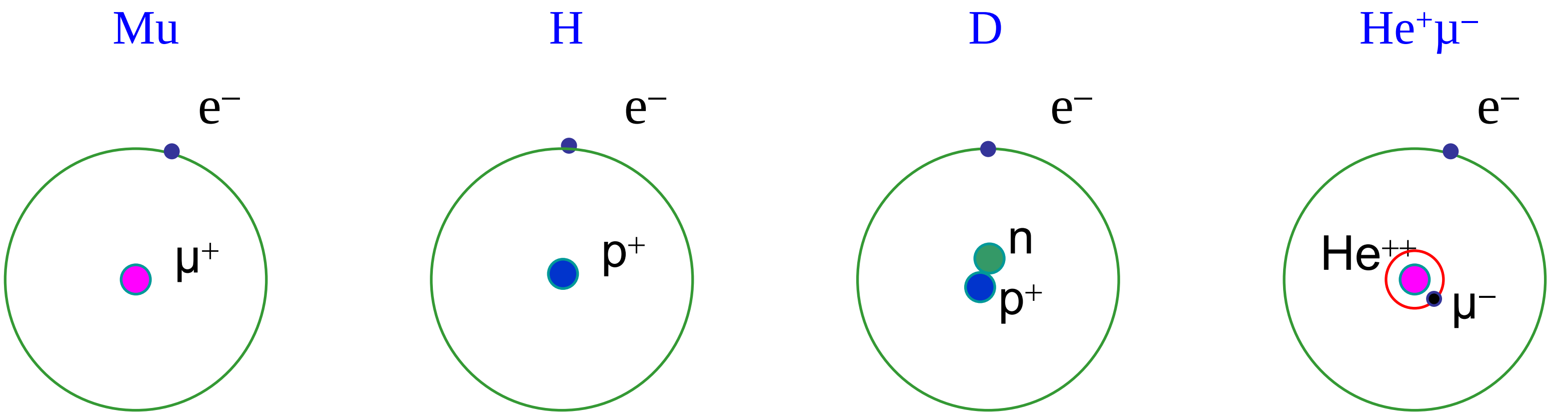
Fundamental Kinetic Studies: H + H_2



Experimental tests of reaction rate theory: Mu+H_2 and Mu+D_2
Fleming et al, J. Chem. Phys. 1987

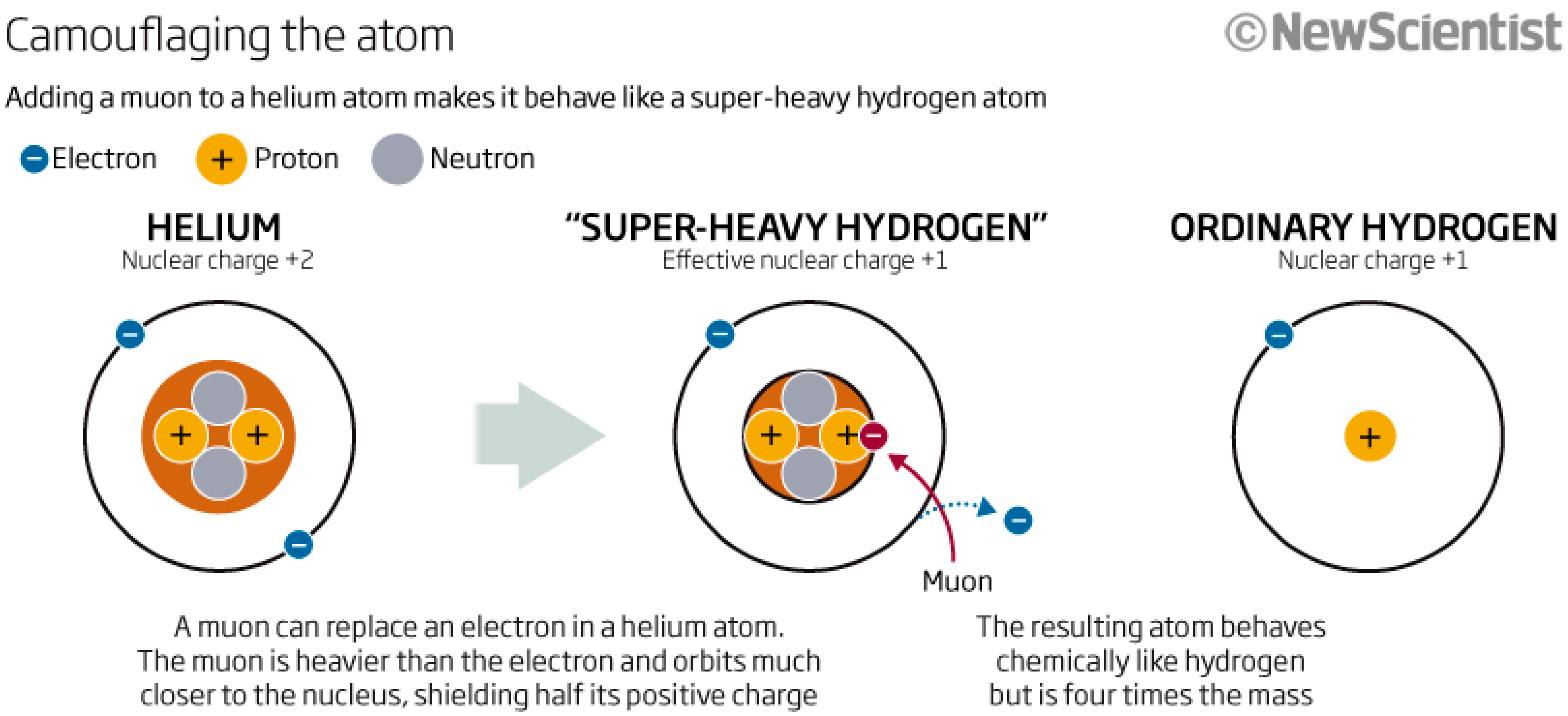
Quasiclassical trajectory (and variational transition state theory) study of the rates and temperature-dependent activation energies of the reactions Mu+H_2 (completely thermal) and H, D, and Mu+H_2 (v=0, j=2)
Truhlar et al, J. Chem. Phys. 1983

Hydrogen Isotopes



$^{0.11}\mathrm{H}$ $^{1}\mathrm{H}$ $^{2}\mathrm{H}$ $^{4.1}\mathrm{H}$

Muonic Helium is a heavy isotope of hydrogen



Camouflaging the atom

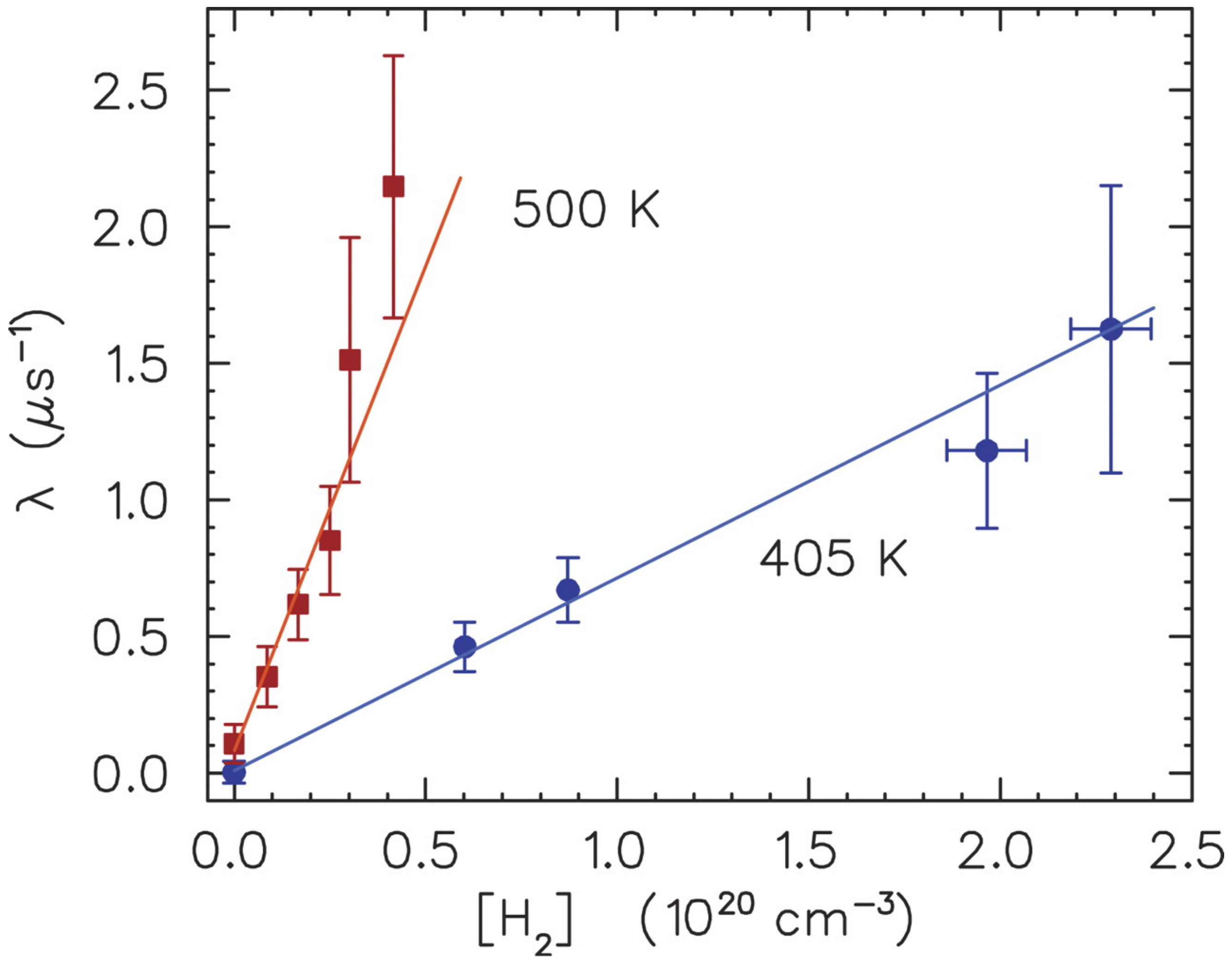
Adding a muon to a helium atom makes it behave like a super-heavy hydrogen atom

