Electron transfer theory and electrocatalysis

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Outline

- ## Molecular theory of redox reactions

  Marcus theory – ion transfer – proton transfer – bond breaking – role of (metal) catalyst

- ## Thermodynamic theory of multiple proton-electron transfer

  Sabatier principle – density functional theory – scaling relations – role of catalyst and solution pH

Butler-Volmer rate law
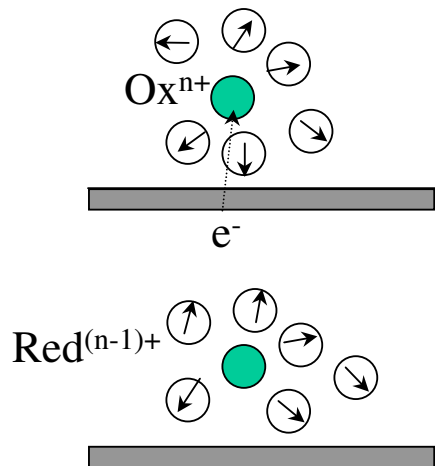
Redox reaction: Red $\rightarrow$ Ox + e$^-$

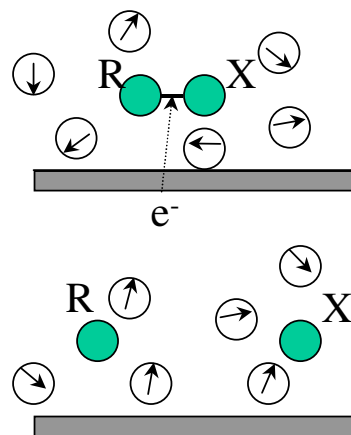Oxidation rate constant:

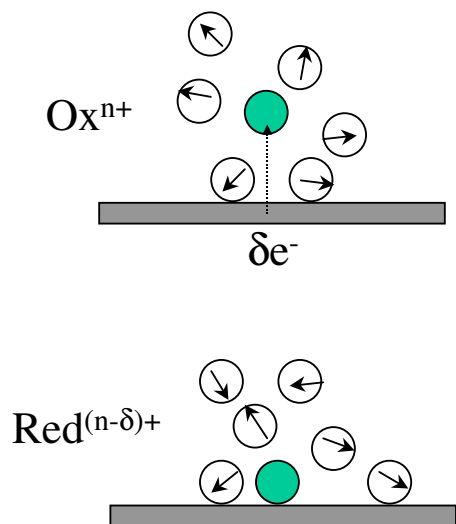$$k = k_s \exp[\alpha F(E-E_0)/RT]$$

What is k_s ?
What is α ?

Outer-Sphere Electron Transfer

Ox^{n+}

e^-

$Red^{(n-1)+}$

Bond Breaking Electron Transfer

R X

e^-

R X^-

Ion Transfer

Ox^{n+}

δe^-

$Red^{(n-\delta)+}$

Dissociative Adsorption - Electron Transfer

X_2

transition state

$X^{\delta-}$ $X^{\delta-}$

X^- X^-
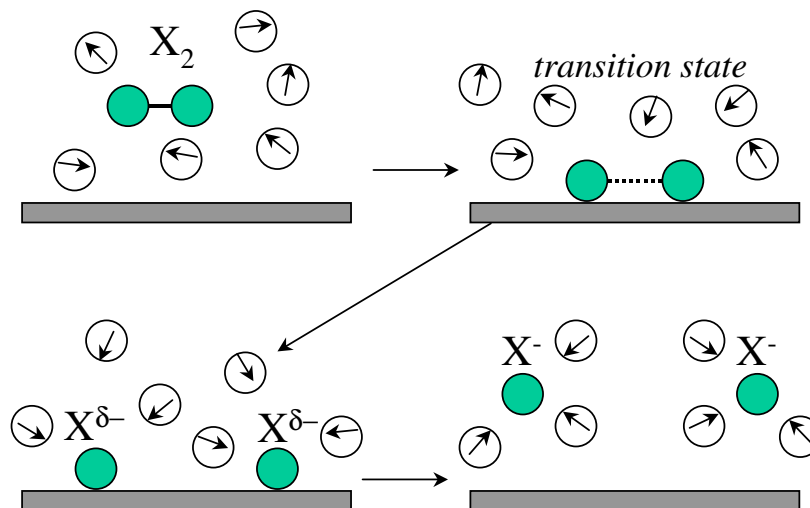
Arrhenius' law

Rate processes are *rare events*

$$k = A \exp(-E_{act} / k_B T)$$

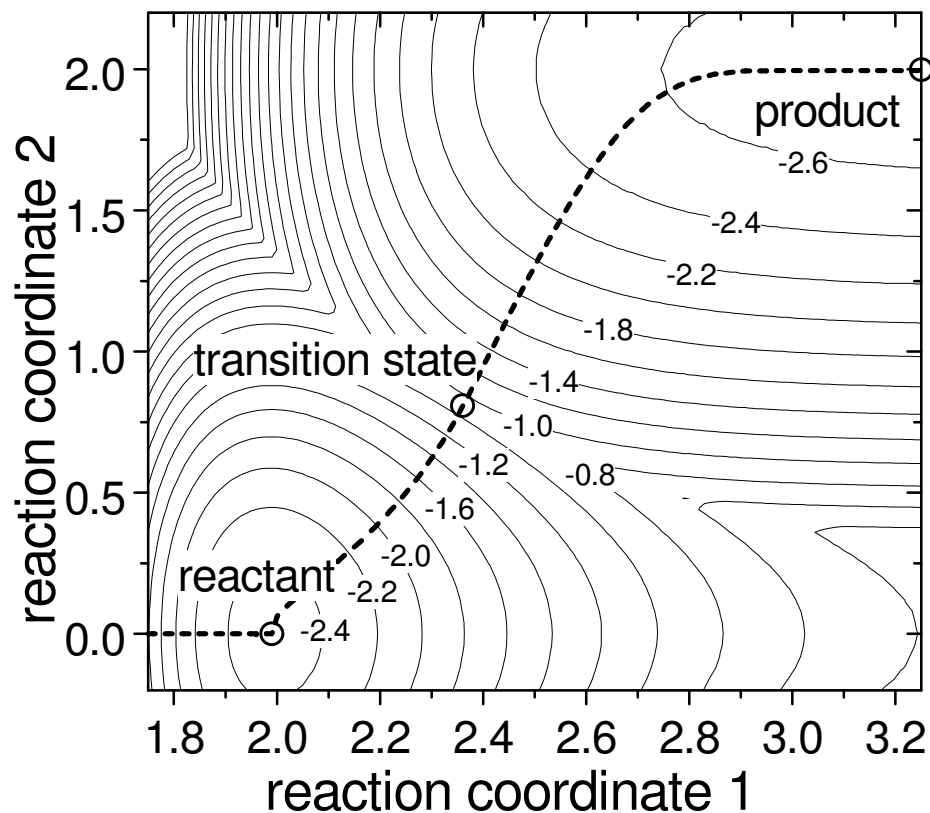Arrhenius' law implies *equilibrium* between normal reactants and active reactants, i.e. the "activated complex".

*Van 't Hoff (1884)*   *Arrhenius (1889)*

The Potential Energy Surface (PES)

Activated complex is the saddle point ("col") of the potential energy surface = transition state

Transition-State Theory - Assumptions

1. Every time the system reaches the transition state, it unavoidably progresses in the direction of the product state. There is no recrossing of the barrier.

2. The energy distribution among the reactant molecules follows the Maxwell-Boltzmann distribution. Hence the concentration of activated complexes can be calculated from equilibrium theory.

3. Separability of the motion through the transition state from the non-reactive motions.

4. Motion over the barrier is classical - no quantum effects accounted for.
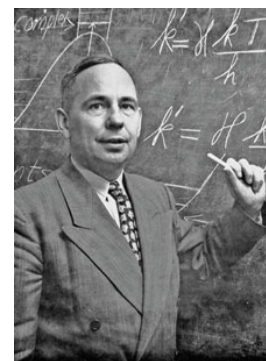
Eyring (1935), Evans & Polanyi (1935)

Transition-State Theory - Rate Expression

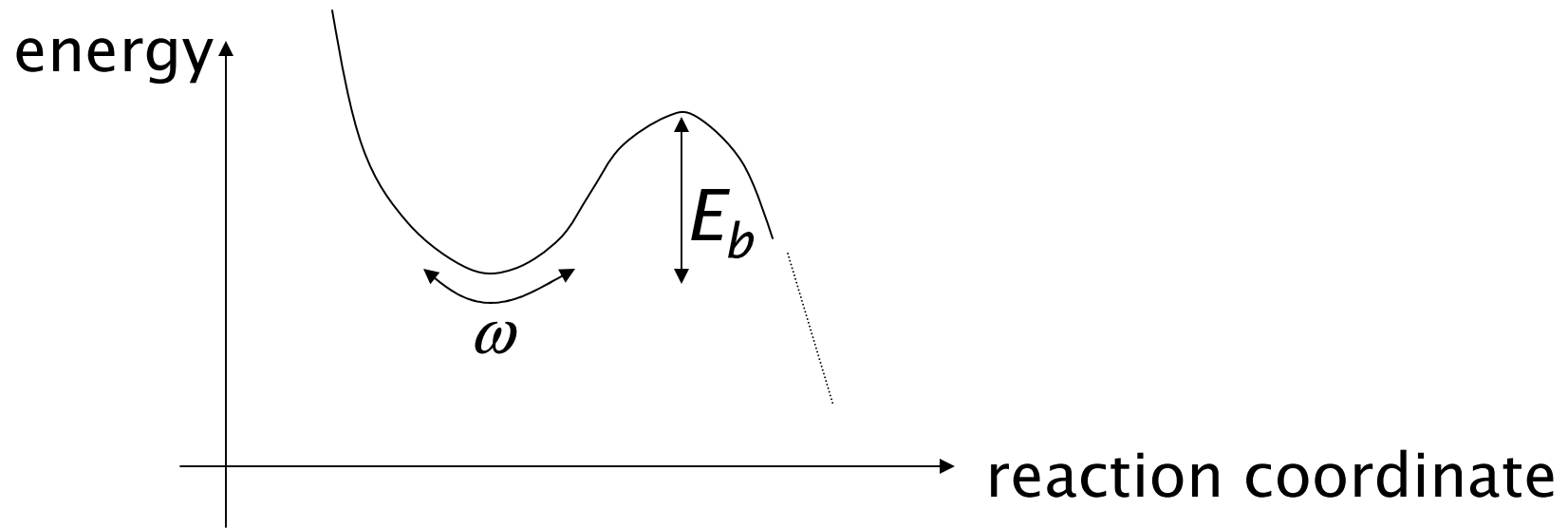$$k = \frac{k_B T}{h} \frac{Z^{\neq}}{Z_R} \exp(-E_b / k_B T)$$

h, Planck's constant

$Z^{\neq}$, partition function of the non-reactive modes at the transition state

Z_R, partition function of the reactant(s)

E_b, energy difference between activated complex and reactant state ("barrier height")

TST rate for escape from 1-D well
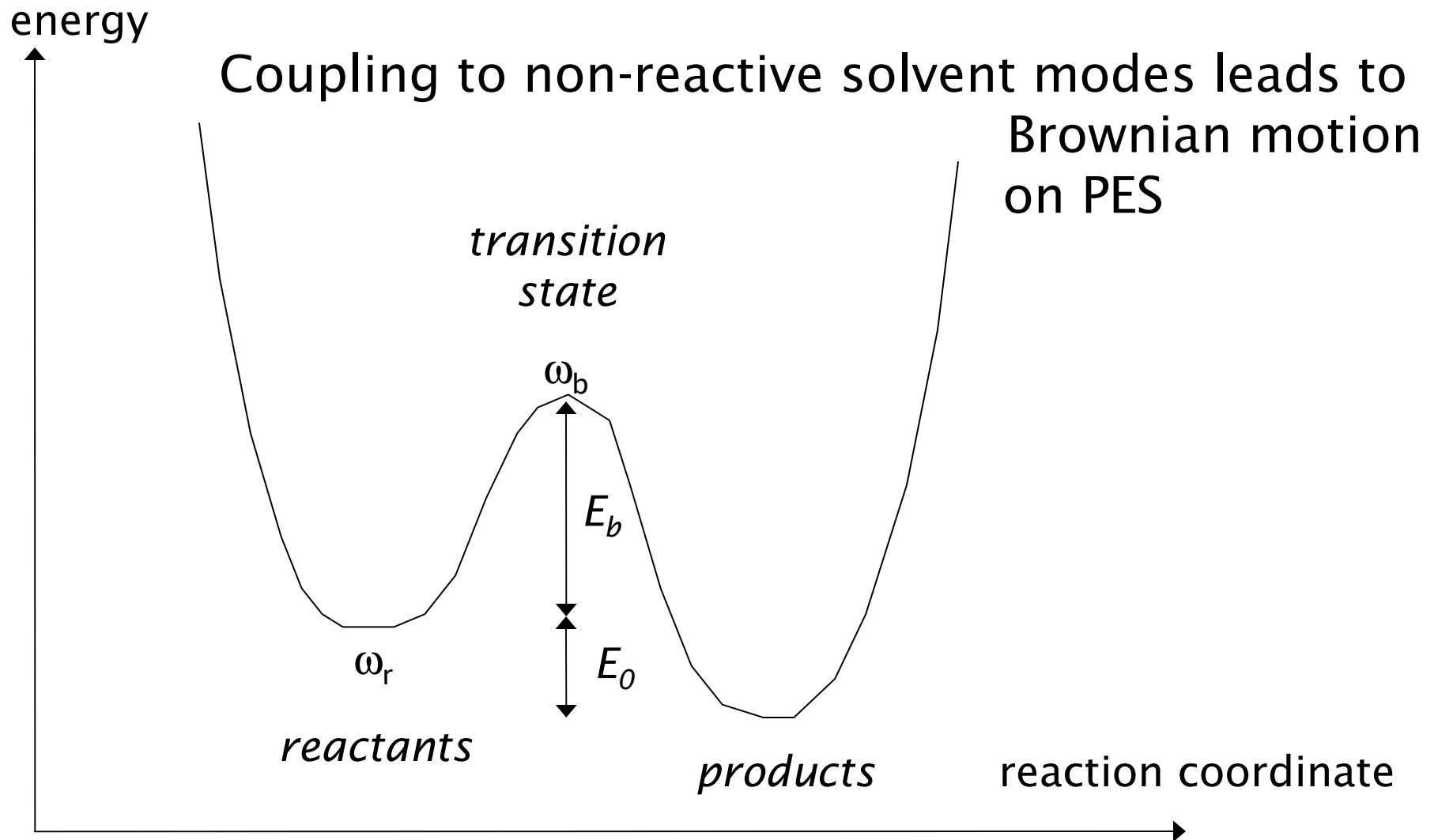

$$Z^{\neq} = 1$$

$$Z_R = \frac{1}{1 - \exp(-h\omega / 2\pi k_B T)} \approx \frac{2\pi k_B T}{h\omega}$$

