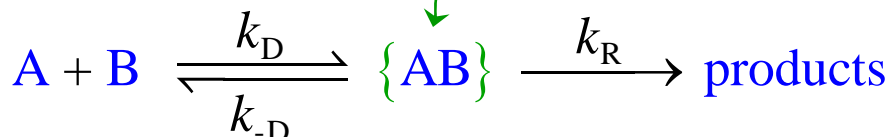


Diffusion-limited Kinetics

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



Apply the steady-state approximation to $\{AB\}$:

$$\frac{d}{dt}[\{AB\}] = k_D[A][B] - (k_{-D} + k_R)[\{AB\}] = 0$$

$$\text{rate} = k_R[\{AB\}] = \frac{k_D k_R}{k_{-D} + k_R} [A][B]$$

The effective rate constant has two limits:

Slow diffusion: $k_{\text{eff}} = \frac{k_D k_R}{k_{-D} + k_R} \rightarrow k_D$ if $k_R \gg k_{-D}$

Fast diffusion: $k_{\text{eff}} \rightarrow \frac{k_D k_R}{k_{-D}} = K_{\{AB\}} k_R = k_{\text{act}}$ if $k_{-D} \gg k_R$

Intermediate situations can be described by:

$$k_{\text{eff}} = \frac{k_D k_R}{k_{-D} + k_R} = \frac{k_D (k_D k_R / k_{-D})}{k_D + (k_D k_R / k_{-D})} = \frac{k_D k_{\text{act}}}{k_D + k_{\text{act}}}$$

Take the inverse:

$$\frac{1}{k_{\text{eff}}} = \frac{1}{k_D} + \frac{1}{k_{\text{act}}}$$

Diffusion-limited Rate Constants

The diffusion –limited rate constant can be calculated:

Smoluchowski $k_D = 4\pi r_{AB} D_{AB}$ (m³ molecule⁻¹ s⁻¹)

$$4000\pi r_{AB} D_{AB} N_{Av} \text{ (dm}^3 \text{ mol}^{-1} \text{ s}^{-1}\text{)}$$

with encounter distance $r_{AB} = r_A + r_B$

coefficient of mutual diffusion $D_{AB} = D_A + D_B$ (m²s⁻¹)

D_A, D_B can be estimated from the

Stokes-Einstein equation $D = \frac{k_B T}{\pi\beta\eta r_s}$

η is the viscosity of the solvent, r_s is the hydrodynamic radius

$\beta = 6$ for ideal Stokes diffusion (continuous medium)

$\beta = 4$ for the opposite limit (solute radius \approx solvent radius)

Assuming the hydrodynamic radius \approx reaction radius,

$$k_D = \frac{4k_B T}{\beta\eta} \left[\frac{1}{r_A} + \frac{1}{r_B} \right] (r_A + r_B) = \frac{4k_B T}{\beta\eta} \left[2 + \frac{r_B}{r_A} + \frac{r_A}{r_B} \right]$$

For reactants of similar size,

$$k_D \approx \frac{16k_B T}{\beta\eta_s} \approx 1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} \quad \text{in water at 300 K}$$

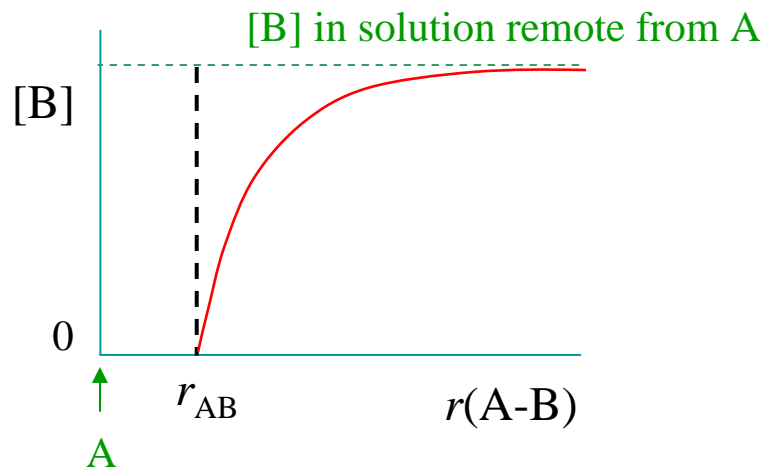
The rate constant is determined by solvent properties!