A muon can replace an electron in a helium atom. The muon is heavier than the electron and orbits much closer to the nucleus, shielding half its positive charge

The resulting atom behaves chemically like hydrogen but is four times the mass

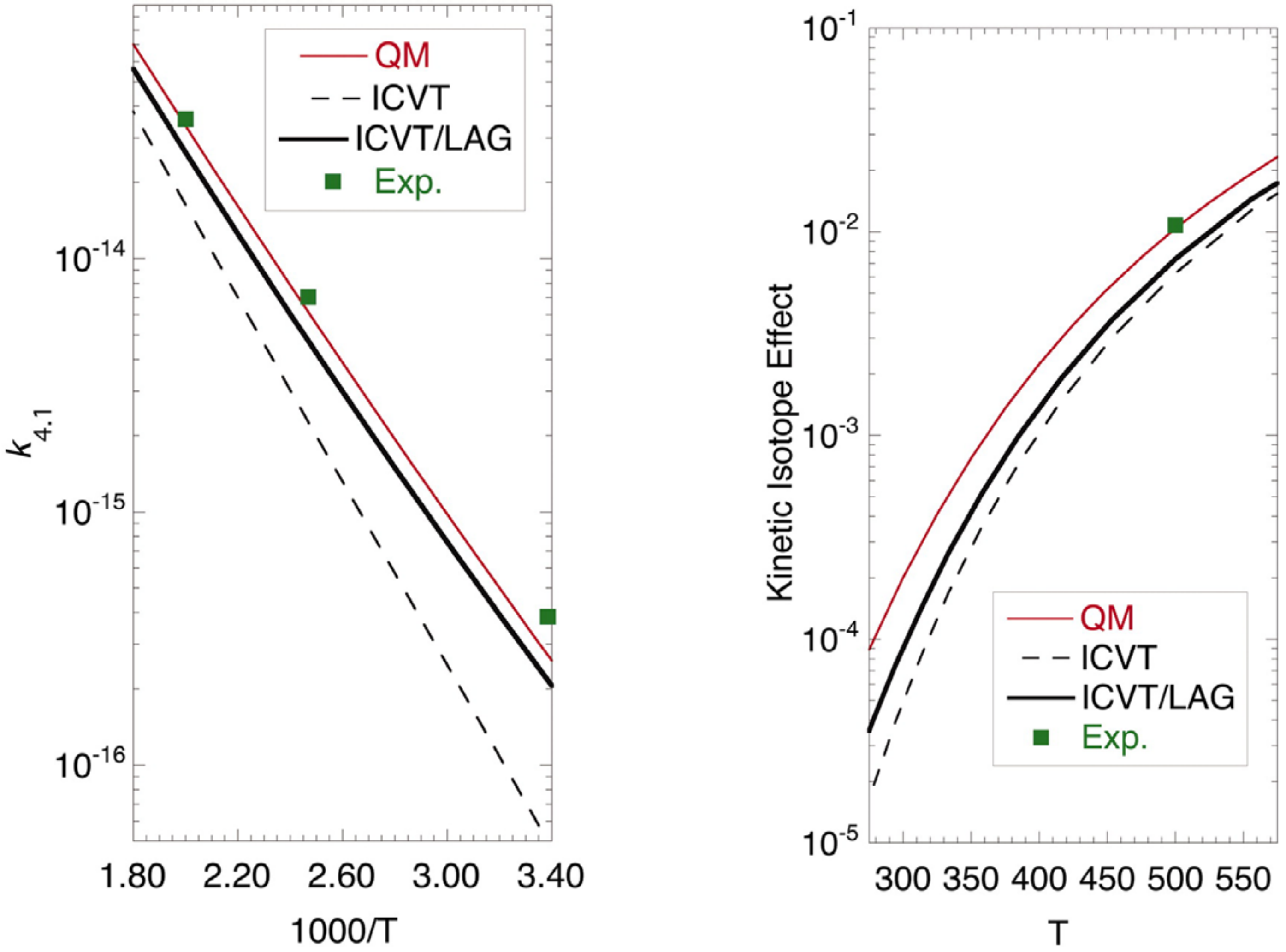
Taken from a comment on a TRIUMF experiment by Don Fleming et al.

D G Fleming et al. Science 2011; 331: 448-450



Published by AAAS

D G Fleming et al. Science 2011; 331: 448-450



$k_{0.11}/k_{4.1}$

Published by AAAS

Muonium Isotope Effects

The chemistry of an atom depends primarily on

⌑ the ionization potential	How easy is it to remove an electron?
⌑ the radius	How are the electrons distributed?

For Mu these are almost the same as for H

However, for molecular vibrations involving Mu,

Mu—X

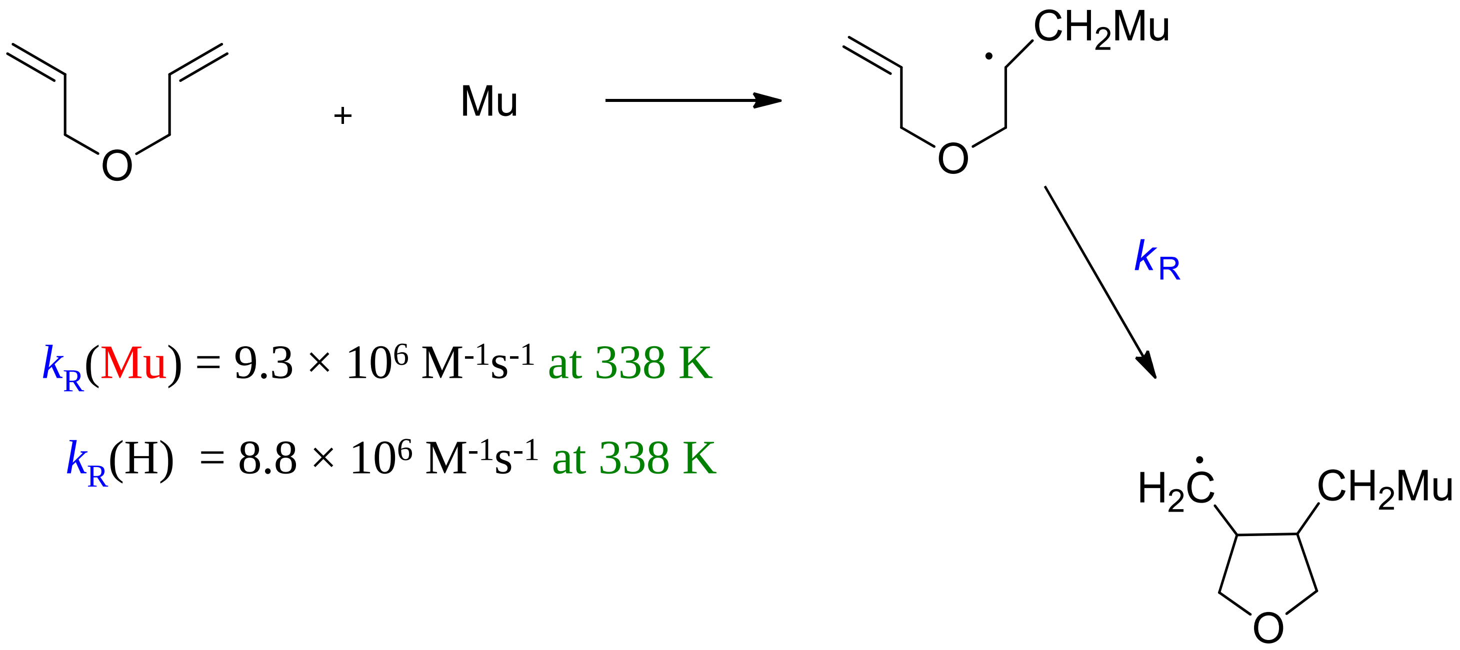
$$m_r = \frac{m_\mu m_X}{m_\mu + m_X} \approx m_\mu \qquad \therefore\ \upsilon_{MuX} = \sqrt{\frac{m_{HX}}{m_{MuX}}}\,\upsilon_{HX} \approx 3\upsilon_{HX}$$

if $m_X >> m_\mu$

⇒ Vibrational frequencies involving Mu are higher than for H

The Muon as Spectator

in a free radical rearrangement



k_R(Mu) = 9.3×10^6 $M^{-1}s^{-1}$ at 338 K

k_R(H) = 8.8×10^6 $M^{-1}s^{-1}$ at 338 K

Mu does not affect the reaction rate because it is remote from the reaction site

Burkhard, Roduner, Hochmann and Fischer (1983)

Arrhenius Temperature Dependence

The Arrhenius "law" is an empirical description of the T dependence of the rate constant:

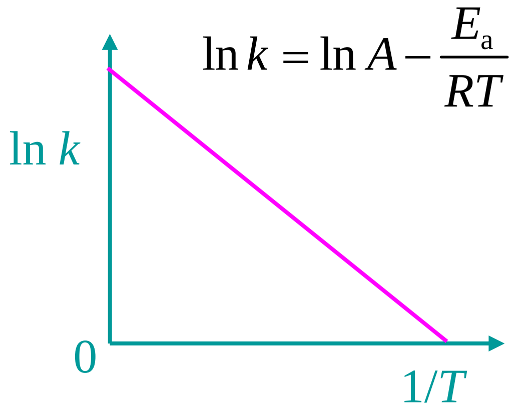
$$k = A\mathrm{e}^{-E_\mathrm{a}/RT}$$

The pre-exponential factor is often interpreted as a collision rate.

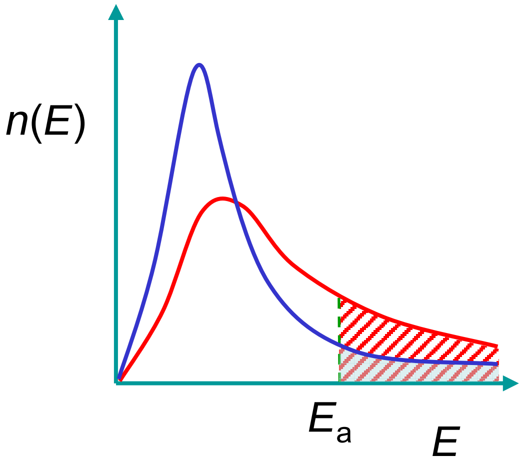
Collision theory predicts $T^{½}$ dependence for A.