$$k = \frac{\omega}{2\pi} \exp(-E_b / k_B T)$$

Where is the quantum mechanics ?

1. The PES is calculated from quantum-mechanical principles, on the basis of the Born-Oppenheimer approximation. The electronic motion is considered to be *adiabatic*.

2. Nuclear motion is treated classically. Nuclear tunneling effects are included in so-called Quantum TS Theory or Quantum Kramers Theory.

Reactions in solution

Coupling to non-reactive solvent modes leads to Brownian motion on PES

transition state

ω_b

E_b

E_0

ω_r

reactants

products

energy

reaction coordinate

Kramers' theory

Motion on PES is described by Smoluchowski equation:

$$\frac{\partial p(x,t)}{\partial t} = D\frac{\partial^2 p(x,t)}{\partial x^2} + k_B T D \frac{dU(x)}{dx}\frac{\partial p(x,t)}{\partial x}$$

With $p(x,t)$ = probability density of finding the system at reaction coordinate x at time t

$$D = \frac{k_B T}{\zeta}$$ ζ, friction coefficient

Solvent friction related to solvent fluctuations by fluctuation-dissipation theorem

Kramers' rate expression

$$k = \frac{\omega_b}{\zeta} \frac{\omega_r}{2\pi} \exp(-E_b / k_B T) = \kappa k_{TST}, \quad \kappa = \frac{\omega_b}{\zeta}$$

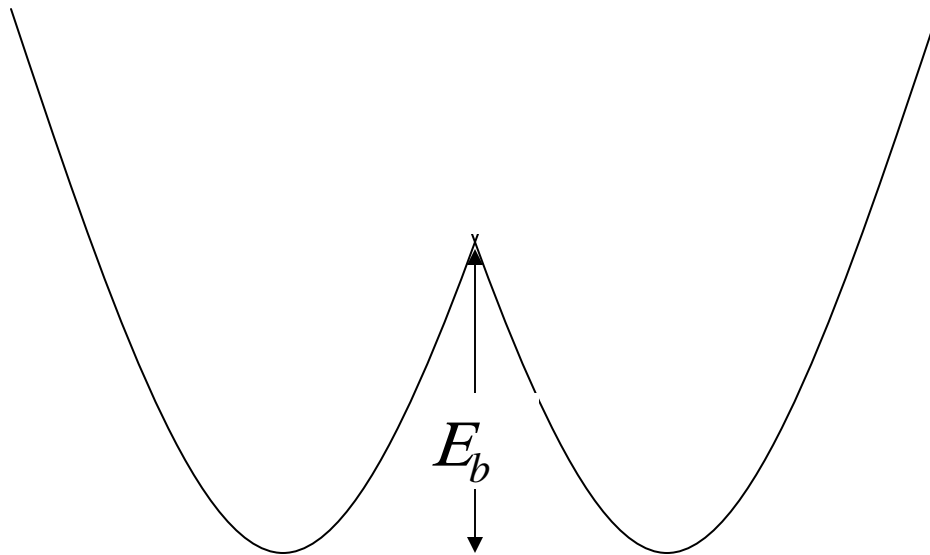valid for strong friction, the "overdamped" limit.

For moderate friction, Kramers derived:

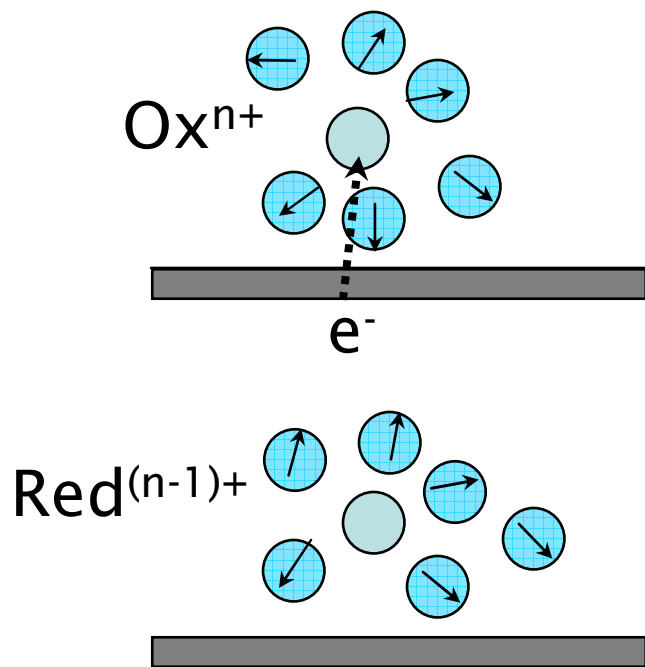$$\kappa = \frac{\left[\dfrac{\zeta^2}{4} + \omega_b^2 \right]^{1/2} - \dfrac{\zeta}{2}}{\omega_b}$$

Kramers' rate for cusp-shaped barrier

$$k = \frac{\omega_r^2}{2\pi\zeta}\left(\frac{\pi E_b}{k_B T}\right)^{1/2}\exp(-E_b/k_B T)$$

Electron transfer reactions at electrodes

Ox^{n+}

e$^-$

Red$^{(n-1)+}$

Electron is transferred from a continuum of levels on the electrode. Effectively, an electron is transferred from the Fermi level.

By changing the electrode potential, the metal levels shift with respect to the electron energy level on the donor or acceptor ion.

Outer-Sphere Electron Transfer

$$Ox^{n+} + e^- \rightleftharpoons Red^{(n-1)+}$$
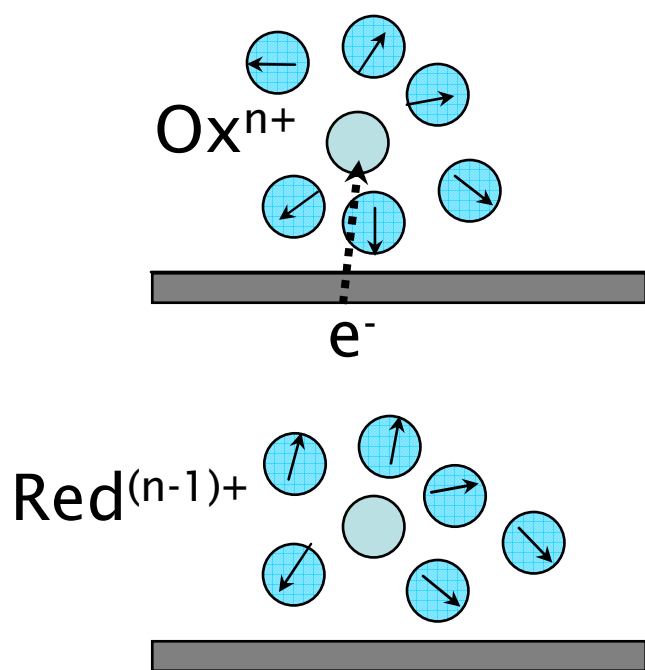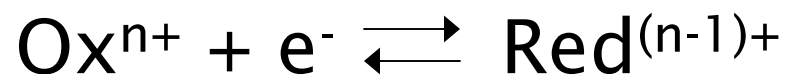
Sequence of events:

1. The reactant moves close to the electrode surface, but does not adsorb (outer Helmholtz plane, say)
2. The solvent assumes a suitable intermediate non-equilibrium configuration (the transition state)
3. The electron is exchanged radiationless
4. The system (solvent) relaxes to its new equilibrium configuration

The Marcus Potential Energy Surface

free energy

transition state

V_{Red}

V_{Ox+e}

n-1

n

generalized solvent coordinate q
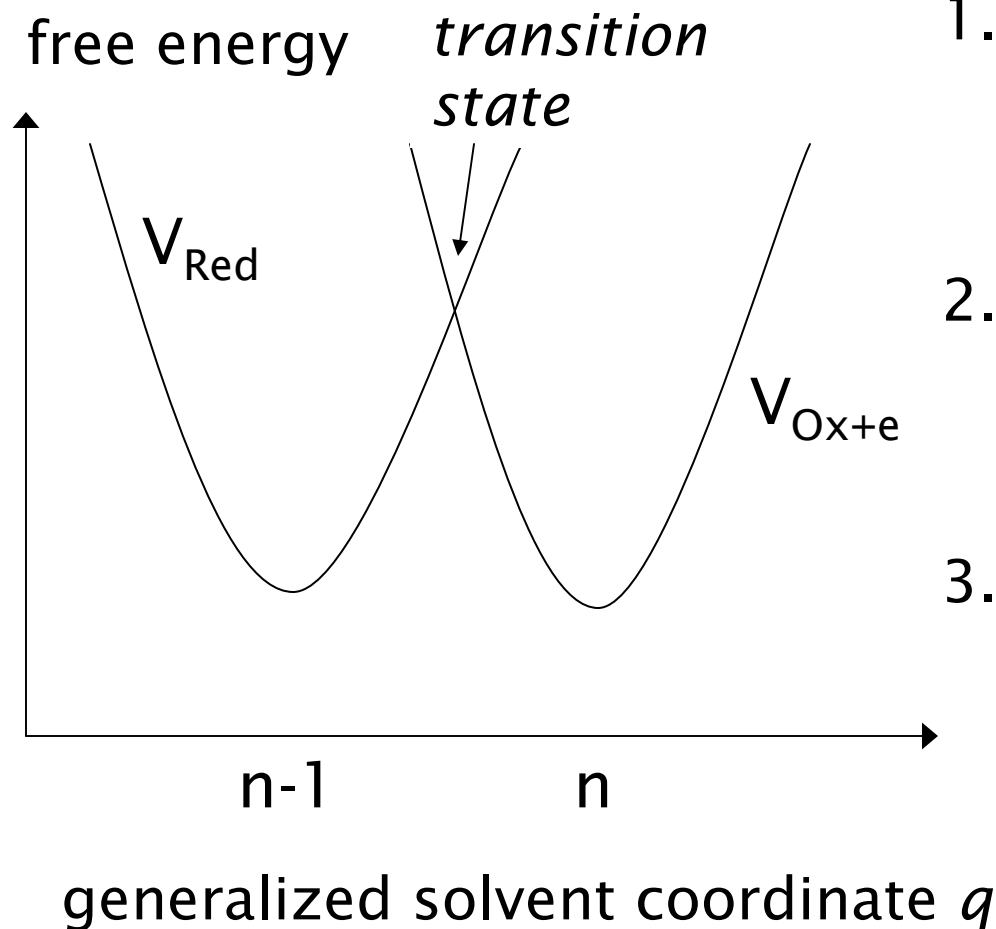
1. Minima at $q = $ n-1 (Red) and $q = $ n (Ox + e$^-$) because these are the equilibrium solvent configurations.
2. Deviations from equilibrium are assumed to be harmonic; V_{Red} and V_{Ox+e} are parabolic in q.
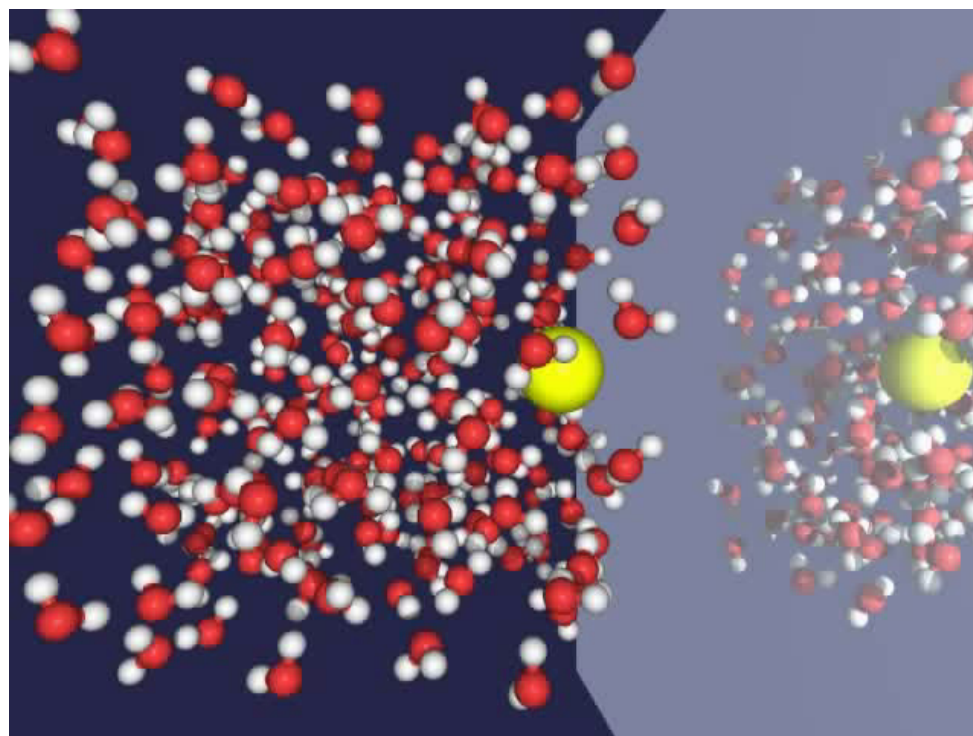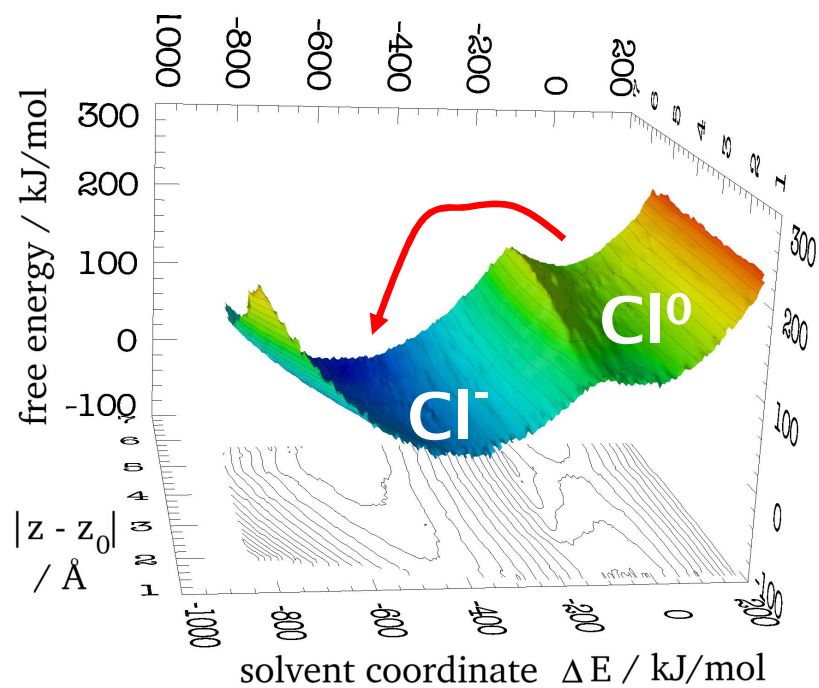3. V_{Ox+e} can be shifted up and down by changing the electrode potential.