The viscosity dominates the temperature dependence.

What if the Diffusion is not at Equilibrium?

This can happen when a reactant suddenly 'appears' in a homogeneous solution of its reaction partner.

e.g. photogeneration of a transient species,
or stopping a particle (muon, positron, ...) from a beam.



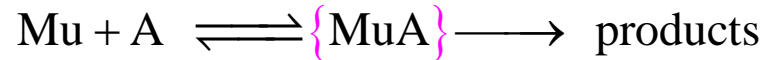
At short times the reaction rate is enhanced by 'contact' pairs.

In general, the rate "constant" is time dependent:

$$k_{\text{AB}}(t) = k_{\infty} \left(1 + \frac{r_{\text{AB}}}{\sqrt{\pi D_{\text{AB}} t}} \right)$$

Diffusion-Reaction Kinetics

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



diffusion

reaction

$$k_{\text{obs}} = \frac{k_{\text{diff}} k_{\text{act}}}{k_{\text{diff}} + k_{\text{act}}}$$

or

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

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

slow diffusion limit

$$k_{\text{act}} = f_{\text{R}} A \exp(-E_a / RT)$$

fast diffusion limit, "reaction controlled"

where

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

p_{R} = orientation factor

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

Diffusion-Reaction Kinetics – 2

$$k_R = \frac{p_R Z_{\text{coll}}}{\tau_{\text{enc}}^{-1} + p_R Z_{\text{coll}}} A e^{-E/RT}$$

$$\frac{1}{k_R} = \frac{1}{A e^{-E/RT}} + \frac{\tau_{\text{enc}}^{-1}}{p_R Z_{\text{coll}} A e^{-E/RT}} = \frac{1}{k_{\text{liq}}} + \frac{1}{k_{\text{gas}}}$$

where $k_{\text{gas}} = \frac{(p_R Z_{\text{coll}})(A e^{-E/RT})}{\tau_{\text{enc}}^{-1}} = p_R \left(\frac{\tau_{\text{enc}}}{\tau_{\text{coll}}} \right) k_{\text{liq}}$

Note that $Z_{\text{coll}} = \tau_{\text{coll}}^{-1}$ depends on pressure,
i.e. it corresponds to the low pressure rate constant.

Overall we have found that: $\frac{1}{k_{\text{obs}}} = \frac{1}{k_{\text{diff}}} + \frac{1}{k_{\text{liq}}} + \frac{1}{k_{\text{gas}}}$