Transition-state theory predicts linear T dependence for A.

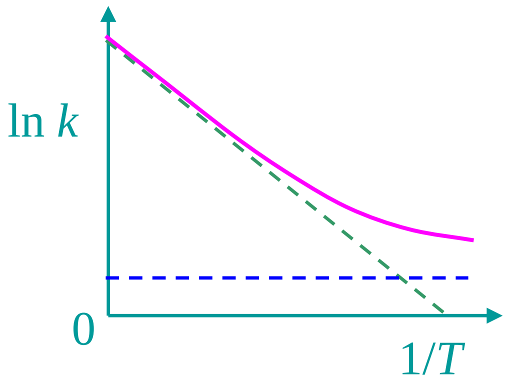
The exponential factor describes the fraction of collisions with sufficient energy for reaction, as predicted by the Boltzmann distribution



$$\ln k = \ln A - \frac{E_\mathrm{a}}{RT}$$

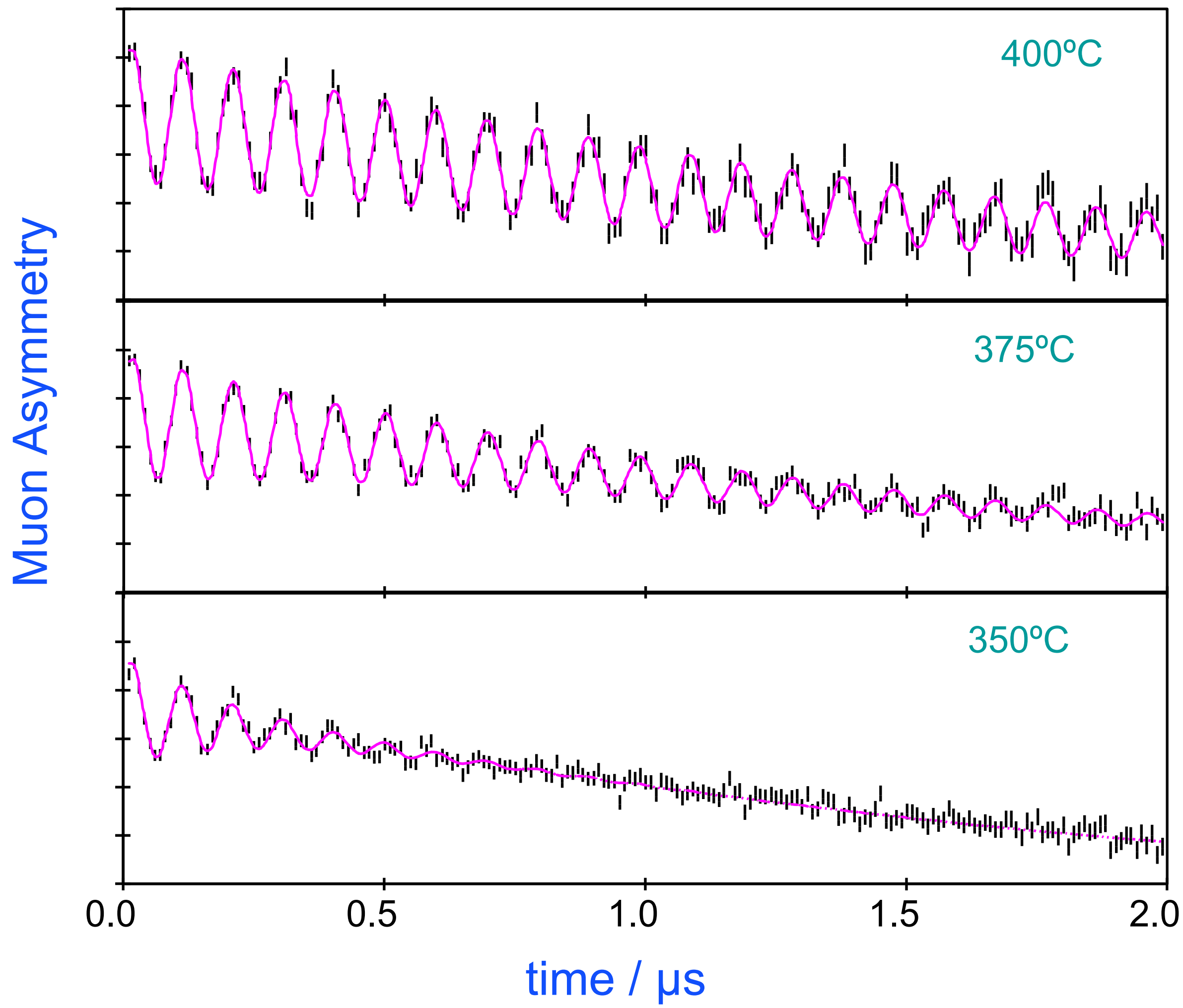


Curvature in the Arrhenius plot is often attributed to tunneling, but there are many other potential reasons.



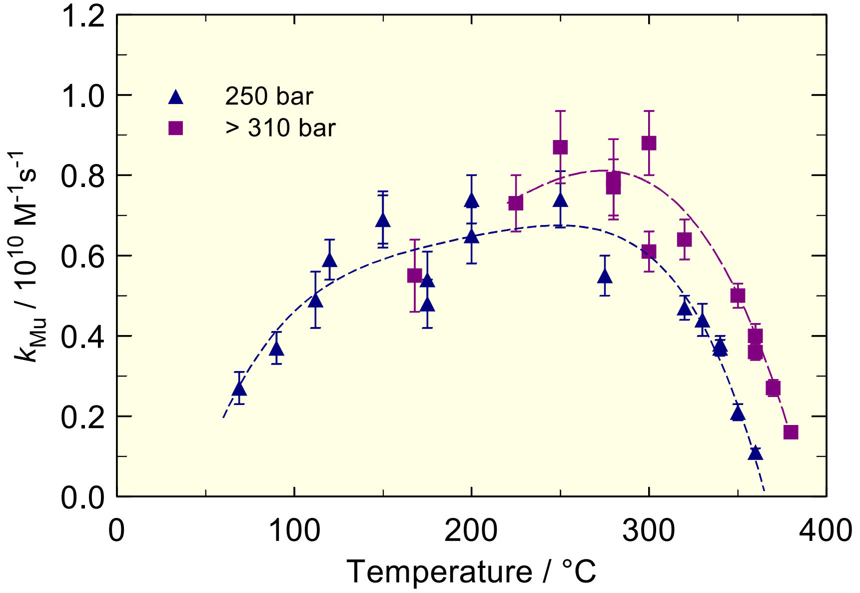
Negative Temperature Dependence!