The solvent reorganization energy λ

free energy

Red   Ox

λ

q
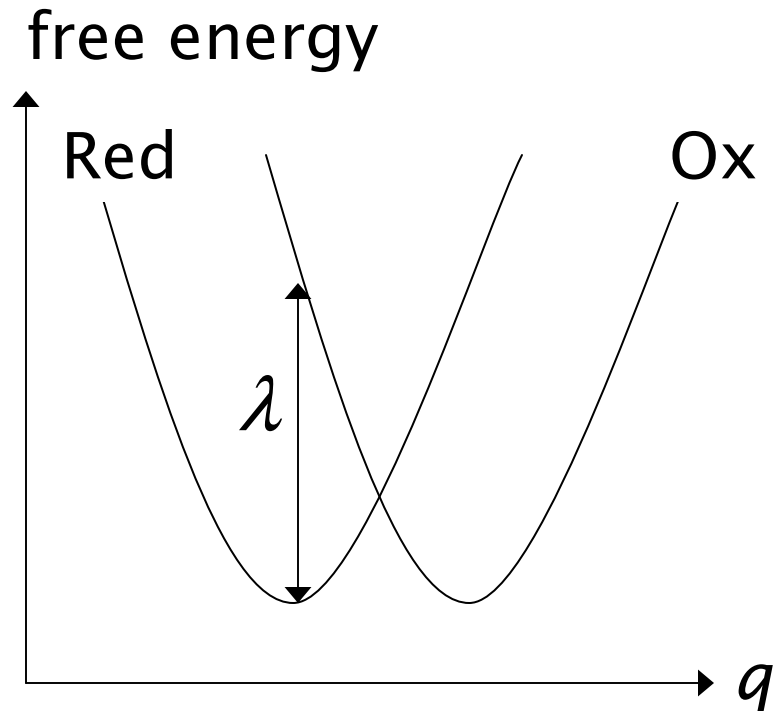
λ is the difference in energy between a non-equilibrium Ox species with a Red solvation shell and an Ox species with its proper equilibrium solvation shell, taking into account only the slow modes of solvation (i.e. the electronic polarization is always equilibrated)
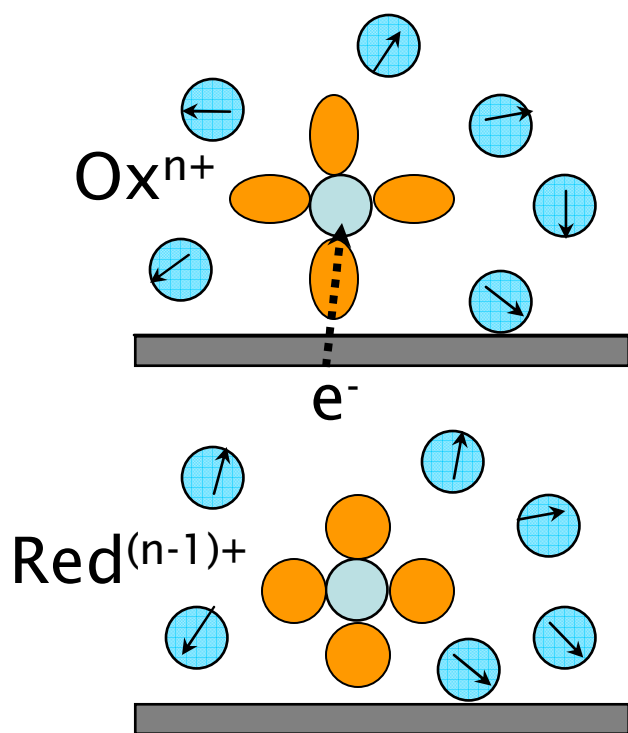
$$\lambda = \frac{e_0^2}{2a}\left(\frac{1}{\varepsilon_{opt}} - \frac{1}{\varepsilon_s}\right) = 50\text{-}200 \text{ kJ/mol}$$

Movie of electron transfer

$$Cl^0 + e^- \Leftrightarrow Cl^-$$

http://www.youtube.com/watch?v=cZslq-h36y0

Inner-sphere and outer-sphere modes

Apart from the reorganization of the solvent (*outer sphere*), ligands or a strongly bound first layer of solvent molecules also reorganizes (*inner sphere*). These modes are usually treated separately.

Activation energy

$V_{Red}(q) = \lambda[q-(n-1)]^2$

$V_{Ox+e}(q) = \lambda[q-n]^2 - \eta$

Transition state: $V_{Red}(q^*) = V_{Ox+e}(q^*)$

Activation energy:

$$\Delta G_{act} = \frac{(\lambda - \eta)^2}{4\lambda}$$

λ = solvent reorganization energy

η = reaction free energy = $e_0(\phi - \phi_0)$

$(\phi - \phi_0)$ = overpotential

Transfer coefficient

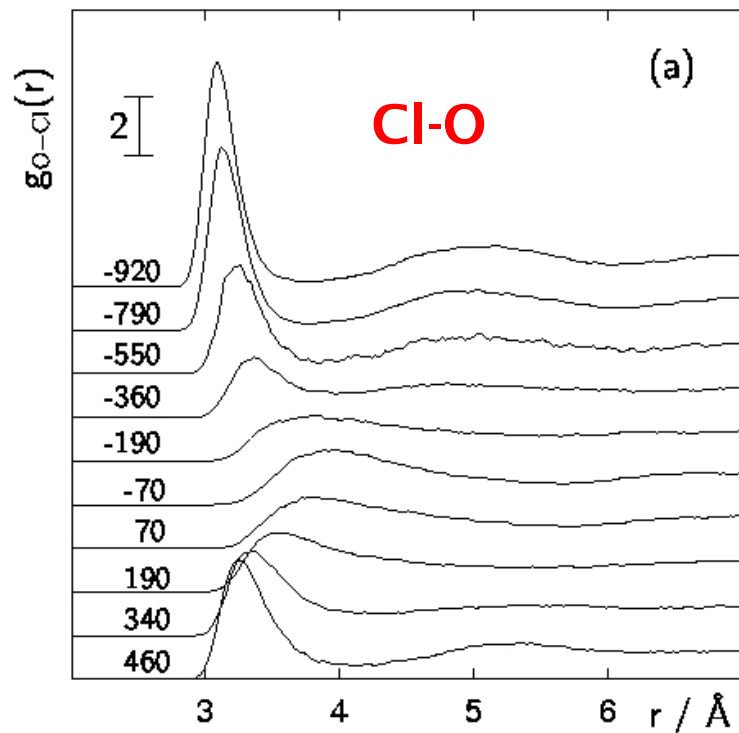Butler-Volmer definition $\alpha = -\, d\Delta G/d\eta$

Marcus theory predicts:

$$\alpha = \frac{1}{2} - \frac{\eta}{2\lambda}$$

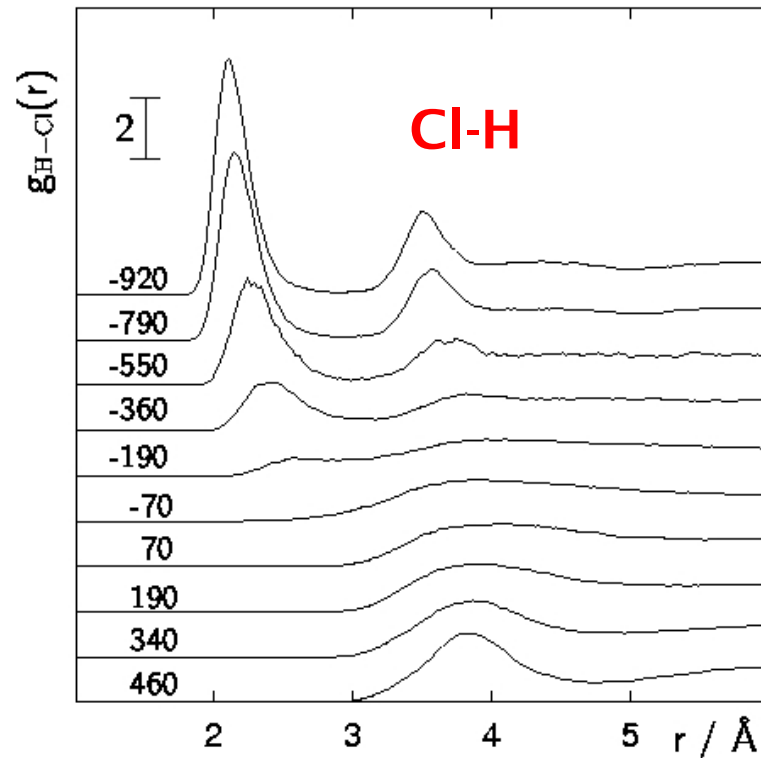α is the amount of charge transferred to the transition state (Hush)

α is potential dependent, leading to a non-linear Tafel plot

α is independent of temperature

# Nonlinear solvent reorganization

Effective radius gets smaller
with higher charge;
Increasing "dielectric saturation
with higher charge

Orientation of water depends
on charge: strongest change
in electrostriction from 0 to -1

C.Hartnig, M.T.M.Koper, J.Chem.Phys. 115 (2001) 8540

Potential dependence of transfer coefficient

Electrochemical ET to a ferrocene tethered to a gold electrode via a alkane thiol chain.