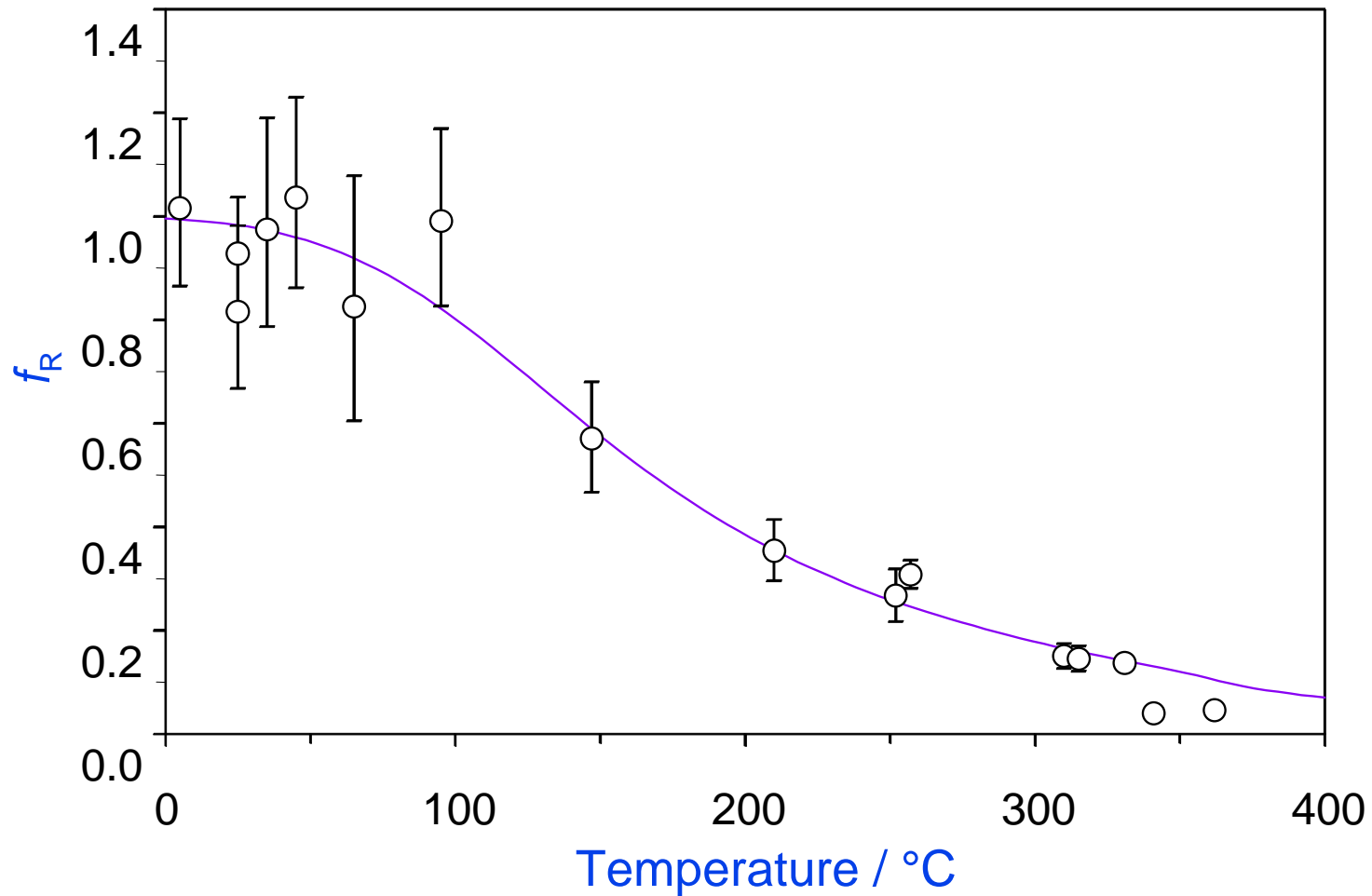
For dense gases Troe derived: $\frac{1}{k_{\text{obs}}} = \frac{1}{k_{\text{diff}}} + \frac{1}{k_{\infty}} + \frac{1}{k_0}$