Muonium Signals in1.4×10^{-4} M (Ni^{2+})$_{aq}$ at 250 atm

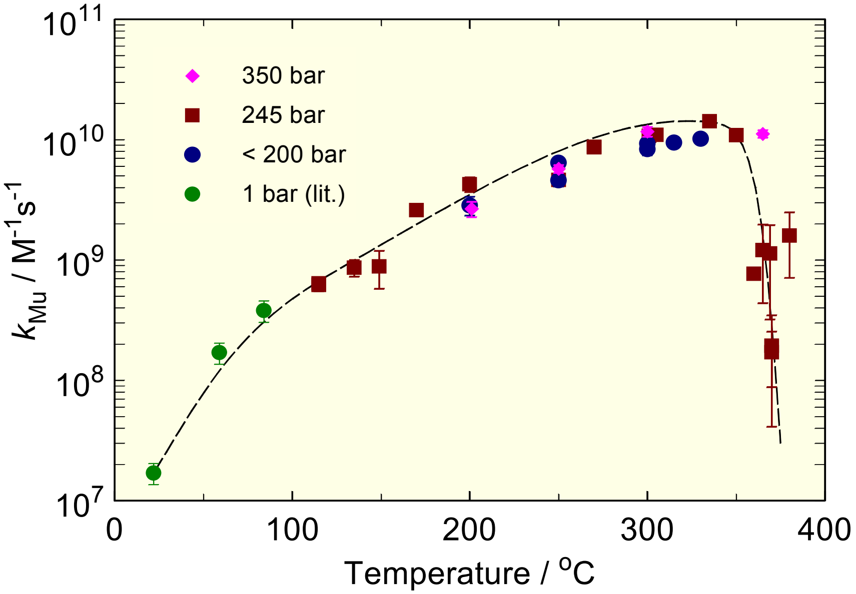


A fall-off of rate is common for reactions in high T water

Mu + Benzene

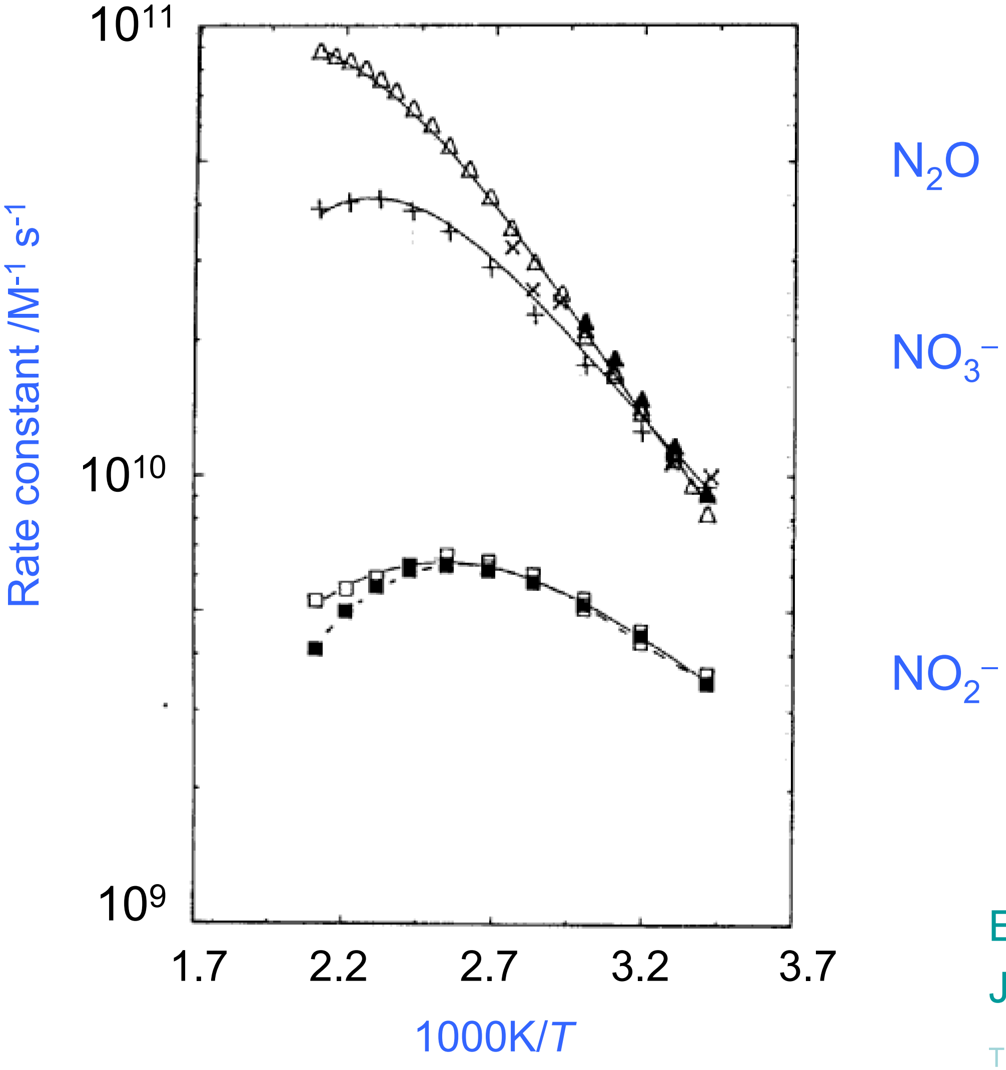


$Mu + OH^- \rightarrow MuOH + e^-_{aq}$



Non-Arrhenius Temperature Dependence

Rate Constants for Reaction of the Hydrated Electron in Water



Elliot, Buxton, et al.,
J C S. Far. Trans. (1990)

Diffusion-Reaction Kinetics

For fast reactions in liquids the rate-determining step can be diffusion of the reactants to form the encounter pair.

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

diffusion reaction

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

or

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

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

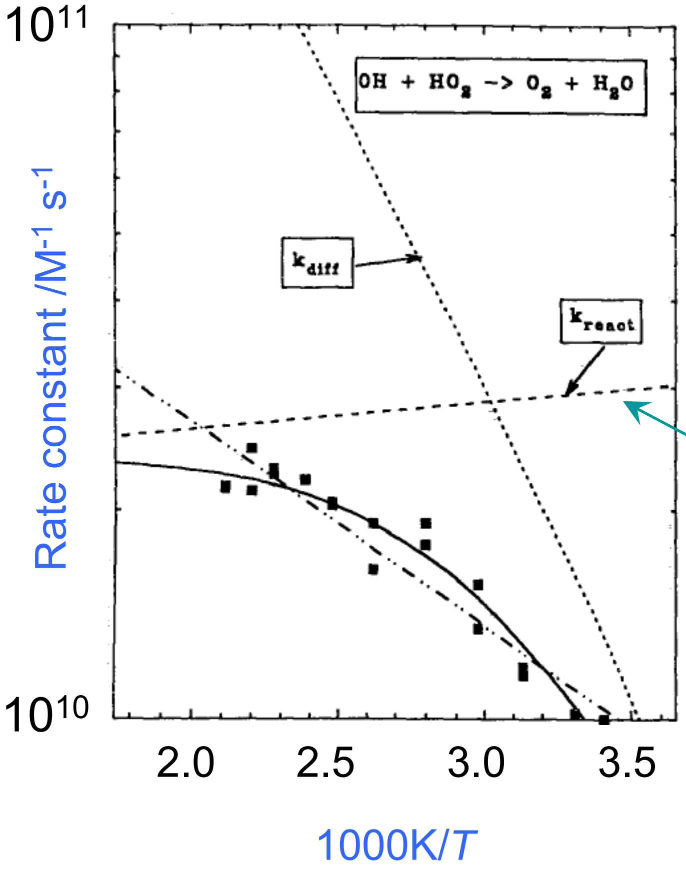
slow diffusion limit

$$k_{\mathrm{act}} = A\exp\left(-E_a / RT\right)$$

fast diffusion limit, “reaction controlled”

Non-Arrhenius Temperature Dependence – 2

Example: Reaction of the Hydroxyl Radical with Hydroperoxyl



$$\frac{1}{k_{\text{obs}}} = \frac{1}{k_{\text{diff}}} + \frac{1}{k_{\text{react}}}$$

negative activation energy?

Elliot et al.,
AECL Report 11073 (1994)

Diffusion-Reaction Kinetics – Modified

For fast reactions in liquids the rate-determining step can be diffusion of the reactants to form the encounter pair.

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

diffusion reaction

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

or

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

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

slow diffusion limit

$$k_{\mathrm{act}} = f_{\mathrm{R}}\, A \exp\left(-E_a / RT\right)$$

fast diffusion limit, “reaction controlled”

where

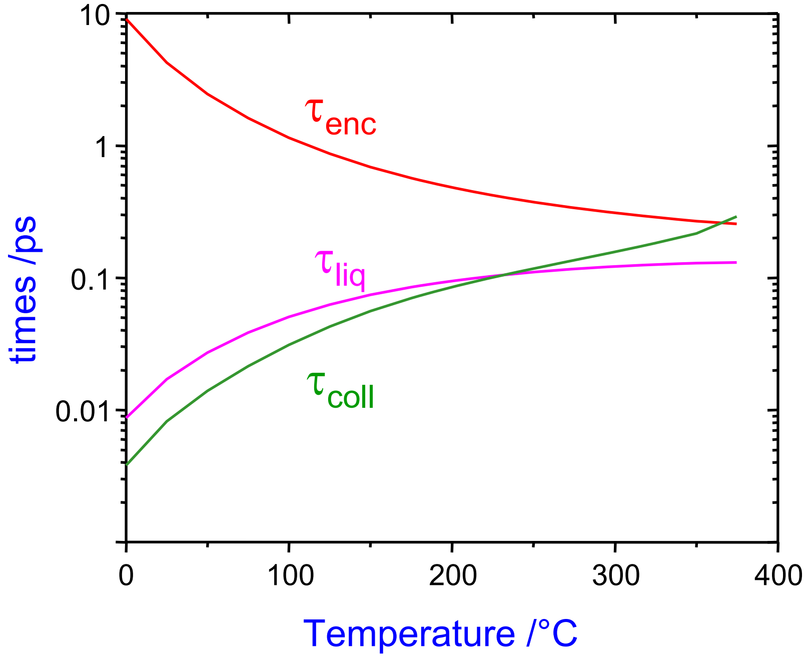
$$f_{\mathrm{R}} = \frac{p_{\mathrm{R}} Z_{\mathrm{coll}}}{\tau_{\mathrm{enc}}^{-1} + p_{\mathrm{R}} Z_{\mathrm{coll}}}$$

p_{R} = orientation factor

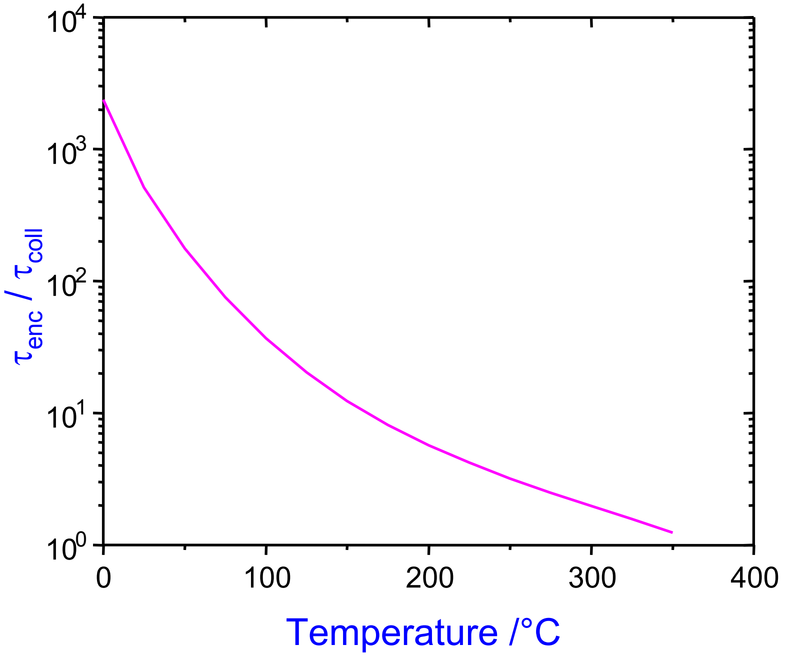
The reaction efficiency depends on the number of collisions of the reactant molecules per encounter.