C.E.D.Chidsey, Science 251 (1991) 919
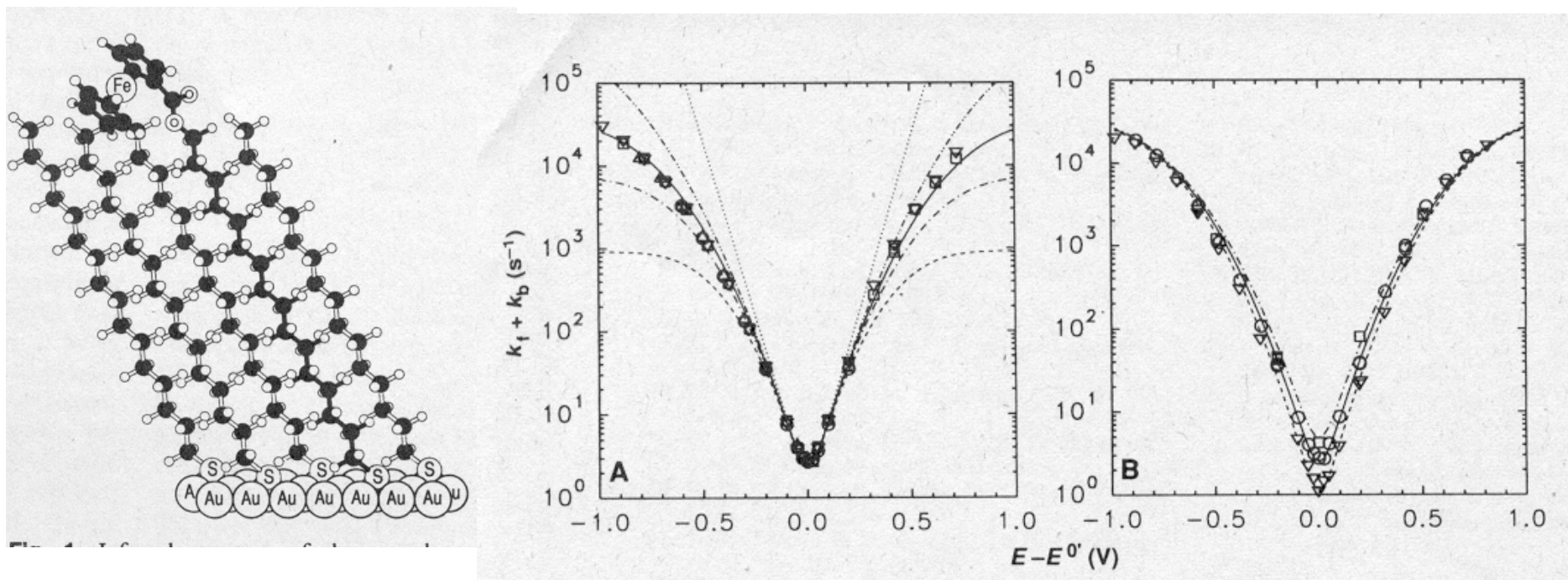
What happened to the prefactor ?

$$k = \nu_n \exp(-\Delta G_b / k_B T)$$

Marcus suggested the reaction to be adiabatic and ν_n to be a collision frequency of the two reactants.

However, it is more likely to be a typical frequency of the solvent motion or the inner-sphere vibration, whichever is dominant.

$$\nu_n = \frac{\omega_{in}}{2\pi}$$

Non-adiabatic ET

Electron tunneling at the TS is rate determining in case of weak electronic coupling (small orbital overlap H_{ab})

$$k = v_{el} \exp(-\Delta G_b / k_B T)$$

$$v_{el} = \frac{2H_{ab}^2}{\hbar} \left(\frac{\pi}{\lambda_{tot} k_B T} \right)^{1/2}$$

(Calculated by application of Fermi's Golden Rule for electronic transitions.)

Evidence for adiabatic ET

Adiabatic ET: reaction rate depends only on solvent fluctuations, not on electron tunneling probability. There should be no metal dependence of the reaction rate.

$[Ru(NH_3)_6]^{2+/3+}$ couple

metal	k (cm s^{-1})
Pt	1.2
Pd	1.0
Au	1.0
Cu	1.2
Ag	1.2
Pt/Tl$_{ad}$	1.3

T.Iwasita, W.Schmickler, J.W.Schultze, Ber.Bunsenges.Phys.Chem. 89 (1985) 138

Evidence for non-adiabatic ET

Non-adiabatic ET: reaction rate depends explicitly on the strength of the electronic coupling, i.e. the electron tunneling probability. A distance dependence of the reaction rate is expected.

$$H_{AB}(R) = H_{AB}^0 \exp(-\beta R)$$

Ferrocene couple attached to Au through alkyl thiol tail.
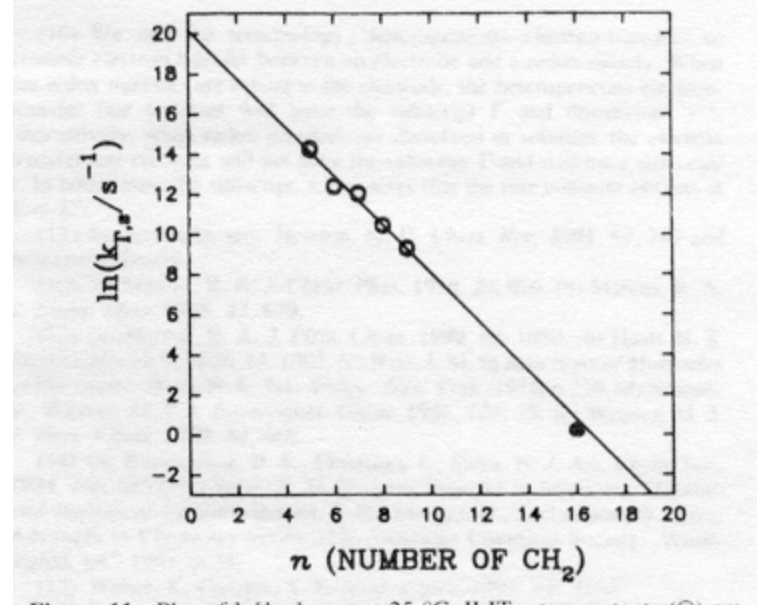
Smalley et al. J.Phys.Chem.99 (1995) 13141

Electron transfer rate to cytochrome *c'*

Rate limited by reorganization

Electron tunneling

$$k = e^{-d/\beta}$$

β = 1.09 per methylene

Au-HS-(CH$_2$)$_n$-COOH

ln(k$_{app}$/s^{-1})

n (thiol length)
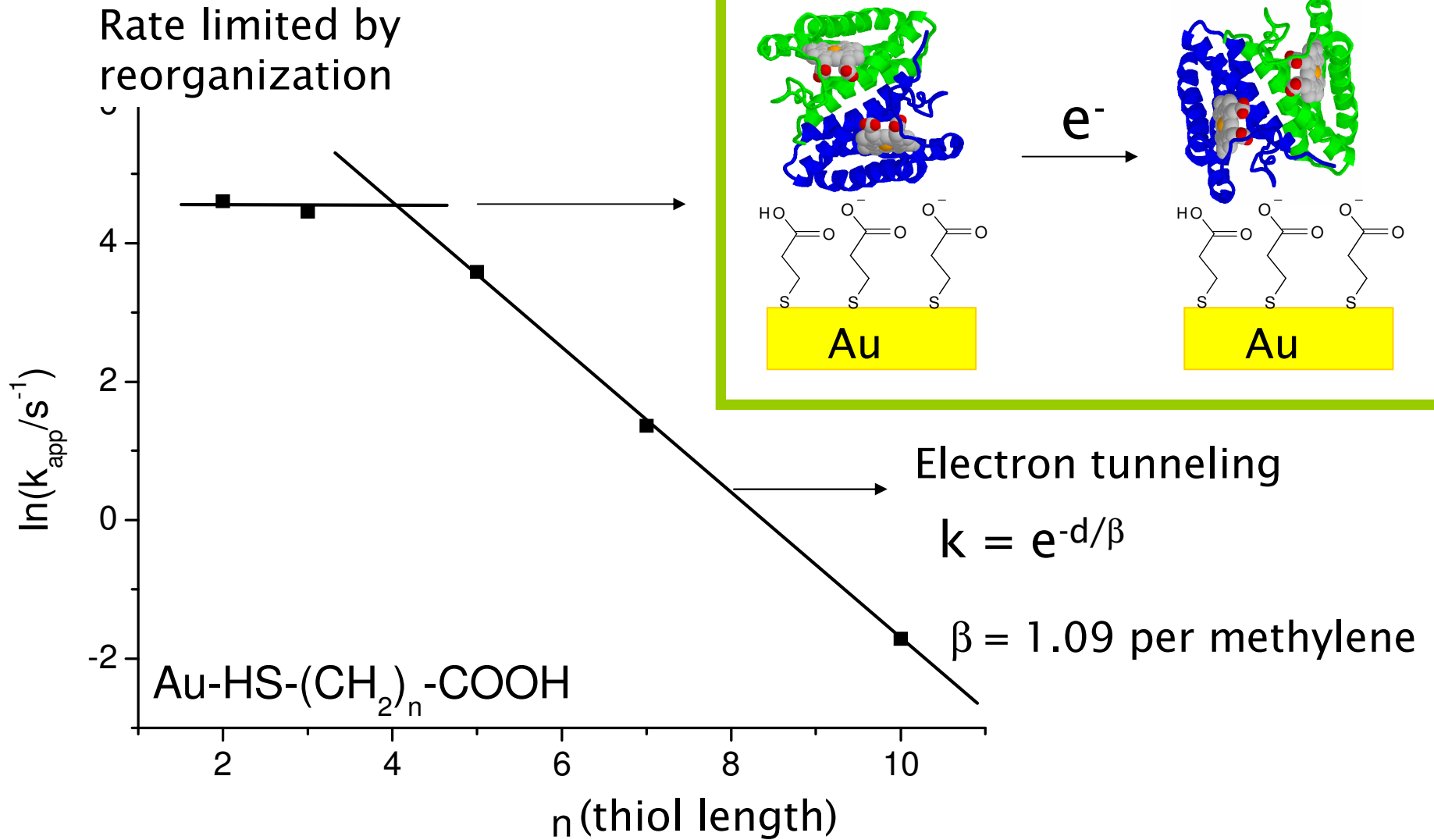
Zusman's theory

Dielectric friction is related to longitudinal relaxation time:

$$\zeta_{dielec} = \omega_s^2 \tau_L$$

Together with Kramers' "overdamped" rate expression for a cusp-shaped barrier, this gives:

$$k = \frac{1}{\tau_L} \left(\frac{\lambda}{16\pi k_B T} \right)^{1/2} \exp(-\lambda / 4k_B T)$$

L.D.Zusman, Chem.Phys. 49 (1980) 295

Evidence for slow solvent dynamics

Plots of log k vs. -log t_L may indicate some solvent dynamical effects for high-friction ("slow") solvents.
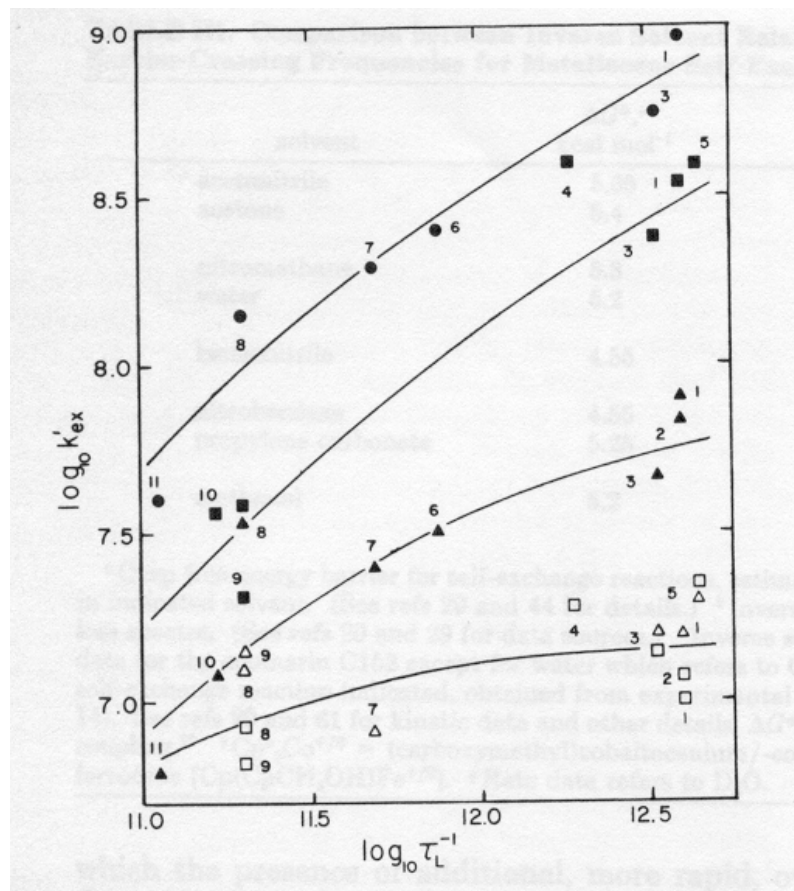
Fe^+/Fe and Co^+/Co with different ligands in different solvents

Electrochemical ion transfer

Ox^{n+}

δe^-

$Red^{(n-\delta)+}$
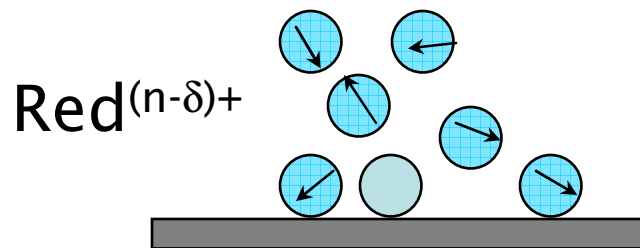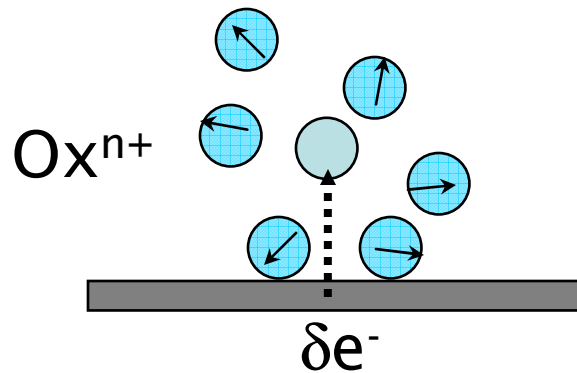
e.g. halide adsorption

$$I^- \longrightarrow I^{(1-\delta)-} + \delta e^-$$
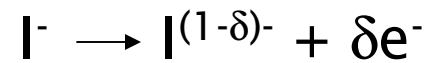
or metal deposition

$$Zn^{2+} + 2e^- \longrightarrow Zn_{ad} \text{ or } Zn(Hg)$$
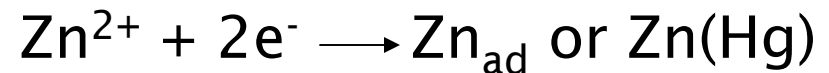
The ion has to penetrate the electric double layer and lose part of its solvation shell.
In the adsorbed state, the ion may be only partially (dis)charged.