low pressure,
(P-proportional)
rate constant

high pressure limit

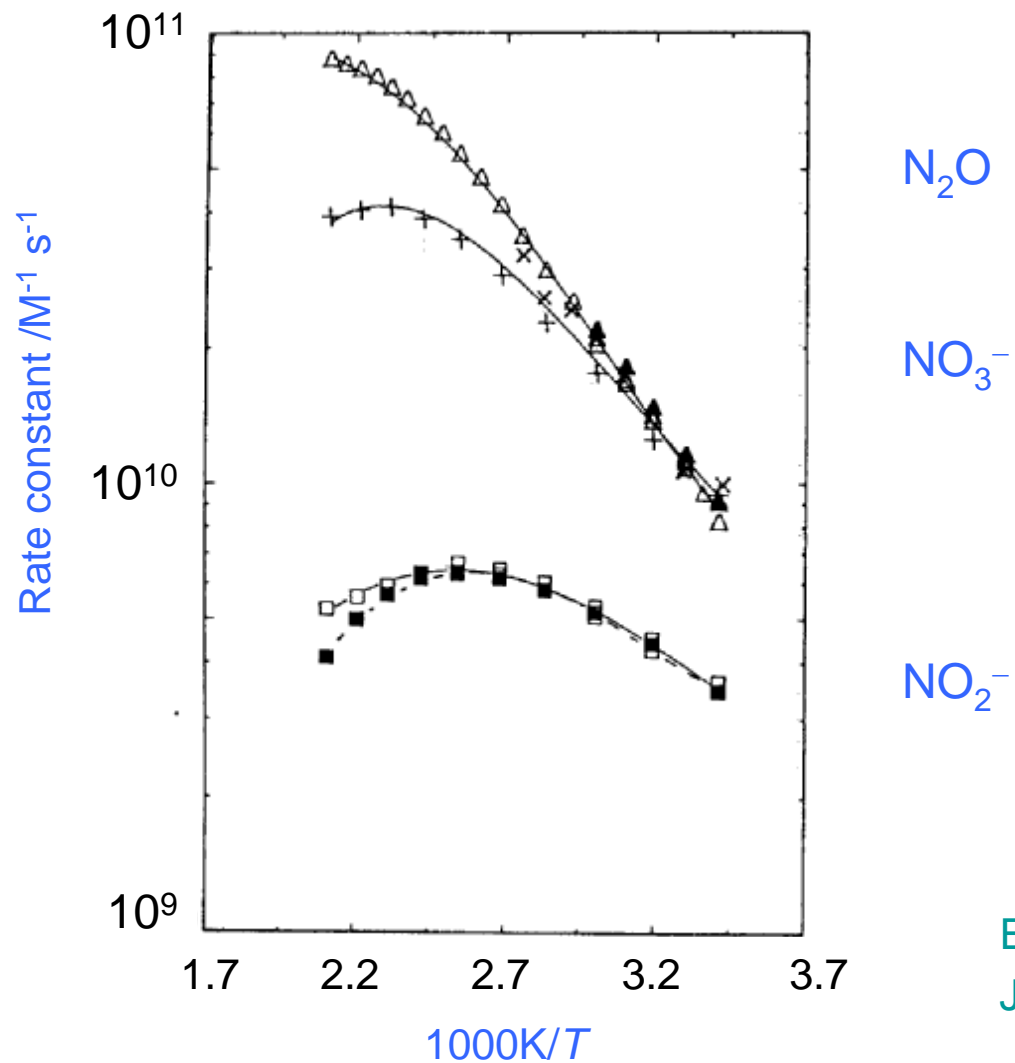
Diffusion-Reaction Kinetics – 3

Reaction Efficiency for Mu + Hydroquinone in water



Non-Arrhenius Temperature Dependence

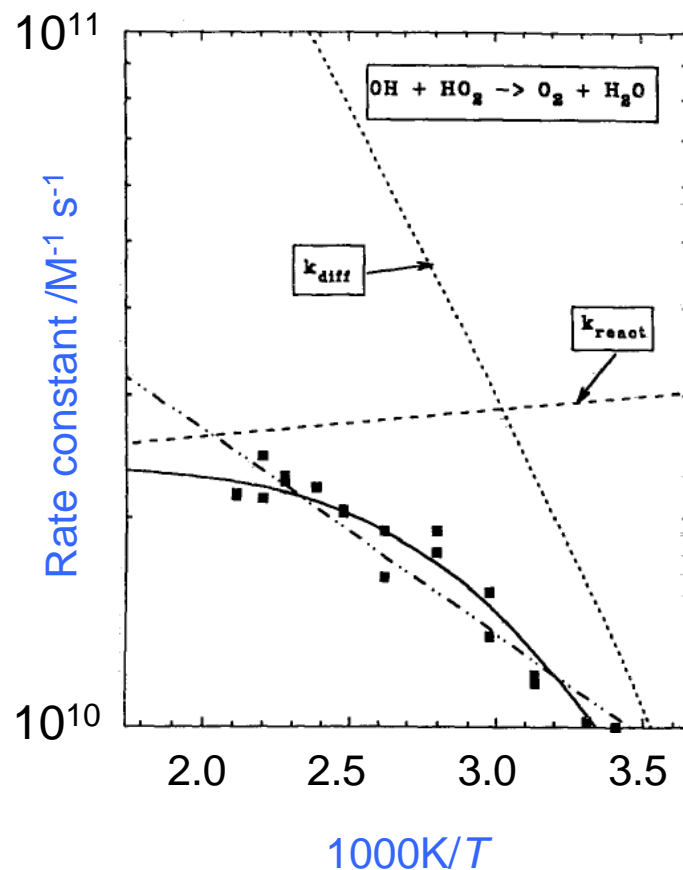
Rate Constants for Reaction of the Hydrated Electron in Water



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

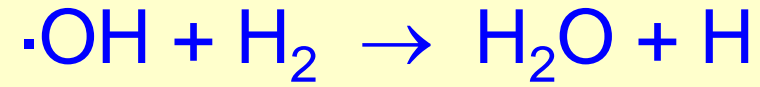
Non-Arrhenius Temperature Dependence – 2