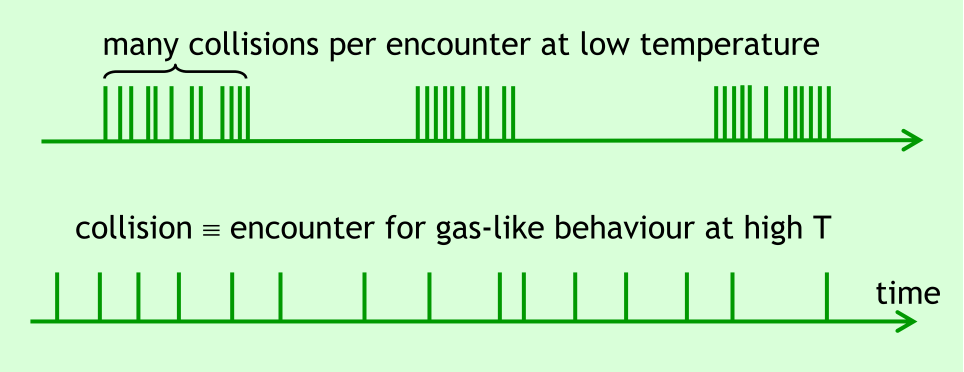
Collisions per Encounter

calculated for Mu + hydroquinone



$$\tau_{enc} = \frac{8k_D^{-1}}{[H_2O]} \qquad \tau_{liq} = \frac{\rho d^2}{6\eta} \qquad \tau_{coll} = \frac{D_{liq}}{D_{gas}} Z_{gas}^{-1}$$



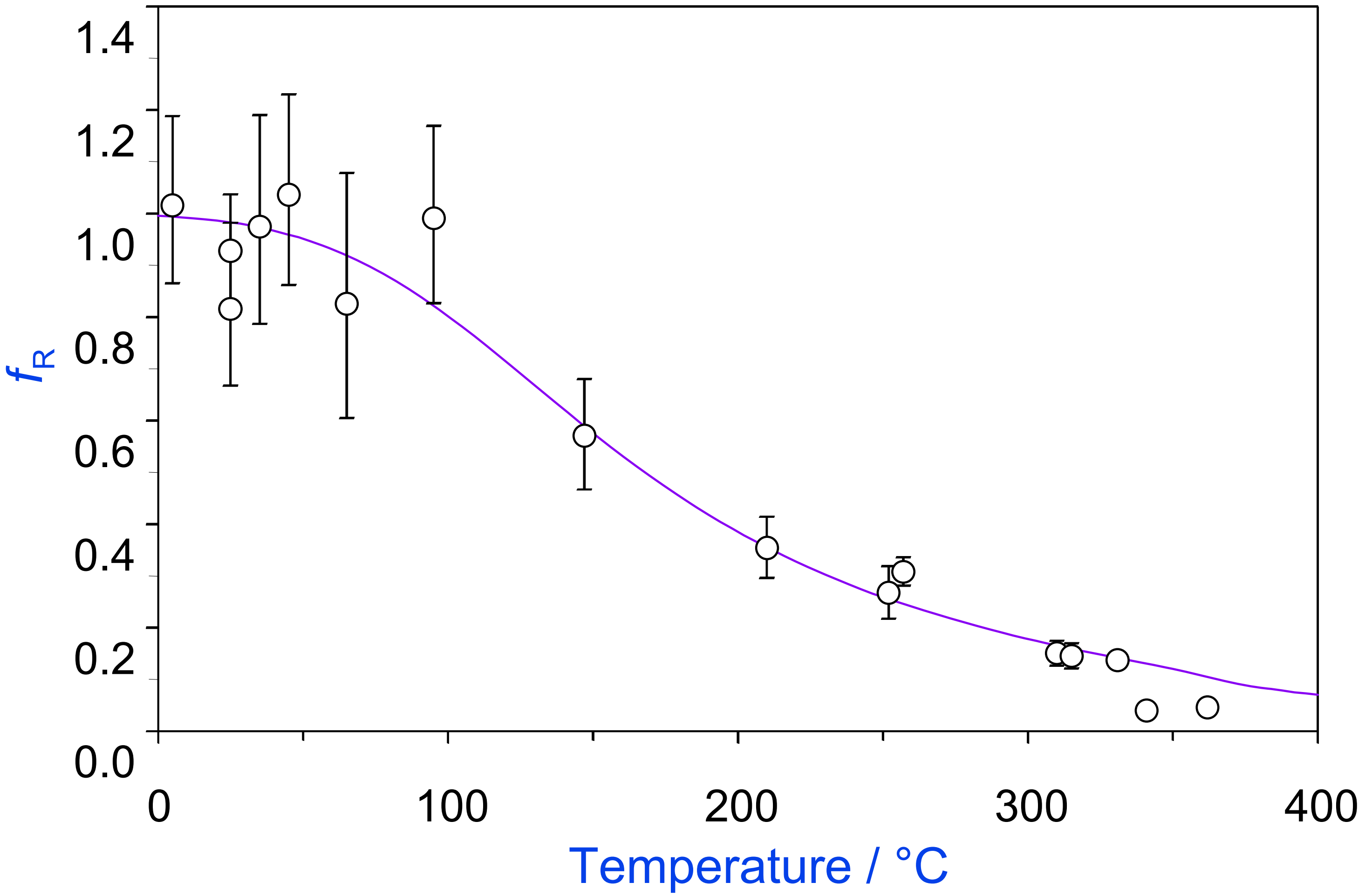


many collisions per encounter at low temperature

collision ≡ encounter for gas-like behaviour at high T

Diffusion-Reaction Kinetics – 3

Reaction Efficiency for Mu + Hydroquinone in water

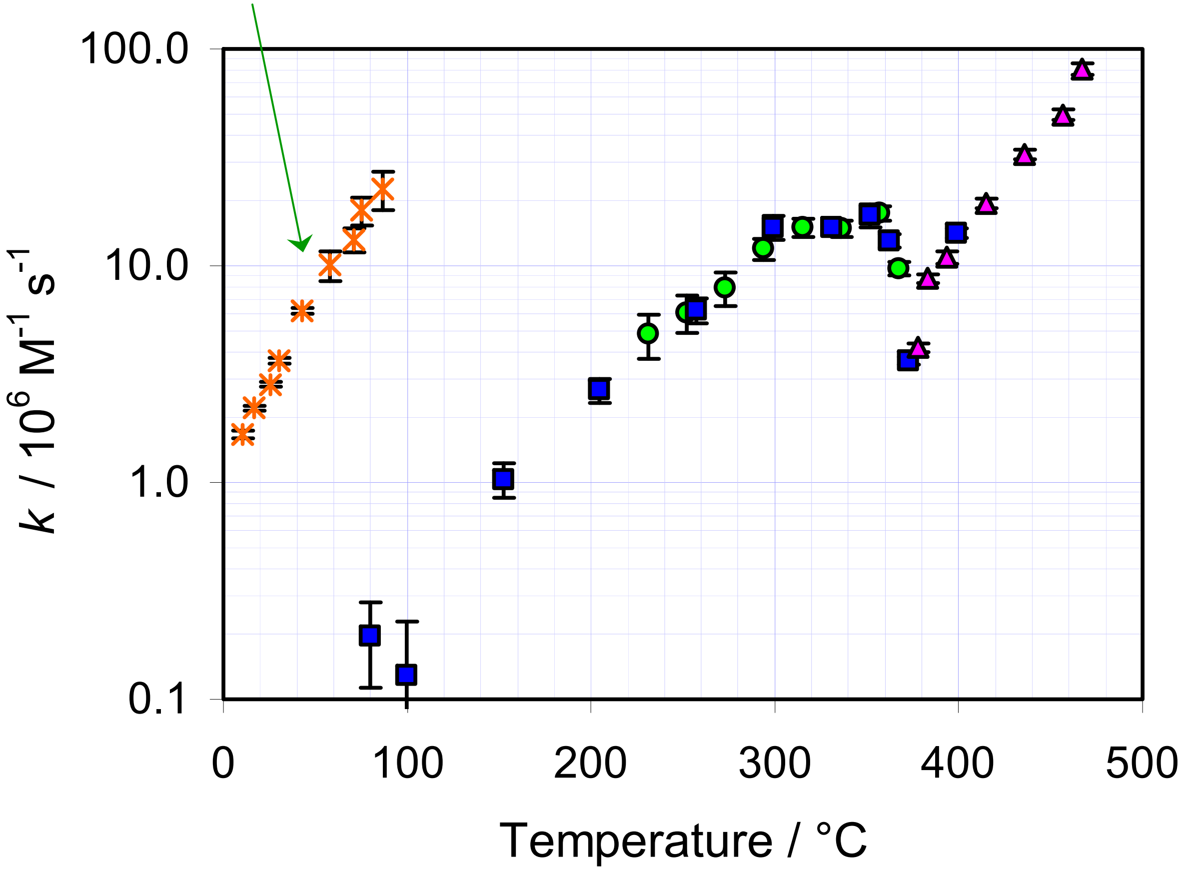


H abstraction from methanol by Mu (H)