Anderson-Newns Hamiltonian

describes the exchange of an electron between an isolated
orbital (the adsorbate) and a continuum of levels (metal).
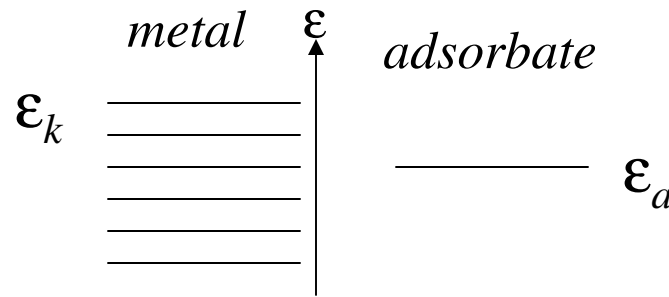
Electronic part:

$$H_{elec} = \varepsilon_a\, n_a + \sum_k \varepsilon_\kappa n_k + \sum_k [V_{ak}\, c_a{}^+ c_k + V_{ka}\, c_k{}^+ c_a]$$

Solvent part:

$$H_{solv} = \lambda q^2 + 2\lambda(z - n_a)q$$

The electronic interaction parameter Δ

$$\Delta = 2\pi\Sigma_k|V_{ak}|^2\delta(\epsilon-\epsilon_k)$$
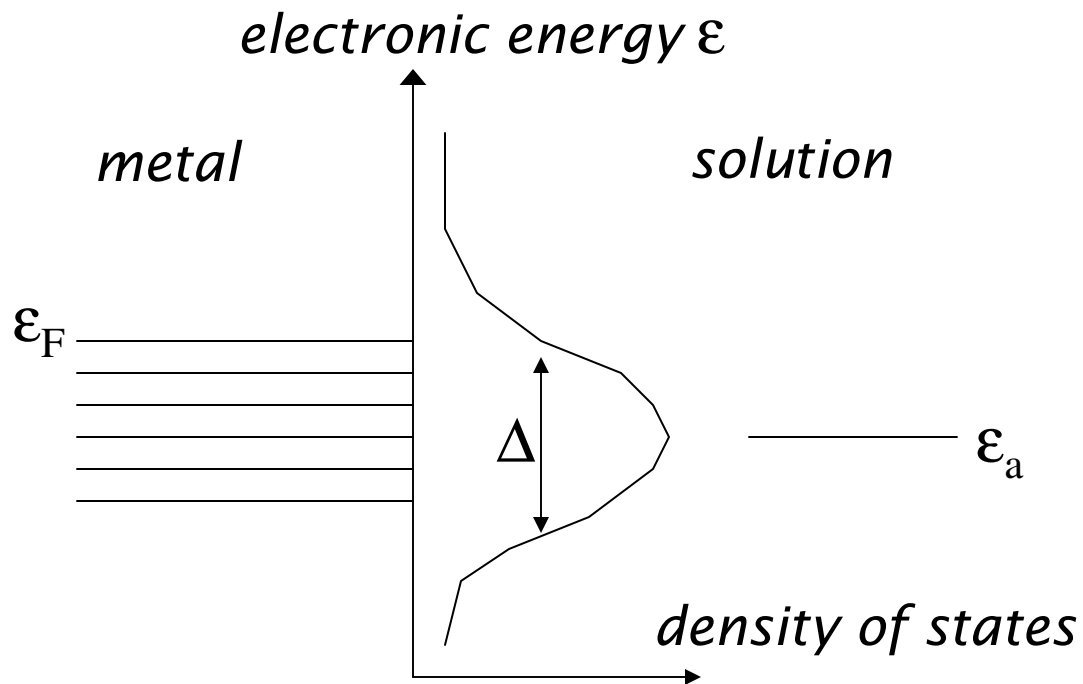
Δ describes the broadening of the adsorbate energy level due to electron exchange.

Schmickler's model for ion transfer

1. distance dependent reorganization energy λ, taken from molecular dynamics simulations.

2. distance dependent electronic interaction, taken from quantum chemical calculations

$$\Delta(x) = \Delta_0 \exp(-x/l)$$

Solvation energy vs. distance

Energy of the chloride-solvent and chlorine-solvent interaction as a function of the distance from the electrode surface.
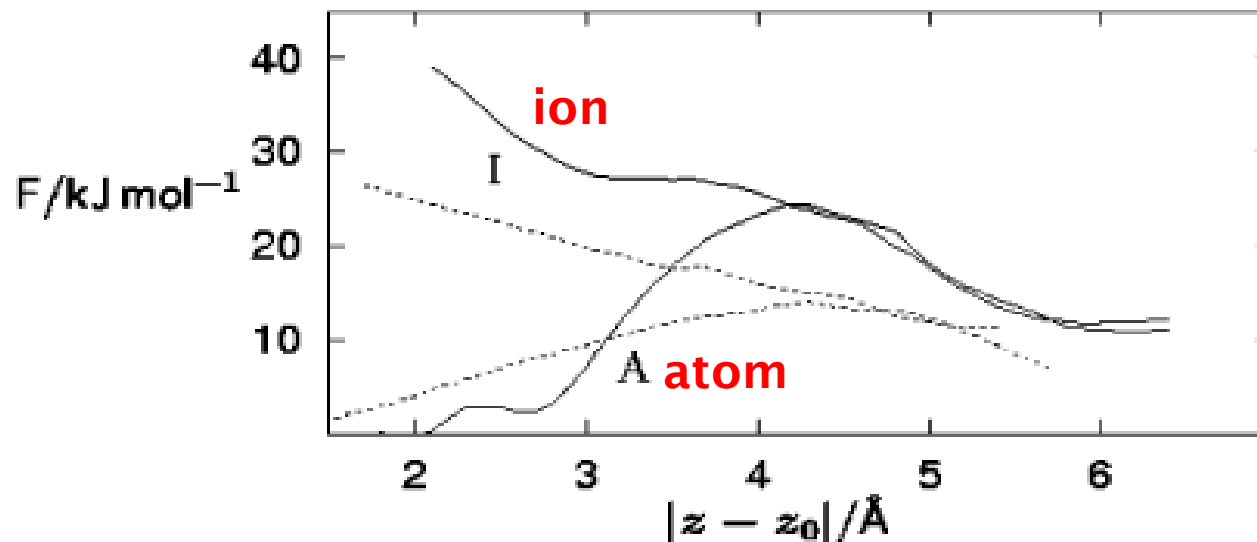

Figure 3. Free energy profiles for the minima in Figure 2 as a function of distance from the surface. Solid lines are the curves for the atom ("A") and ion ("I") with the corrugated metal−water potential; dashed lines are the curves for the atom and ion with the smooth metal−water potential.
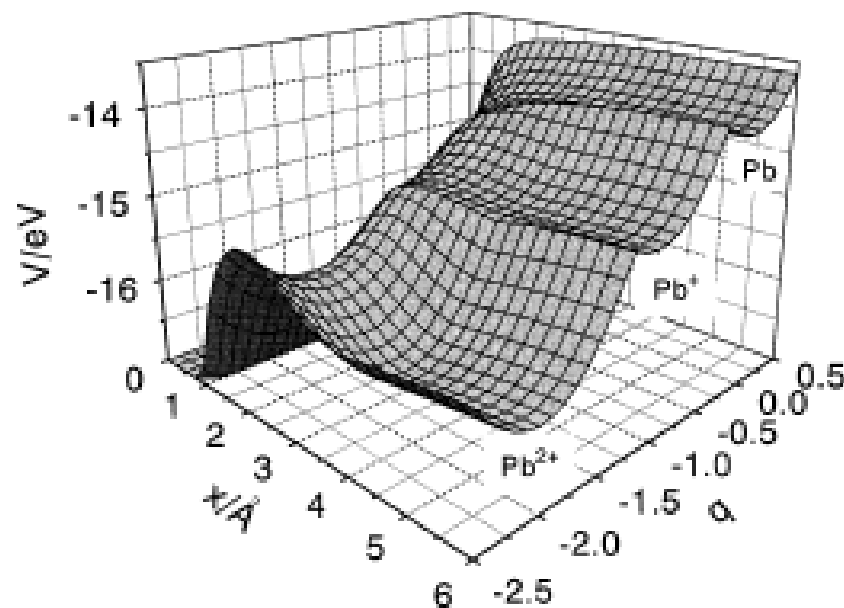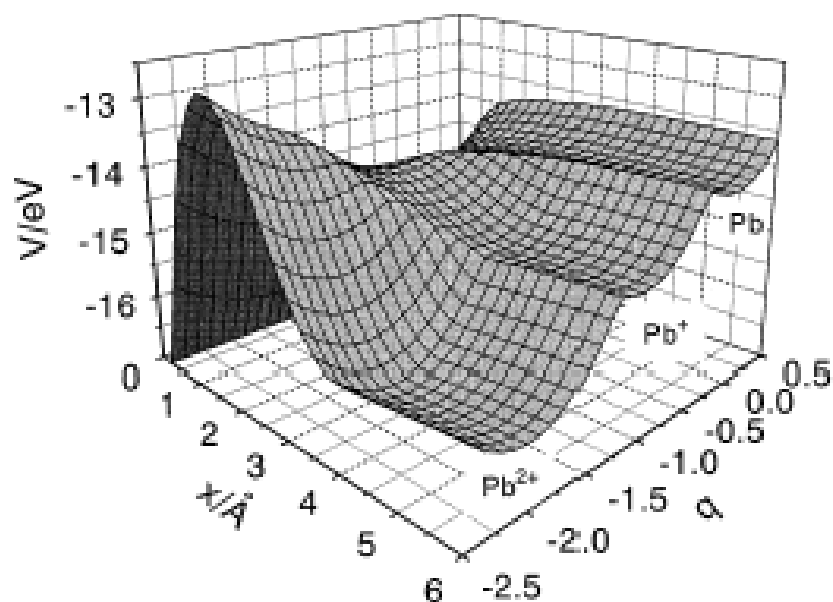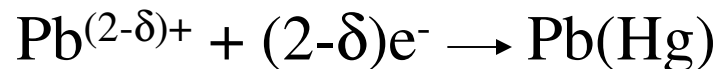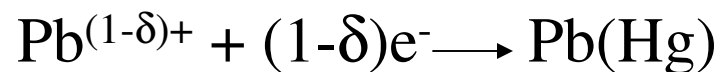
E.Spohr, Chem.Phys.Lett. 207 (1993) 214
C.Hartnig, M.T.M.Koper, J.Phys.Chem.B 108 (2004) 3824