Example: Reaction of the Hydroxyl Radical with Hydroperoxyl



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

Elliot et al.,
AECL Report 11073 (1994)



Marin, Jonah and Bartels, Chem. Phys. Lett. (2003)

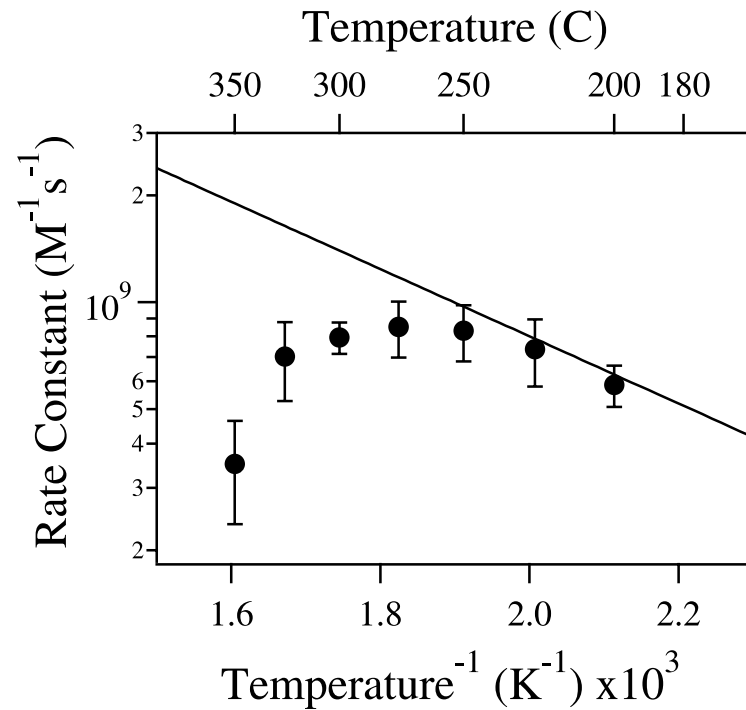
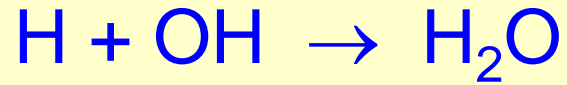


Fig. 2. Arrhenius plot for reaction (1). The solid line represents an extrapolation of previously reported data available up to 230 °C [6,7].