H + CH_3OH

Mezyk and Bartels, 1994

Percival et al., 2007



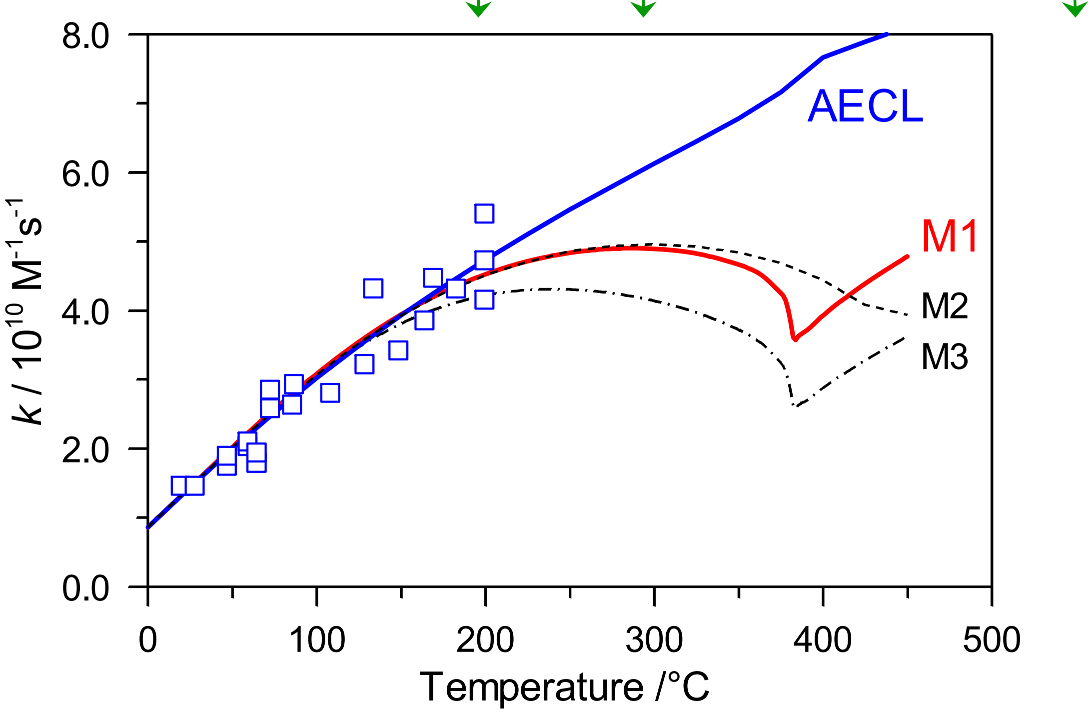
$H + OH \rightarrow H_2O$

Data limited to 200°C

current PWR reactors

Buxton and Elliot,
JCS Far. Trans. 89 (1993) 485

next generation reactors



Ghandi and Percival, J. Phys. Chem. A 107 (2003) 3006

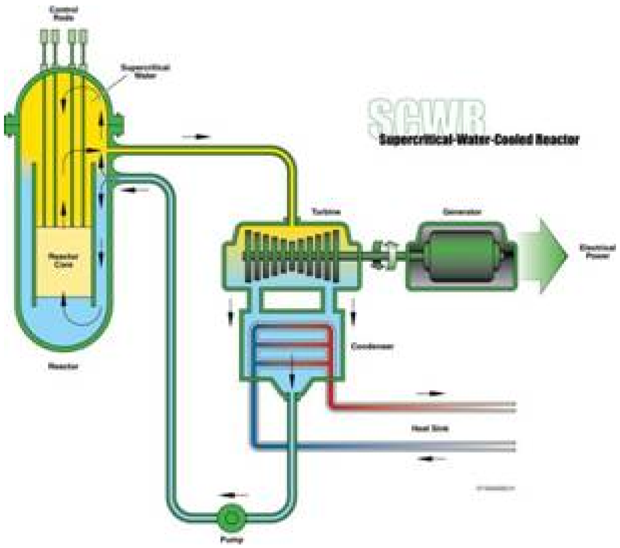
Supercritical-Water-Cooled Reactor

Canada is one of ten countries (the Generation IV International Forum) working together to lay the groundwork for fourth generation nuclear reactor systems.

The priority R & D areas for Canada include
"improved understanding of radiolysis under supercritical water conditions and the effect of radiolysis products on corrosion and stress corrosion cracking".

The Supercritical-Water-Cooled Reactor (SCWR) system is a high-temperature, high-pressure water cooled reactor that operates above the thermodynamic critical point of water (374°C, 22 Mpa)

The SCWR system is primarily designed for efficient electricity production.



Pressure Dependence of Reaction Rates

From classical thermodynamics $dG = VdP - SdT$ $\left(\frac{\partial G}{\partial P}\right)_T = V$ $\left(\frac{\partial \Delta G}{\partial P}\right)_T = \Delta V$

For a reaction at equilibrium $\left(\frac{\partial \ln K}{\partial P}\right)_T = -\frac{1}{nRT}\left(\frac{\partial \Delta G}{\partial P}\right)_T = -\frac{\Delta \bar{V}^\circ}{RT}$

$$\Delta \bar{V}^\circ = \bar{V}_{\text{prod}} - \bar{V}_{\text{react}} = \left(\bar{V}^\ddagger - \bar{V}_{\text{react}}\right) - \left(\bar{V}^\ddagger - \bar{V}_{\text{prod}}\right) = \Delta^\ddagger \bar{V}_1{}^\circ - \Delta^\ddagger \bar{V}_{-1}{}^\circ$$

Since $K = k_1 / k_{-1}$ $\left(\frac{\partial \ln k_1}{\partial P}\right)_T - \left(\frac{\partial \ln k_{-1}}{\partial P}\right)_T = -\frac{\Delta^\ddagger \bar{V}_1{}^\circ}{RT} + \frac{\Delta^\ddagger \bar{V}_{-1}{}^\circ}{RT}$

Most books state $\left(\frac{\partial \ln k_1}{\partial P}\right)_T = -\frac{\Delta^\ddagger \bar{V}_1{}^\circ}{RT}$ $\left(\frac{\partial \ln k_{-1}}{\partial P}\right)_T = \frac{\Delta^\ddagger \bar{V}_{-1}{}^\circ}{RT}$

This neglects the difference between K° and K_c only different for $\Delta\nu \neq 0$

Since $K_c = \bar{V}^\circ K^\circ$ for $\Delta\nu = -1$

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = -\frac{\Delta^\ddagger \bar{V}^\circ}{RT} - \kappa_0$$

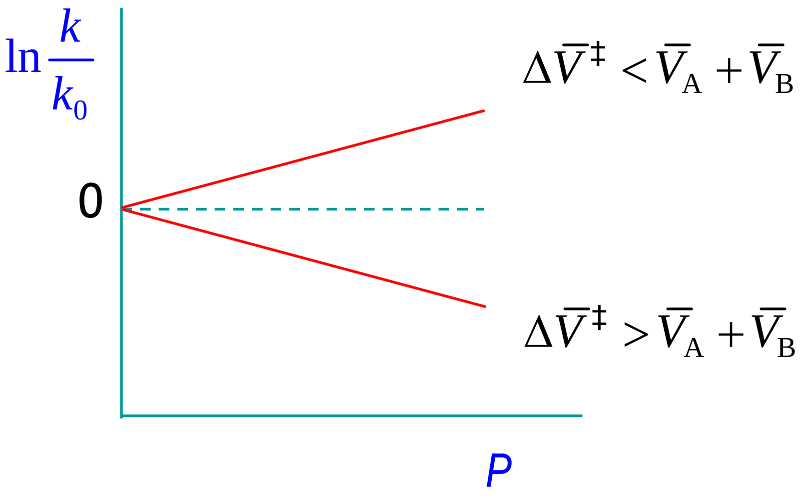
volume of activation

compressibility of the solvent $\left(\frac{\partial \ln V}{\partial P}\right)_T = \frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$

Pressure Dependence – 2

Neglecting κ_0

$$\ln k = \ln k_0 - \frac{\Delta \overline{V}^{\ddagger}}{RT} P$$

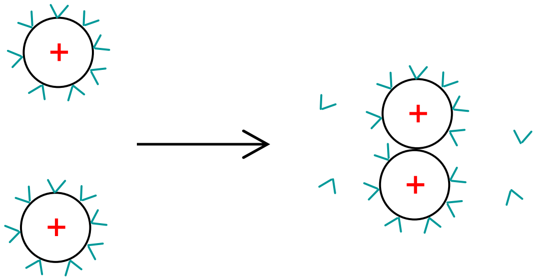


If reactants..	expect
combine	$\Delta \overline{V}^{\ddagger} < 0$
dissociate	$\Delta \overline{V}^{\ddagger} > 0$
have like charges	$\Delta \overline{V}^{\ddagger} < 0$
unlike charges	$\Delta \overline{V}^{\ddagger} > 0$

similar effects for polar molecules (dipoles)

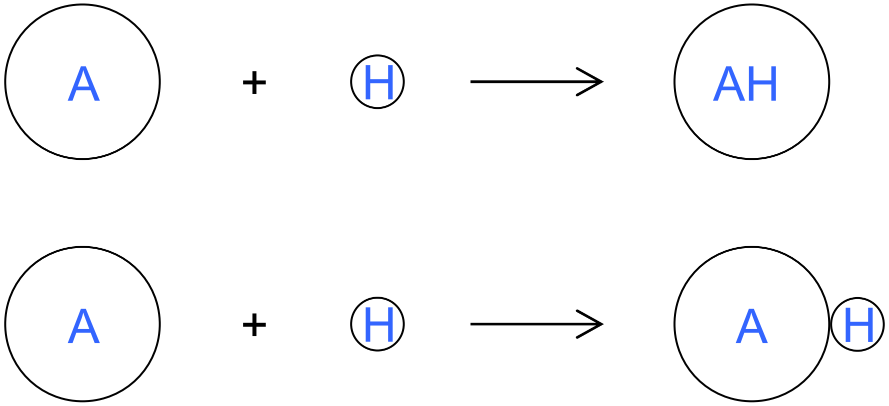
Solvent effects are often dominant

Electrorestriction



ordering of the solvent molecules reduces their effective volume

Volume of Activation for H Atom Reactions

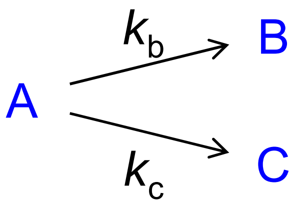


$$\Delta\bar{V}^{\ddagger} = \bar{V}_{\mathrm{AH}} - \bar{V}_{\mathrm{A}} - \bar{V}_{\mathrm{H}} \approx -\bar{V}_{\mathrm{H}}$$

$$\Delta\bar{V}^{\ddagger} \approx V_{\mathrm{w}}(\mathrm{H}) - \bar{V}_{\mathrm{H}}$$

Comparison of $\Delta\bar{V}^{\ddagger}(\mathrm{H})$ and $\Delta\bar{V}^{\ddagger}(\mathrm{Mu})$ shows that V(Mu) > V(H) in water.

Parallel Reactions – Competition



Consider a molecule that can react by two different routes:

Define a = [A], b = [B], c =[C].