Thallium reduction on Hg

$$Tl^+ + \delta e^- \longrightarrow Tl^{(1-\delta)+}$$

$$Tl^{(1-\delta)+} + (1-\delta)e^- \longrightarrow Tl(Hg)$$
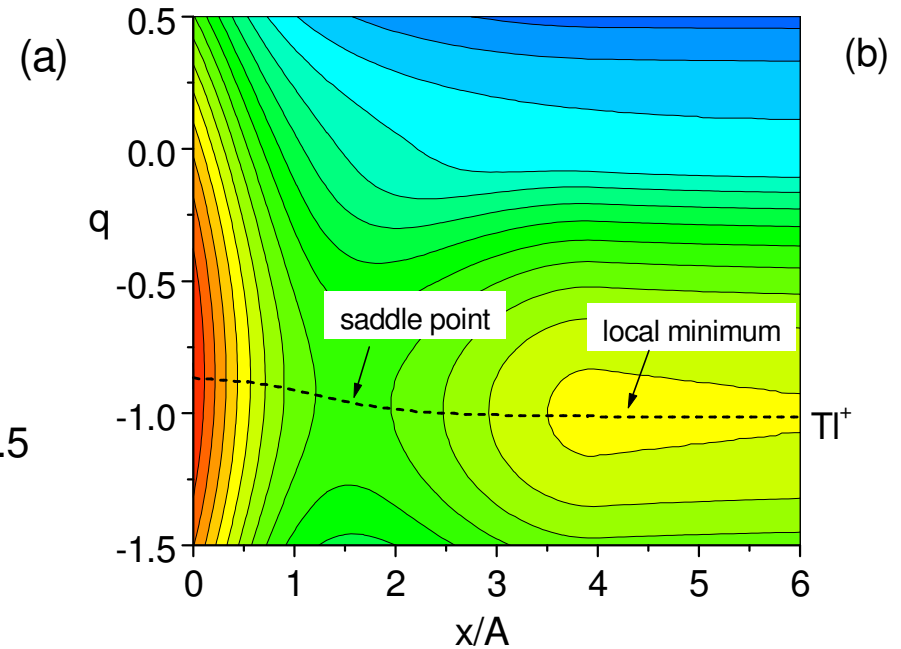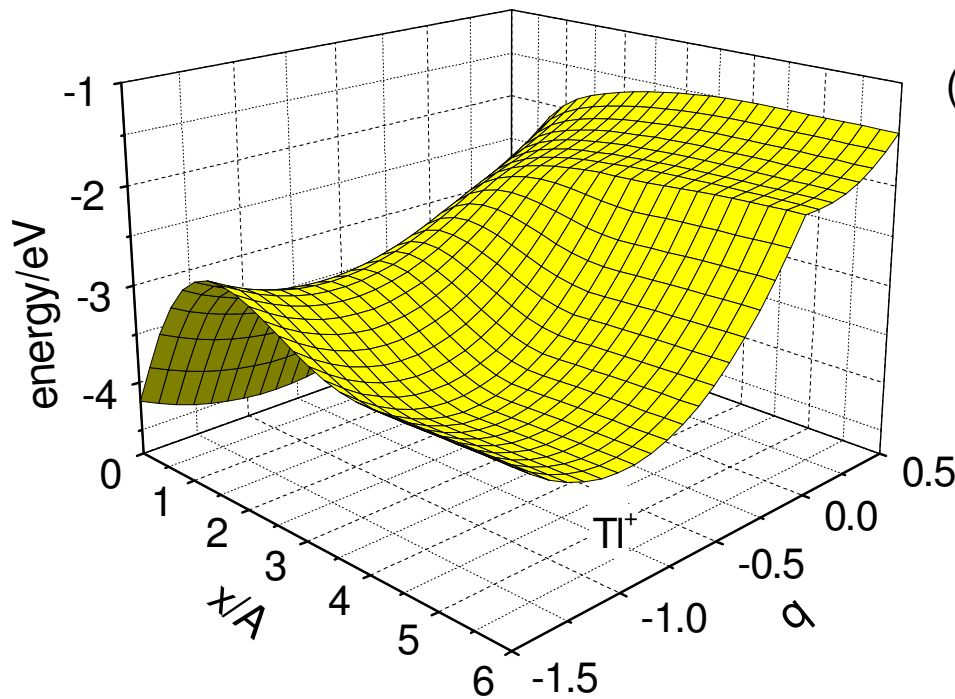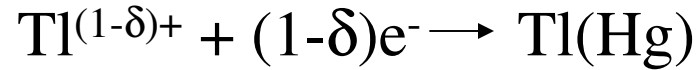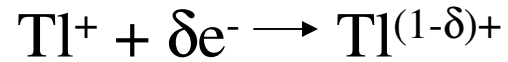
Transfer coefficient: fraction of the double-layer potential traversed at the transition state.

Lead reduction on Hg: two mechanisms

$$Pb^{2+} + e^- \longrightarrow Pb^+$$
$$Pb^+ + \delta e^- \longrightarrow Pb^{(1-\delta)+}$$
$$Pb^{(1-\delta)+} + (1-\delta)e^- \longrightarrow Pb(Hg)$$

$$Pb^{2+} + \delta e^- \longrightarrow Pb^{(2-\delta)+}$$
$$Pb^{(2-\delta)+} + (2-\delta)e^- \longrightarrow Pb(Hg)$$
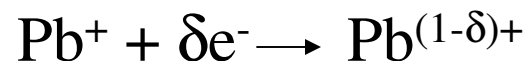
# Electron and ion transfer compared

Electron transfer

· reaction occurs at a distance from the surface due to strongly inner solvation sphere
· reaction coordinate: solvent and/or inner-sphere reorganization
· transfer coefficient = 1/2 at equilibrium
· transfer coefficient is potential dependent
· transfer coefficient is <u>not</u> temperature dependent

Ion transfer

· reaction involves penetration of the electric double layer
· reaction coordinate is mainly the distance from the electrode surface
· activation energy correlates with the ion solvation energy
· transfer coefficient depends on the structure of the double layer
· transfer coefficient is temperature dependent

Concerted bond breaking and electron transfer
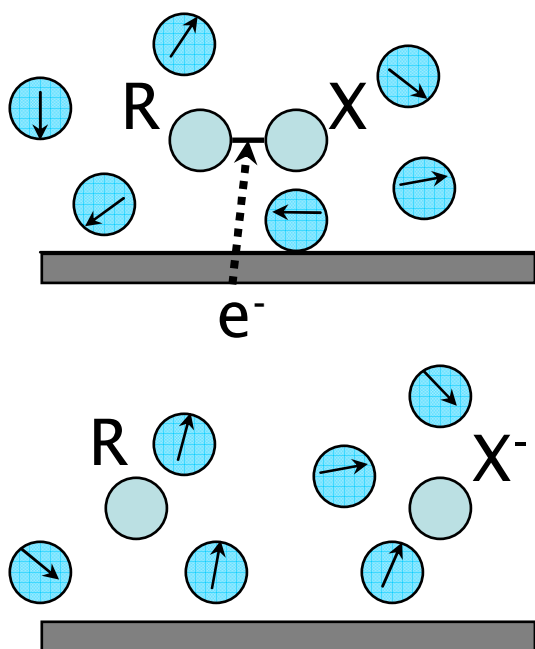
e.g. methylchloride reduction

$$CH_3Cl + e^- \longrightarrow CH_3 + Cl^-$$
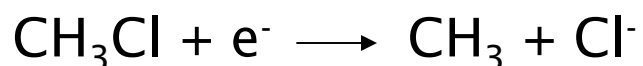
The methylchloride does <u>not</u> adsorb onto the metal electrode

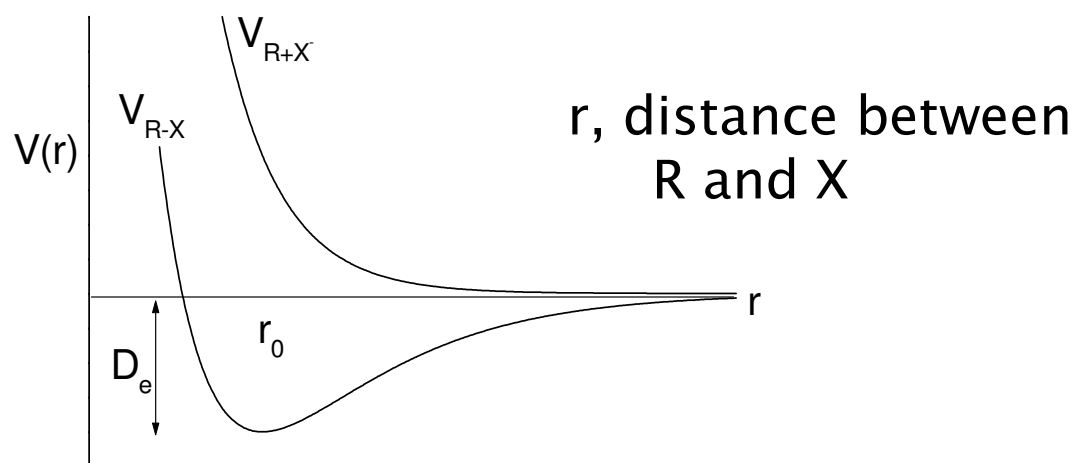*J.M.Saveant, J.Am.Chem.Soc. 109 (1987) 6788*

Hamiltonian for bond breaking ET

$H = H_{elec} + H_{solv} + H_{bond\text{-}breaking}$
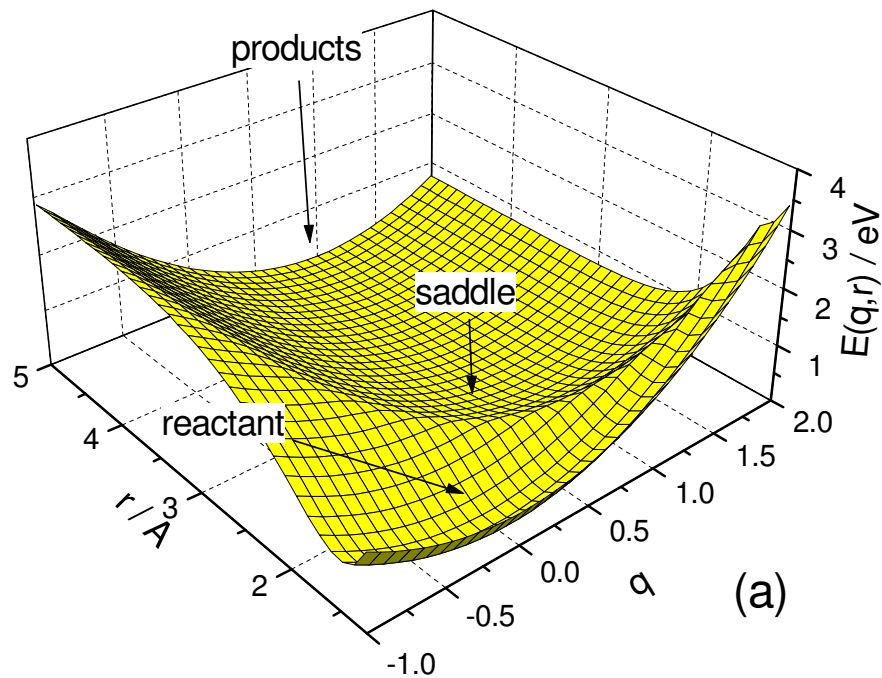
$H_{bond\text{-}breaking}$ is modeled by a kind of switching function:

$H_{bond\text{-}breaking} = [1 - n_a] V_{R\text{-}X} + n_a V_{R+X^-}$

where n_a is the number operator of the antibonding LUMO orbital of the R-X molecule

r, distance between R and X

PES for BBET
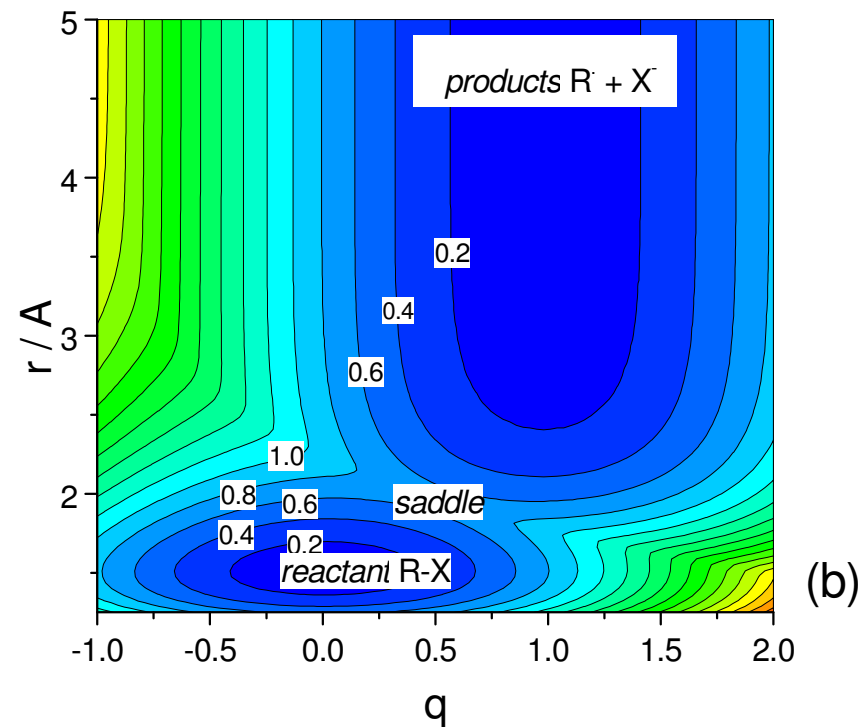
Small Δ, weak electronic interaction