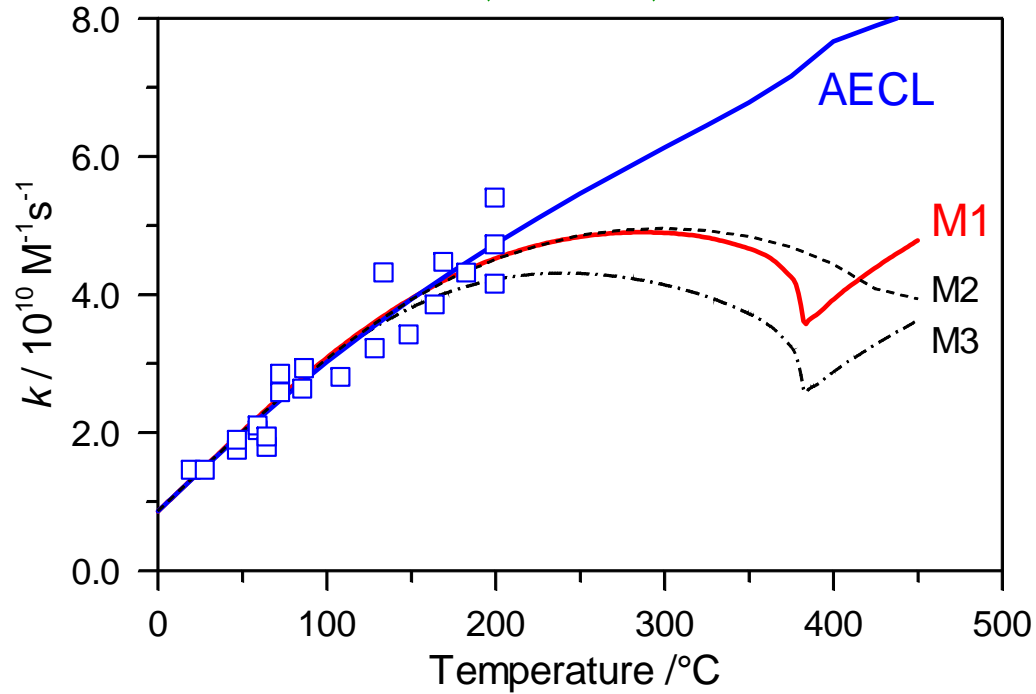


Data limited to 200°C

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

current PWR reactors

next generation reactors

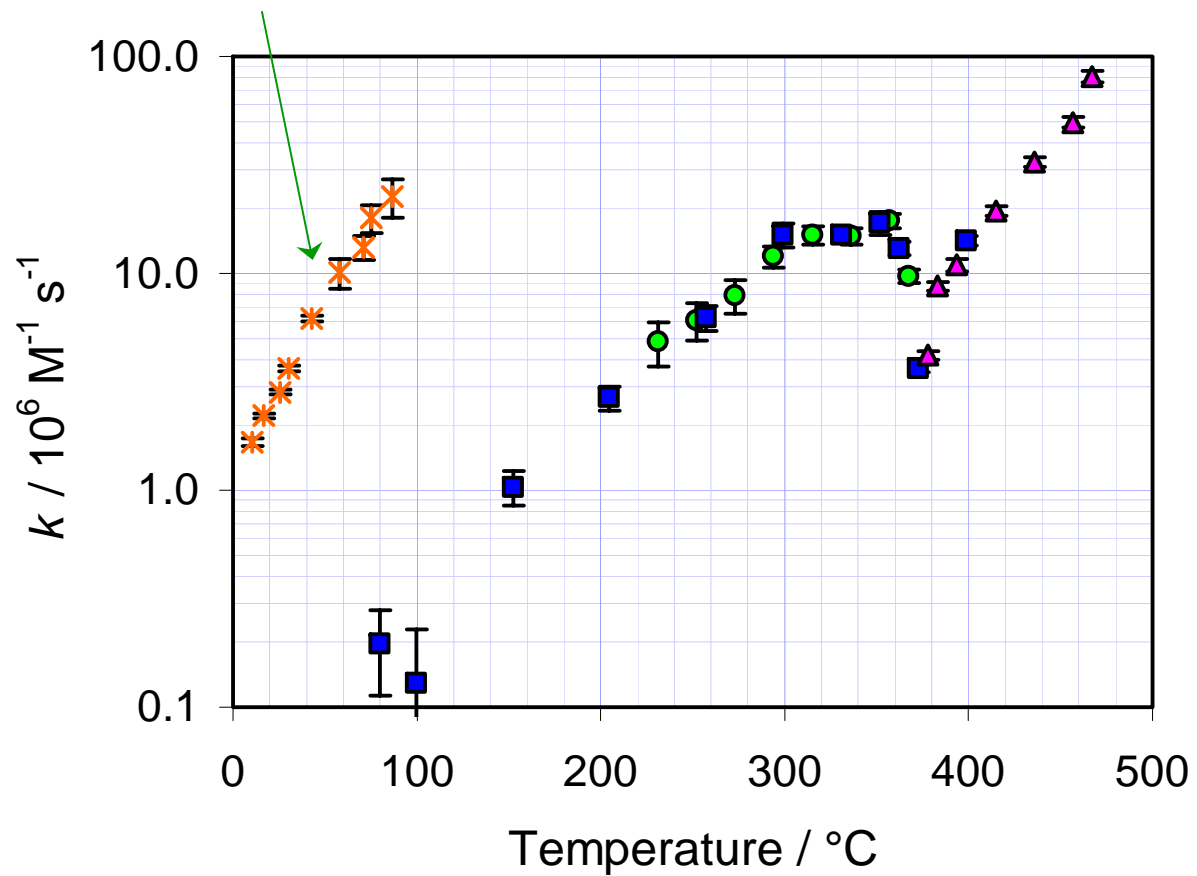


Ghandi and Percival, J. Phys. Chem. A 107 (2003) 3006

H abstraction from methanol by Mu (H)