The overall decay of A depends on both reactions:

$$-\frac{da}{dt} = k_b a + k_c a = (k_b + k_c)a \qquad \Rightarrow \qquad a = a_0 e^{-(k_b+k_c)t}$$

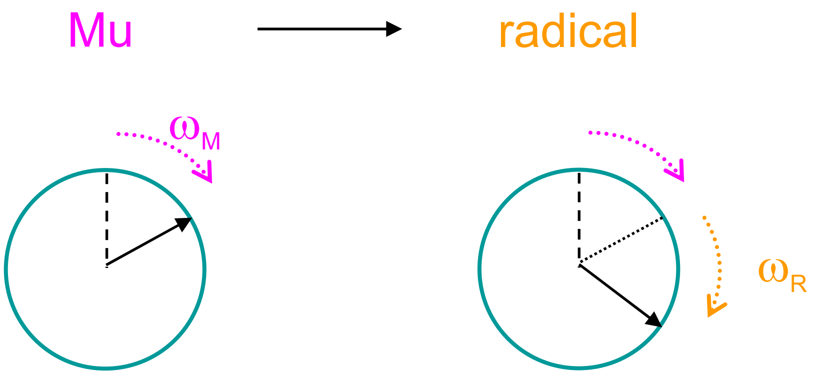
The rate of formation of each product depends on both rate constants:

$$\left.\begin{aligned} \frac{db}{dt} &= k_b a = k_b a_0 e^{-(k_b+k_c)t} \\ \frac{dc}{dt} &= k_c a = k_c a_0 e^{-(k_b+k_c)t} \end{aligned}\right\} \qquad \Rightarrow \qquad \frac{b}{c} = \frac{k_b \int a\,dt}{k_c \int a\,dt} = \frac{k_b}{k_c} = \frac{db/dt}{dc/dt}$$

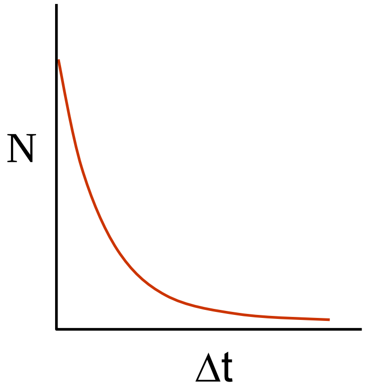
$$\frac{k_b}{k_c} = \frac{[\mathrm{B}]}{[\mathrm{C}]} = \frac{\text{yield of B}}{\text{yield of C}}$$

This is the basis for competition kinetics, whereby an unknown rate constant is determined from a known rate constant and the ratio of competitive products.

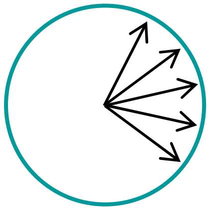
Muon Spin Dephasing During Reaction



Distribution of reaction times



Dephasing of muon spins



Muon Spin Dephasing During Reaction: Theory

high field

$$P_x(\nu_{12}) = \tfrac{1}{2}\left[\frac{c_{\mathrm{M}}^2}{1+\Delta_{1212}^2} + \frac{s_{\mathrm{M}}^2}{1+\Delta_{1412}^2}\right] \qquad P_y(\nu_{12}) = \tfrac{1}{2}\left[\frac{c_{\mathrm{M}}^2\Delta_{1212}}{1+\Delta_{1212}^2} + \frac{s_{\mathrm{M}}^2\Delta_{1212}}{1+\Delta_{1412}^2}\right]$$

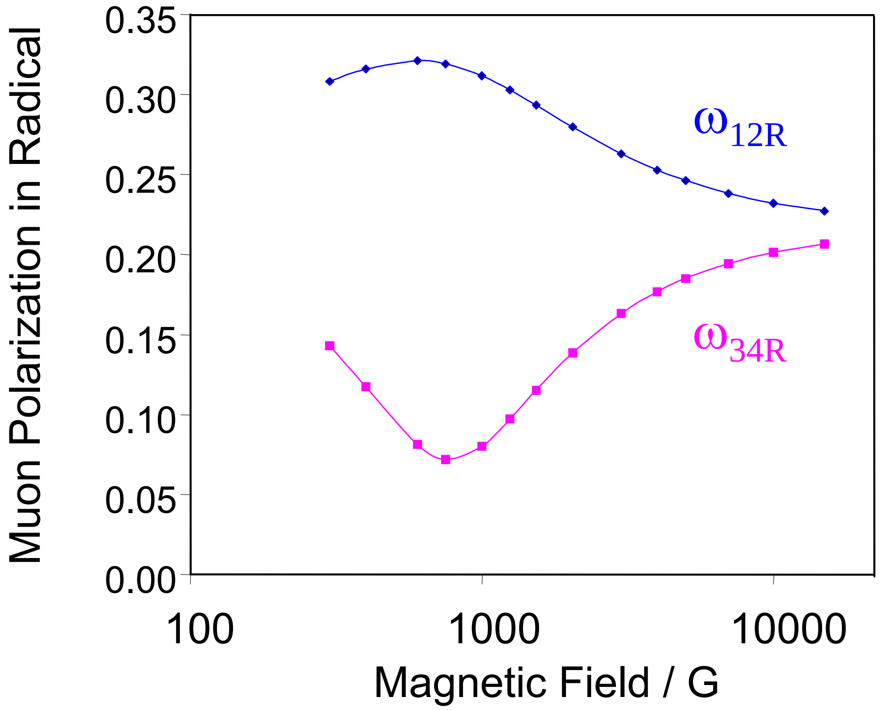
$$P_{\perp}(\nu_{12}) = \left[P_x(\nu_{12})^2 + P_y(\nu_{12})^2\right]^{1/2}$$

$$\Delta_{1212} = (\omega_{12\mathrm{M}} - \omega_{12\mathrm{R}})/\lambda$$

$$\Delta_{1214} = (\omega_{12\mathrm{M}} - \omega_{14\mathrm{R}})/\lambda$$

$$\Delta_{2343} = (\omega_{43\mathrm{M}} - \omega_{23\mathrm{R}})/\lambda$$

$$\Delta_{4343} = (\omega_{43\mathrm{M}} - \omega_{43\mathrm{R}})/\lambda$$

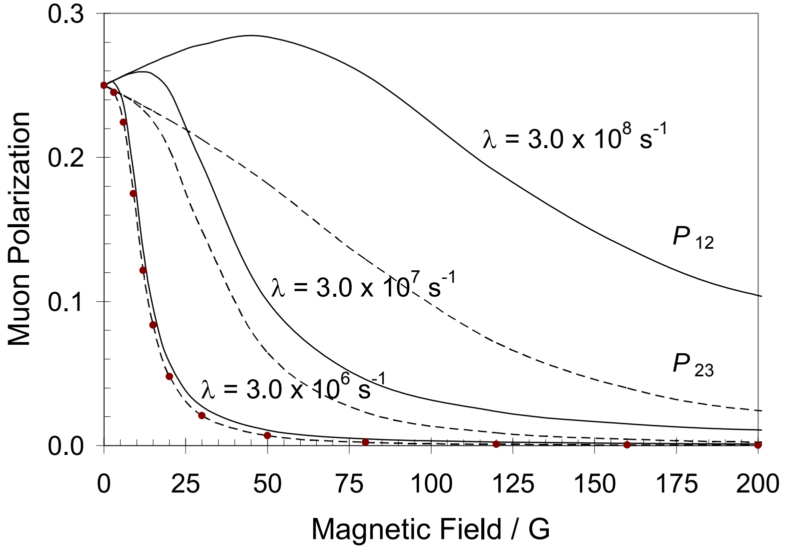


Transfer of Muon Polarization as Mu → Radical

$$P\left(\nu_{12}\right)=\tfrac{1}{2}\left\{\left[\frac{\left(c_{\mathrm{M}}^{2}c_{\mathrm{R}}^{2}+c_{\mathrm{M}}s_{\mathrm{M}}c_{\mathrm{R}}s_{\mathrm{R}}\right)}{1+\Delta_{1212}^{2}}+\frac{\left(s_{\mathrm{M}}^{2}c_{\mathrm{R}}^{2}-c_{\mathrm{M}}s_{\mathrm{M}}c_{\mathrm{R}}s_{\mathrm{R}}\right)}{1+\Delta_{1412}^{2}}\right]^{2}+\left[\frac{\left(c_{\mathrm{M}}^{2}c_{\mathrm{R}}^{2}+c_{\mathrm{M}}s_{\mathrm{M}}c_{\mathrm{R}}s_{\mathrm{R}}\right)\Delta_{1212}}{1+\Delta_{1212}^{2}}+\frac{\left(s_{\mathrm{M}}^{2}c_{\mathrm{R}}^{2}-c_{\mathrm{M}}s_{\mathrm{M}}c_{\mathrm{R}}s_{\mathrm{R}}\right)\Delta_{1412}}{1+\Delta_{1412}^{2}}\right]^{2}\right\}^{1/2}$$

$$P\left(\nu_{23}\right)=\tfrac{1}{2}\left\{\left[\frac{\left(c_{\mathrm{M}}^{2}c_{\mathrm{R}}^{2}+c_{\mathrm{M}}s_{\mathrm{M}}c_{\mathrm{R}}s_{\mathrm{R}}\right)}{1+\Delta_{2323}^{2}}+\frac{\left(s_{\mathrm{M}}^{2}c_{\mathrm{R}}^{2}-c_{\mathrm{M}}s_{\mathrm{M}}c_{\mathrm{R}}s_{\mathrm{R}}\right)}{1+\Delta_{4323}^{2}}\right]^{2}+\left[\frac{\left(s_{\mathrm{M}}^{2}s_{\mathrm{R}}^{2}+c_{\mathrm{M}}s_{\mathrm{M}}c_{\mathrm{R}}s_{\mathrm{R}}\right)\Delta_{2323}}{1+\Delta_{2323}^{2}}+\frac{\left(c_{\mathrm{M}}^{2}s_{\mathrm{R}}^{2}-c_{\mathrm{M}}s_{\mathrm{M}}c_{\mathrm{R}}s_{\mathrm{R}}\right)\Delta_{4323}}{1+\Delta_{4323}^{2}}\right]^{2}\right\}^{1/2}$$

where $\Delta_{1214}=\left(\omega_{12\mathrm{M}}-\omega_{14\mathrm{R}}\right)/\lambda$ etc.