Activation energy of bond breaking

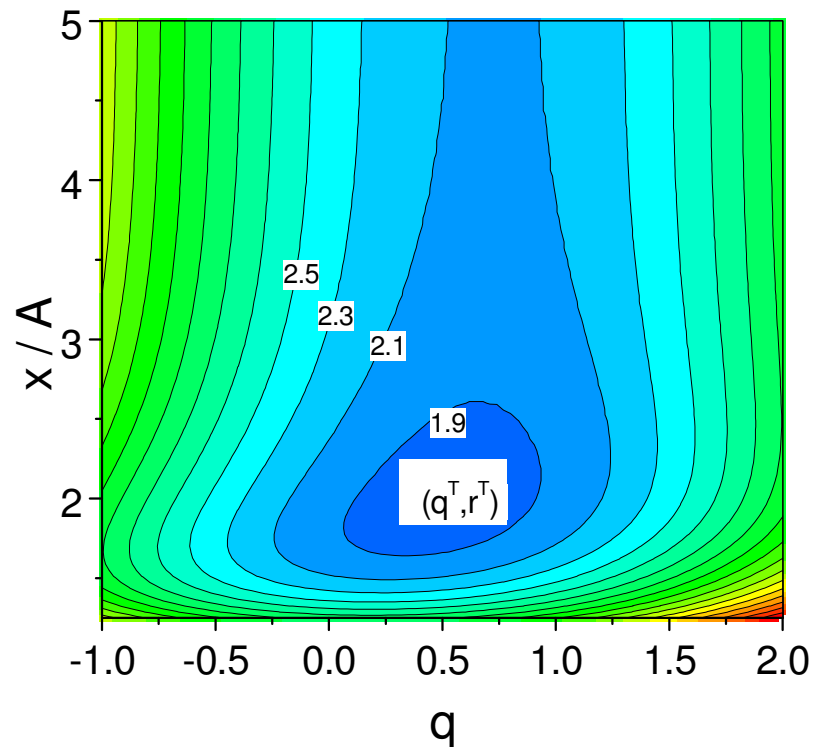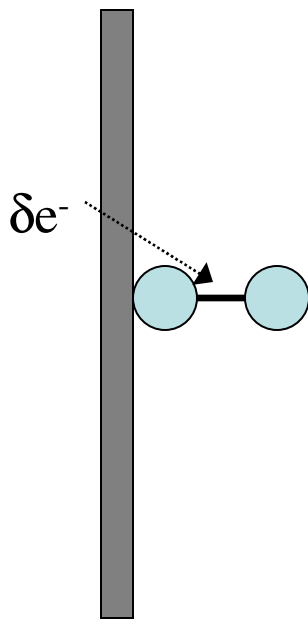$$\Delta G_{act} = \frac{(\lambda + D_e - \eta)^2}{4(\lambda + D_e)}$$

transfer coefficient

$$\alpha = \frac{1}{2} - \frac{\eta}{2(\lambda + D_e)}$$

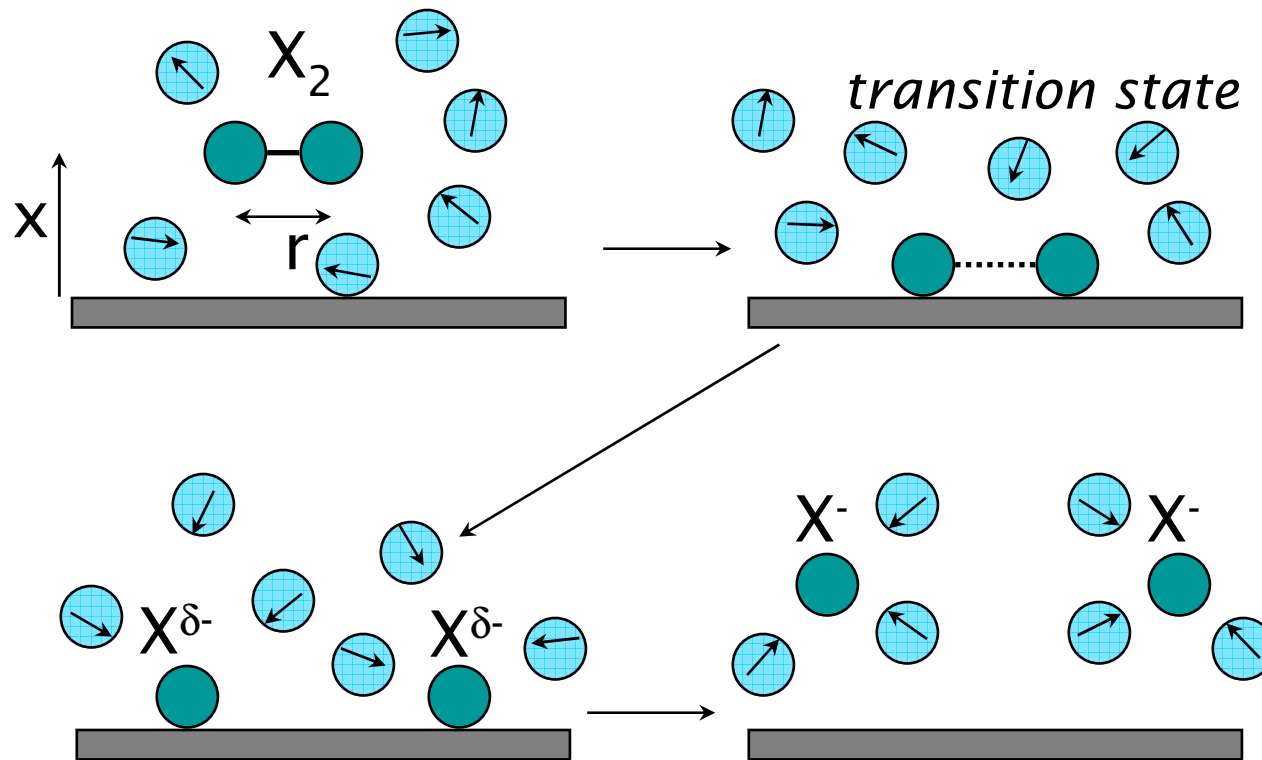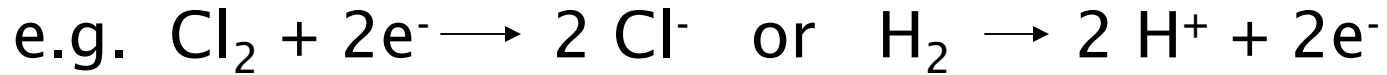amount of charge transferred to the antibonding orbital

Adsorption of molecules: backdonation

the metal donates electronic charge to the antibonding orbital leading to a weakening of the intramolecular bond.

Large Δ, strong electronic interaction leads to chemical bond

Catalysis and electron transfer

e.g. $Cl_2 + 2e^- \longrightarrow 2\,Cl^-$ or $H_2 \longrightarrow 2\,H^+ + 2e^-$
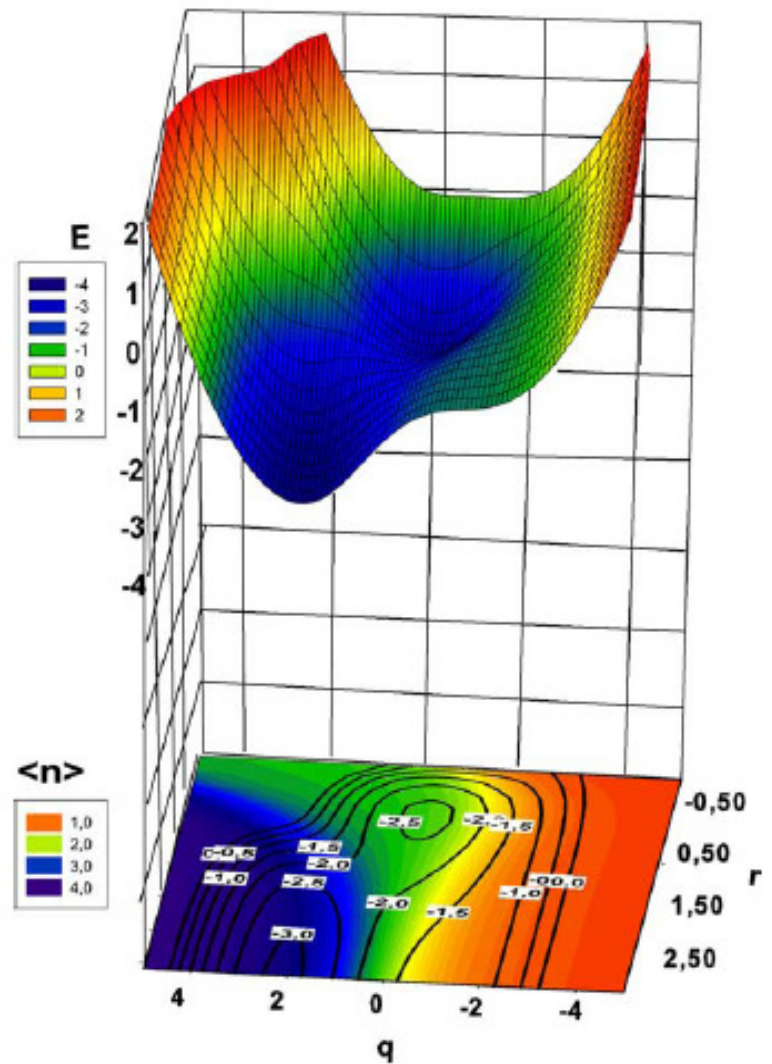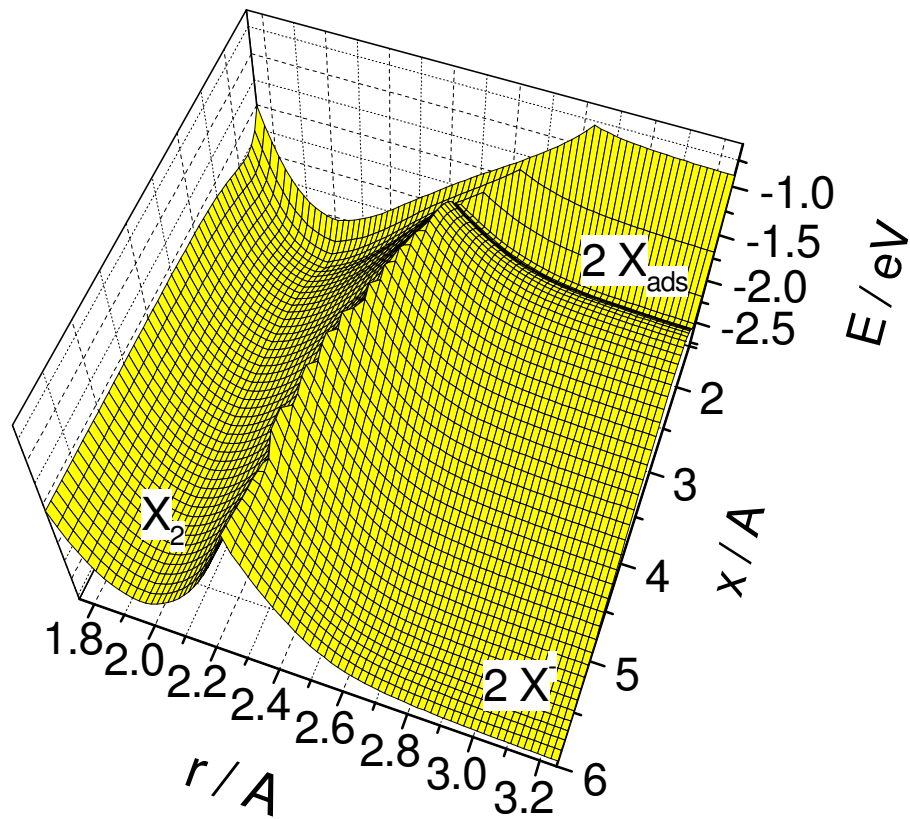
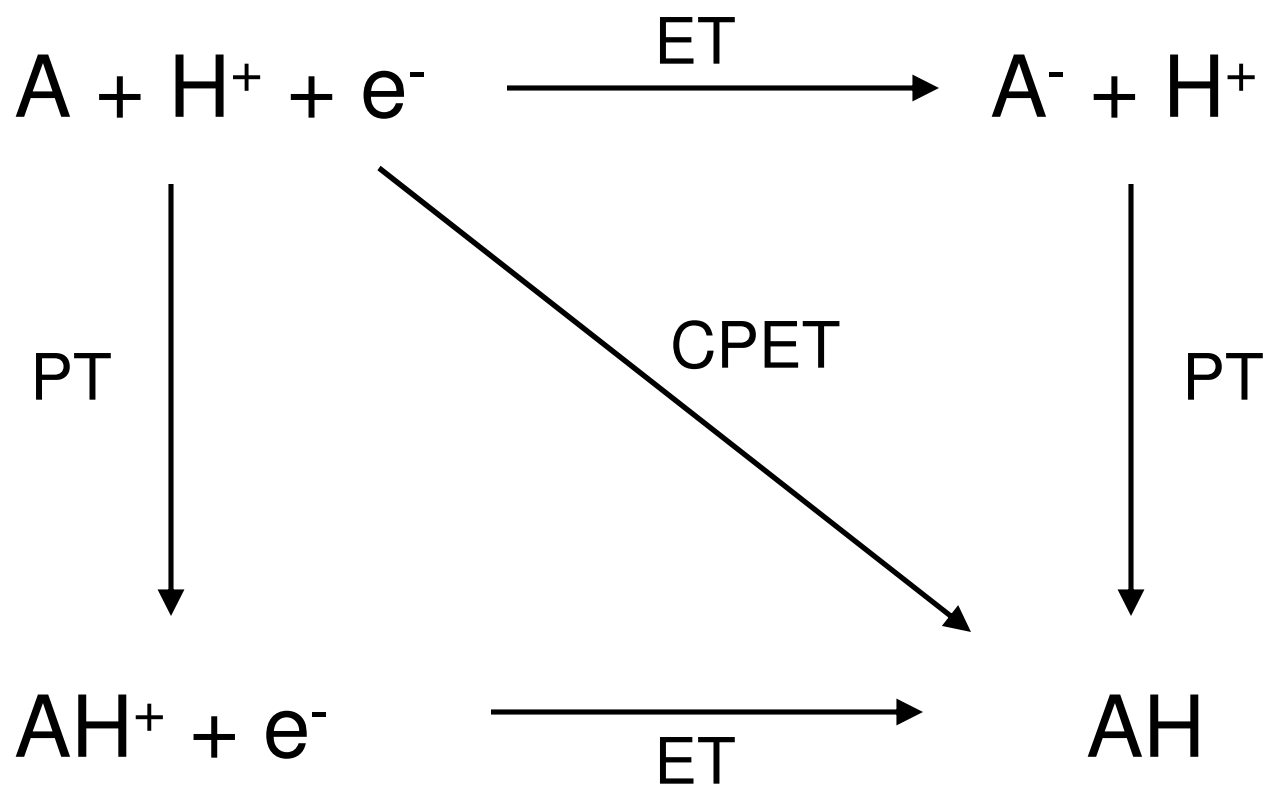M.T.M.Koper, G.A.Voth, J.Chem.Phys. 109 (1998) 1991
E.Santos, M.T.M.Koper, W.Schmickler, Chem.Phys.Lett. 419 (2006) 421
E.Santos, M.T.M.Koper, W.Schmickler, Chem.Phys. 344 (2008) 195
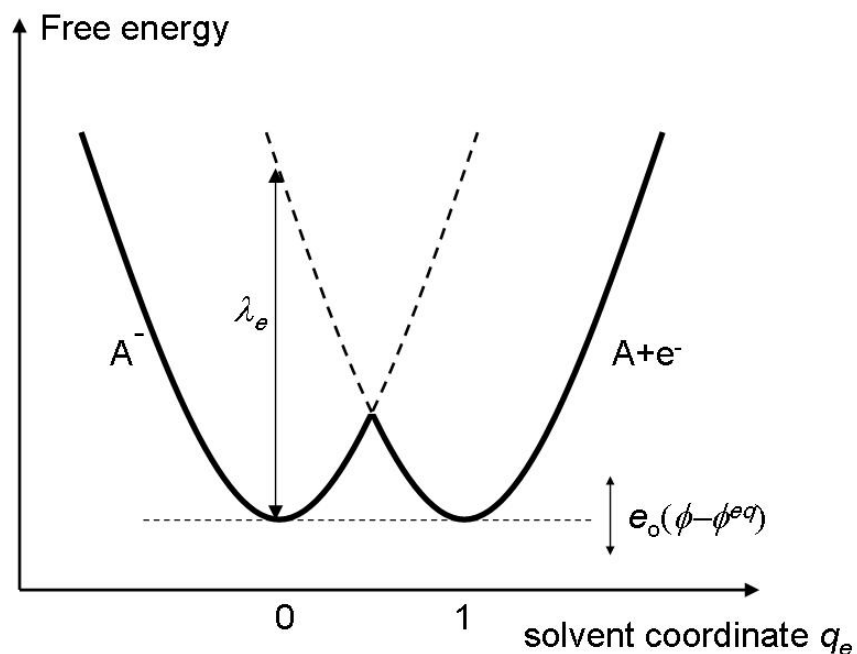
PES of catalytic BBET