H + CH₃OH

Mezyk and Bartels, 1994



Spin Effects in Diffusion-Controlled Reactions

For reactions between pairs of radicals (or other paramagnetic species)

$$k_{\text{diff}} = 4\pi\sigma(R_A + R_B)(D_A + D_B)$$

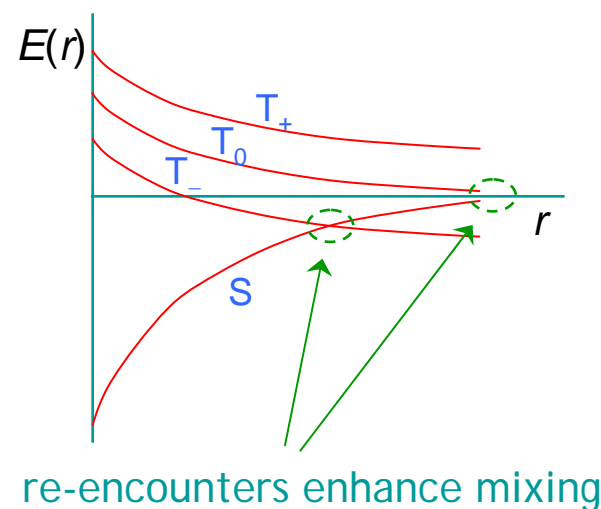
The **spin factor** accounts for spin pairing in chemical bonds.

Thus, $\text{H} + \text{H} \rightarrow \text{H}_2$ has $\sigma = 0.25$ because the singlet spin combination reacts, but not the triplet (three-fold degenerate) $S = 1$ state.

Some radical-radical reactions have higher σ because of spin conversion, either through fast spin relaxation ($\cdot\text{OH}$) or mixing of spin levels.

Selective mixing of spin levels gives rise to:

- CIDNP
- CIDEP
- magnetic field dependent rates
- field dependent fluorescence quenching



Diffusion-Controlled Reactions between Ions

For reactions between pairs of ions the diffusion-limited rate constant is

$$k_{\text{diff}} = 4\pi\sigma D_{\text{AB}} R_{\text{eff}} = 4\pi\sigma D_{\text{AB}} \left\{ \frac{R_c}{e^{-R_c/R_{\text{AB}}} - 1} \right\}$$

The **Onsager escape radius** is the separation at which the electrostatic attraction is balanced by thermal motion (opposite charges)

$$R_c = \left| \frac{z_A z_B e^2}{4\pi\epsilon_r \epsilon_0 k_B T} \right|$$

solvent	ϵ_r	$R_c / \text{\AA}$	factor	
			$z_A z_B = +1,$	-1
water	80	7	0.25	2.6
methanol	33	17	0.02	5.7
ethanol	24	23	0.004	7.7
EtOEt	4.3	130	10^{-17}	43
hexane	1.9	290	10^{-40}	97

$z_A z_B$	$R_c / \text{\AA}$	factor
-2	(-)14	4.7
-1	(-)7	2.6
0	-	1
+1	7	0.25
+2	14	0.04

water; 300 K; $R_{\text{ab}} = 3 \text{\AA}$

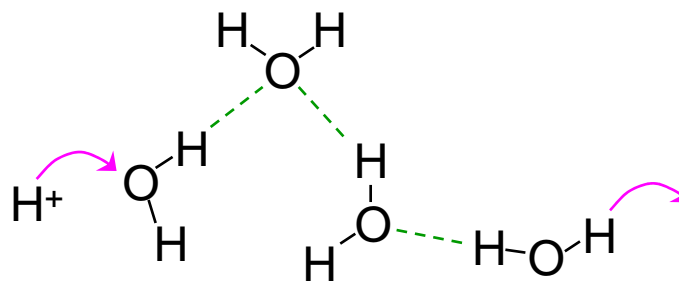
Proton Diffusion

The Onsager correction is insufficient to explain the high rates of many proton reactions, e.g.

$$k_D = 1.4 \times 10^{11} \text{ M}^{-1}\text{s}^{-1} \text{ for } \text{H}^+ + \text{OH}^- \text{ in water}$$

R_{eff} is about 8 Å, consistent with the existence of species such as $[\text{H}_9\text{O}_4]^+$

Grotthuss Mechanism



This is even more efficient in ice, with its regular H-bonded structure.

$$k_D = 8.6 \times 10^{12} \text{ M}^{-1}\text{s}^{-1} \text{ for } \text{H}^+ + \text{OH}^- \text{ in ice}$$