$Mu + CH_2{=}CH_2 \rightarrow MuCH_2\text{-}CH_2\cdot$

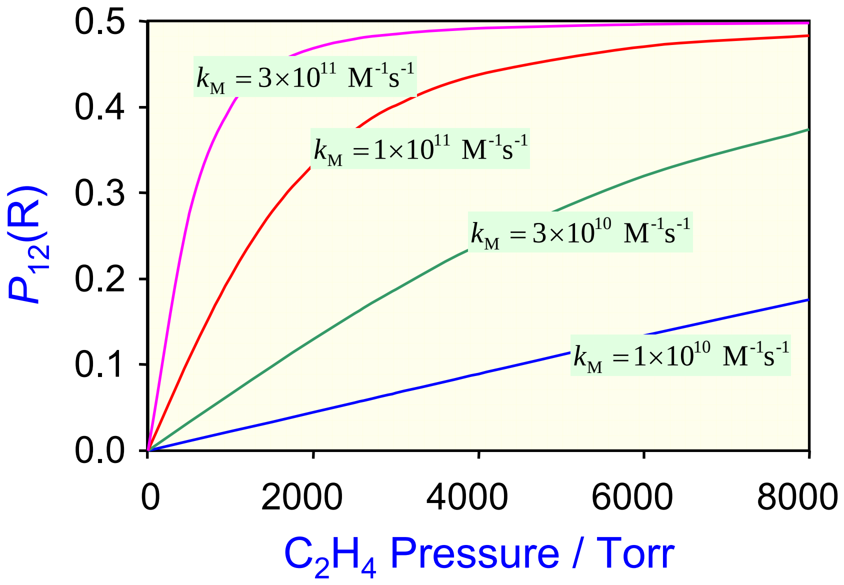
If the radical is formed via muonium there is loss of signal amplitude due to incoherent spin precession in the product. The muon polarization at the lower radical precession frequency is given by:

$$P_{12}(\mathrm{R}) = \tfrac{1}{2} h_{\mathrm{M}} \left[\frac{\lambda^2}{\lambda^2 + \Delta\omega_{12}^2} \right]^{1/2}$$

$h_{\mathrm{M}} =$ initial fraction of muon polarization in Mu

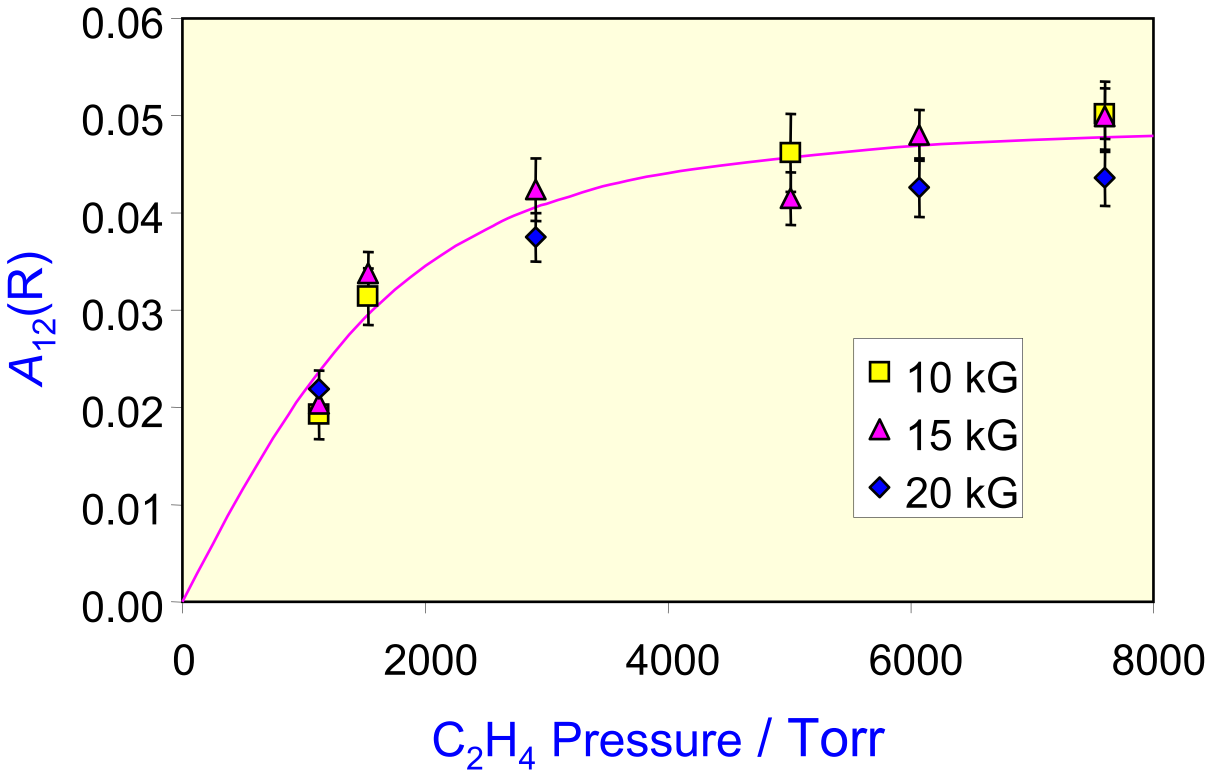
$\lambda = k_{\mathrm{M}}[\text{ethene}] =$ first-order reaction rate

$\Delta\omega_{12} = \omega_{12}^{\mathrm{M}} - \omega_{12}^{\mathrm{R}} =$ change in precession frequency



$Mu + CH_2{=}CH_2 \rightarrow MuCH_2\text{-}CH_2\cdot$

The data for pure ethene can be described by a simple 1-step model in which Mu is converted to a radical.



Transfer of Muon Spin Polarization Between Radicals

$$P(\omega_{12}) = \tfrac{1}{2}\left\{\left[\frac{C}{1+\Delta_{1212}^2}+\frac{S}{1+\Delta_{1412}^2}\right]^2+\left[\frac{C\,\Delta_{1212}}{1+\Delta_{1212}^2}+\frac{S\,\Delta_{1412}}{1+\Delta_{1412}^2}\right]^2\right\}^{1/2}$$

$$P(\omega_{43}) = \tfrac{1}{2}\left\{\left[\frac{C}{1+\Delta_{4343}^2}+\frac{S}{1+\Delta_{2343}^2}\right]^2+\left[\frac{C\,\Delta_{4343}}{1+\Delta_{4343}^2}+\frac{S\,\Delta_{2343}}{1+\Delta_{2343}^2}\right]^2\right\}^{1/2}$$

$$\Delta_{klmn} = (\omega_{kl}-\omega_{mn})/\lambda$$

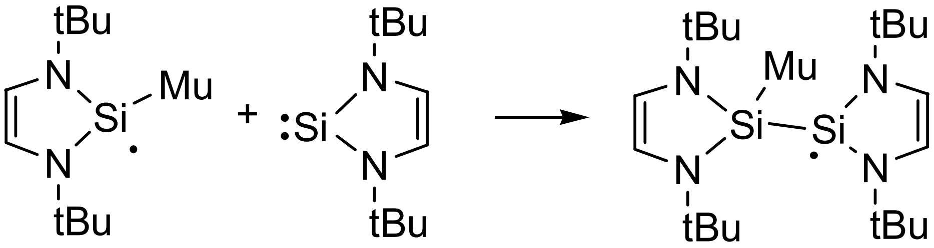
$$C = c_{\mathrm{R1}}^2 c_{\mathrm{R2}}^2 + c_{\mathrm{R1}} s_{\mathrm{R1}} c_{\mathrm{R2}} s_{\mathrm{R2}}$$

$$S = s_{\mathrm{R1}}^2 c_{\mathrm{R2}}^2 - c_{\mathrm{R1}} s_{\mathrm{R1}} c_{\mathrm{R2}} s_{\mathrm{R2}}$$

$$c = \left\{1+\frac{(\omega_{\mathrm{e}}+\omega_{\mu})}{\left[\omega_0^2+(\omega_{\mathrm{e}}+\omega_{\mu})^2\right]^{1/2}}\right\}^{1/2}, \qquad s^2 = c^2 - 1$$

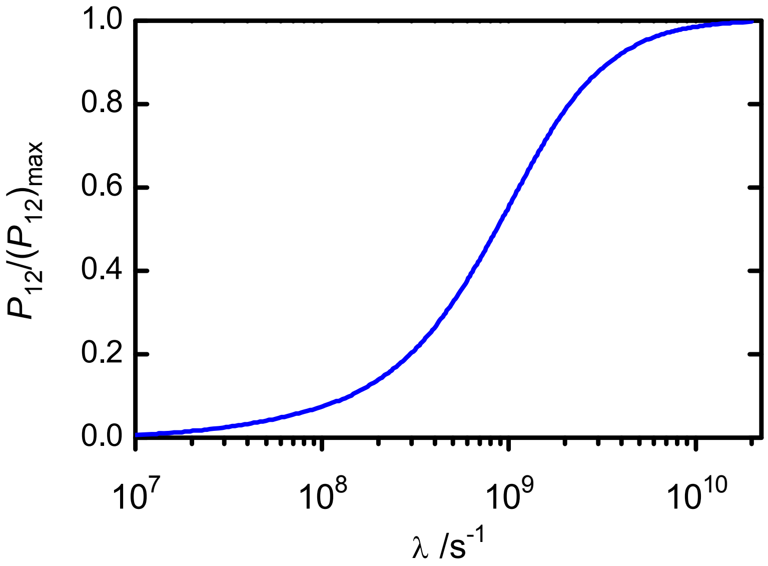
$$P(\omega_{12}) = \tfrac{1}{2}\left[\frac{\lambda^2}{\lambda^2+(\omega_{12\mathrm{R1}}-\omega_{12\mathrm{R2}})^2}\right]^{1/2}$$

Radical Coupling of a Silyl to Form a Disilanyl



R1(hfc 722.5 MHz) → R2(hfc 235.4 MHz)
at 14.5 kG

$$P(\omega_{12}) = \tfrac{1}{2}\left[\frac{\lambda^2}{\lambda^2 + (\omega_{12R1} - \omega_{12R2})^2}\right]^{1/2}$$



Measured polarization = 51% ⇒ $\lambda = 8.9 \times 10^8$ s^{-1}

⇒ $k = 5.7 \times 10^8$ M^{-1}s^{-1}

McCollum, Brodovitch, Clyburne, Percival and West, Physica B, 404 (2009) 940-942.