Proton-coupled electron transfer

$$A + H^+ + e^- \xrightarrow{\text{ET}} A^- + H^+$$

PT $\downarrow$ CPET   PT $\downarrow$

$$AH^+ + e^- \xrightarrow{\text{ET}} AH$$

CPET = Concerted Proton-Electron Transfer

S. Hammes-Schiffer, A.A.Stuchebrukhov, Chem.Rev.110 (2010) 6939
M.T.M.Koper, Phys.Chem.Chem.Phys. 15 (2013) 1399

Hamiltonian of PCET

$$H(q_e, q_p) = \varepsilon_A n_A + \sum_k \varepsilon_k n_k + \sum_k \left(V_k c_k^+ c_A + V_k^* c_A^+ c_k \right) + \varepsilon_{p,1} n_1 + \varepsilon_{p,2} n_2 + V_{pt} c_1^+ c_2 + V_{pt}^* c_2^+ c_1$$

$$+ \lambda_e q_e^2 + \lambda_p q_p^2 - 2\overline{\lambda} q_e q_p - 2\lambda_e q_e - 2\lambda_p q_p + \beta n_A n_2$$
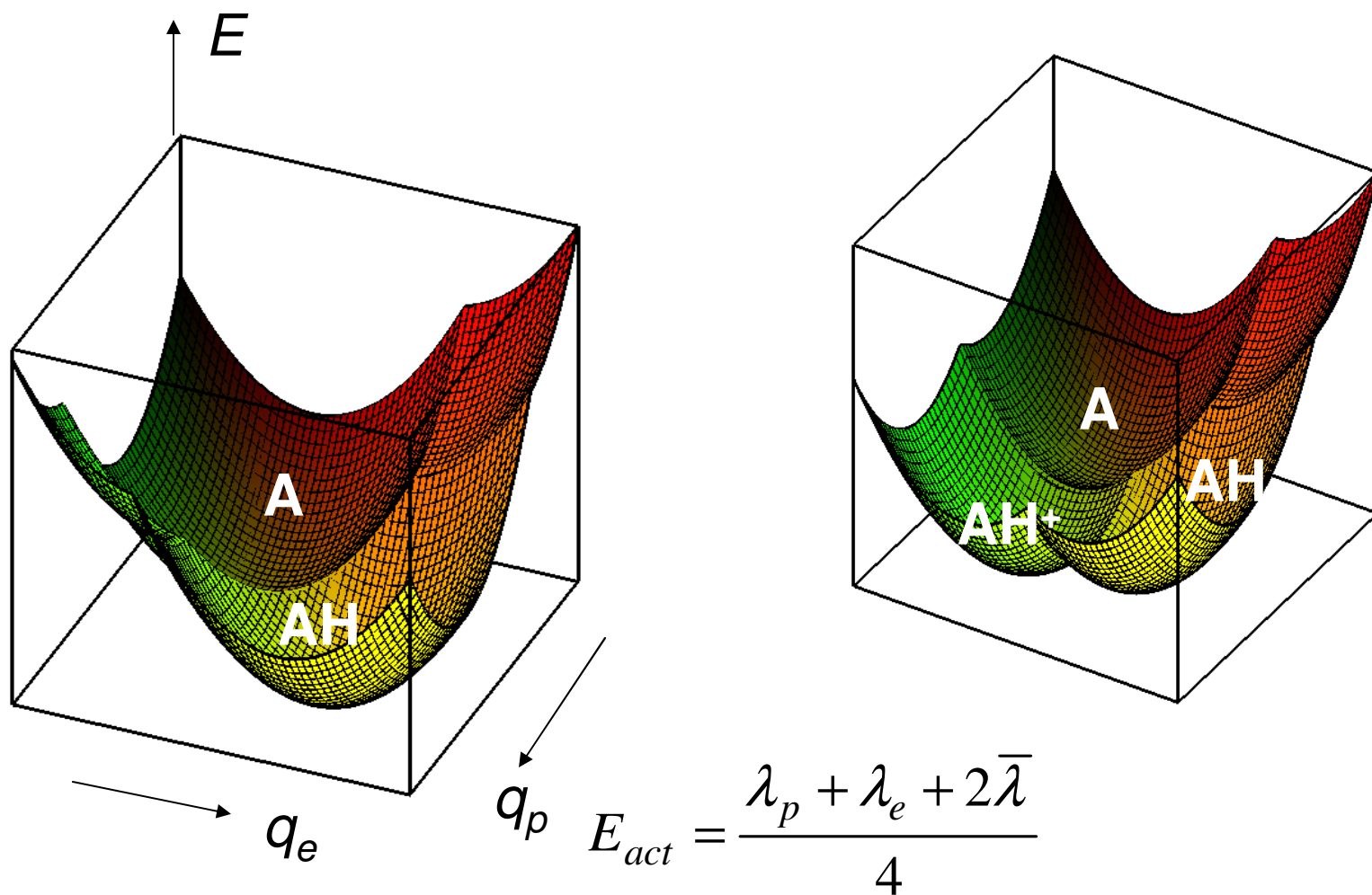

Electron affinity + solvation energy

Proton affinity = pK$_a$(AH$^+$)

j.Grimminger, S.Bartenschlager, W.Schmickler, Chem.Phys.Lett. 416 (2005) 316
M.T.M.Koper, Phys.Chem.Chem.Phys. 15 (2013) 1399
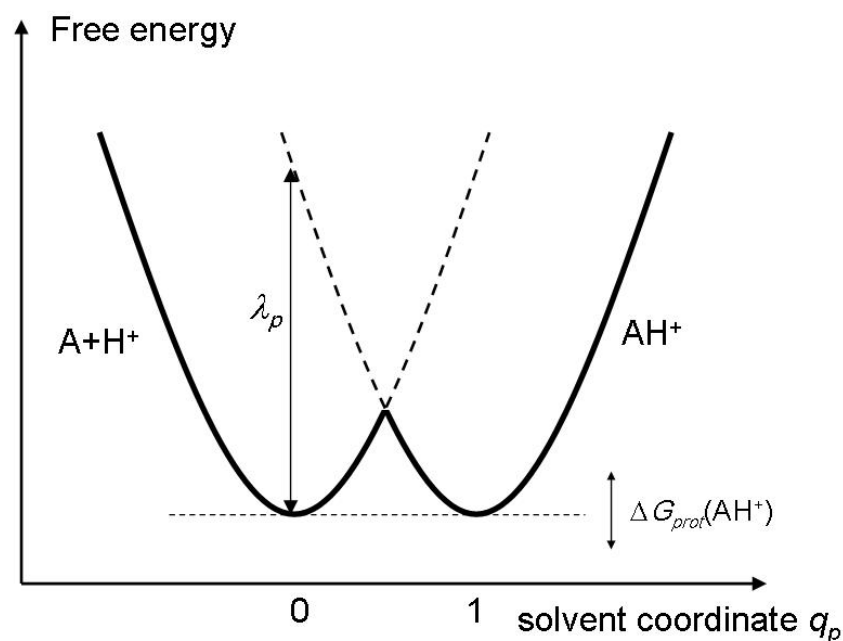
PES for coupled and decoupled PCET

$$E_{act} = \frac{\lambda_p + \lambda_e + 2\overline{\lambda}}{4}$$

M.T.M.Koper, Phys.Chem.Chem.Phys. 15 (2013) 1399

PT reorganization energy λ_p

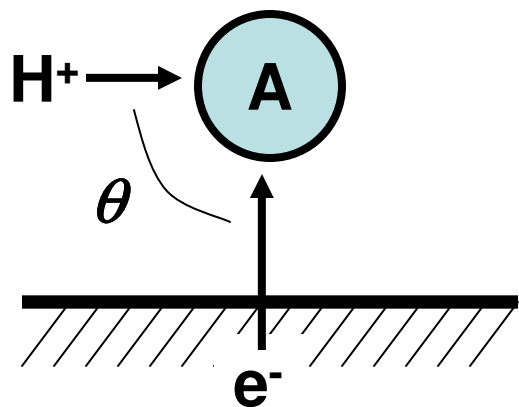HA $\leftrightarrows$ H$^+$ + A$^-$

Electrostatically, this is like the creation or annihilation of a dipole. Reorganization energy of the solvent is then the dielectrically slow part of the solvation energy of a dipole, as given by the Kirkwood-Onsager expression:
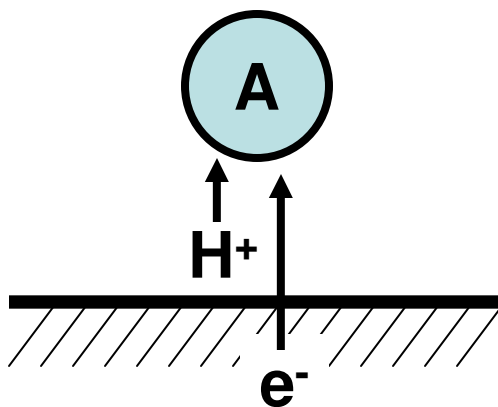
$$\lambda_p = \frac{1}{4\pi\varepsilon_0}\left(\frac{\varepsilon_s - 1}{2\varepsilon_s + 1} - \frac{\varepsilon_{opt} - 1}{2\varepsilon_{opt} + 1}\right)\frac{\mu}{a^3}$$

Cross reorganization energy