Lecture #5 of 12

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Thermal (Dark) Reactions

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Marcus–Hush Theory

$$\underbrace{\mathrm{D} + \mathrm{A}}_{\mathrm{A}} \rightleftharpoons \underbrace{\mathrm{D}^+ + \mathrm{A}^-}_{\mathrm{B}}$$

… but how is this a first-order reaction (s^{-1})?… more on this later…

Marcus–Hush (1950s–1960s)
theoretical (semiclassical) rate constant equation

$$k_{\mathrm{ET}} = \frac{2\pi}{\hbar}|H_{\mathrm{DA}}|^2 \frac{1}{\sqrt{4\pi\lambda_{\mathrm{AB}}k_{\mathrm{B}}T}} \exp\left(-\frac{\Delta G_{\mathrm{AB}}{}^{\neq}}{k_{\mathrm{B}}T}\right)$$

… $\frac{2\pi|H_{\mathrm{DA}}|^2}{\hbar\sqrt{4\pi\lambda k_{\mathrm{B}}T}}$ has units of s^{-1}

$$\mathrm{A} \rightleftharpoons \mathrm{X}^{\neq} \rightleftharpoons \mathrm{B}$$

Eyring–Polanyi–Evans (1930s)
theoretical rate constant equation (from **transition-state theory / activated complex theory**)

$$k_f = \kappa\nu K^{\neq} = \frac{\kappa k_{\mathrm{B}}T}{h}K^{\neq}$$

… with **transmission coefficient**, κ, and **vibrational frequency**, ν (s^{-1})

… and $R = N_A k_{\mathrm{B}}$… and $\frac{\kappa k_{\mathrm{B}}T}{h}$ has units of s^{-1}

$$k_f = \frac{\kappa k_{\mathrm{B}}T}{h}\exp\left(-\frac{\Delta G^{\neq}}{RT}\right) = \frac{\kappa k_{\mathrm{B}}T}{h}\exp\left(\frac{\Delta S^{\neq}}{R}\right)\exp\left(-\frac{\Delta H^{\neq}}{RT}\right)$$

… and so A contains $\Delta S^{\neq}$

… what is the largest predicted pre-exponential factor at 25 °C? **$(161\ \mathrm{fs})^{-1} = (1.61 \times 10^{-13}\ \mathrm{s})^{-1}$**

Outer + Inner Reorganization Energies

(REVIEW)

Marcus–Hush (1950s–1960s)
theoretical (semiclassical) rate constant equation

This theory came about by answering the following question: For an electron-transfer event, how does one satisfy the Franck–Condon principle and the conservation of energy?

- Franck–Condon principle: Nuclei are fixed during electron-transfer between orbitals… Born–Oppenheimer approximation is relevant

$$\lambda_i = \sum_l \lambda_{i,l} = \frac{1}{2}\sum_l f_l\,(\Delta q_{e,l})^2$$

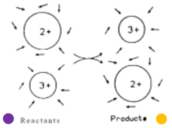
… this is for a harmonic oscillator
… with force constants, f_l…

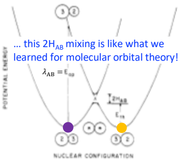
… and yes, it's another parabola!

P. Chen & T. J. Meyer, *Chem. Rev.*, **1998**, *98*, 1439–1477

Electron Transfer in Solution

$$\lambda_{AB} = \lambda_{in} + \lambda_{out}$$





… this $2H_{AB}$ mixing is like what we learned for molecular orbital theory!

N. Sutin, *Acc. Chem. Res.*, **1982**, *15*, 275–282

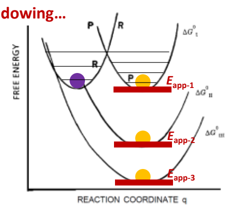
Observation of Inverted Region Behavior

Marcus–Hush (1950s–1960s)
theoretical (semiclassical) rate constant equation

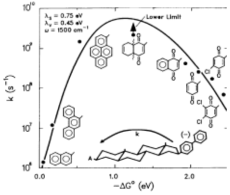
Closs–Miller (1984)
observation of inverted region

Foreshadowing…

The Inverted Region Effect



Experimental Confirmation of Inverted Region



L. T. Calcaterra, J. R. Miller & G. L. Closs, *J. Am. Chem. Soc.*, **1984**, *106*, 3047–3049
G. L. Closs & J. R. Miller, *Science*, **1988**, *240*, 440–447

Today's Critical Guiding Question

What thermodynamic term indicates whether a processes will net occur, or not, for a chemical reaction, and a single species… and uniquely for today, how does it allow us to quantitatively predict kinetic information… for real this time: Part 2?

Thermal (Dark) Reactions

- **Activation energy, Eyring–Polanyi–Evans equation**
- **Marcus–Hush (electron-transfer) theory**
- **Transition-state character, Reorganization energies (outer and inner), Linear free energy relationships**
- **Molecular orbital theory, Huang–Rhys factor**
- **Quantum mechanical tunneling, Superexchange**
- **Inner *versus* Outer sphere reactions, Robin–Day classification**
- Self-exchange reactions, Marcus cross relations
- Charge transfer across electrified interfaces, Butler–Volmer equation, Rate-determining step, Fermi's golden rule, Marcus–Gerischer theory

Linear Free Energy Relationships (LFERs)

Marcus–Hush (1950s–1960s)
theoretical (semiclassical) rate constant equation

Brønsted–Pedersen (1924)
empirical LFER for proton transfer

$$\ln k_{\mathrm{PT}} = -\boldsymbol{\beta}\ \mathrm{p}K_{\mathrm{a}} + C$$
$$\ln k_{\mathrm{PT}} = \boldsymbol{\beta}\ \Delta \mathrm{p}K_{\mathrm{a}} + C'$$

linear free-energy relation

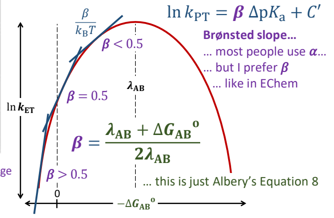
Also contains definition of: linear Gibbs energy relation

A linear correlation between the logarithm of a rate constant or equilibrium constant for one series of reactions and the logarithm of the rate constant or equilibrium constant for a related series of reactions. Typical examples of such relations (also known as linear Gibbs energy relations) are the Brønsted relation, and the Hammett equation.

The name arises because the logarithm of an equilibrium constant (at constant temperature and pressure) is proportional to a standard free energy (Gibbs energy) change, and the logarithm of a rate constant is a linear function of the free energy (Gibbs energy) of activation.

It has been suggested that this name should be replaced by linear Gibbs energy relation, but at present there is little sign of acceptance of this change. The area of physical organic

... trend looks linear over a small enough $\Delta G_{\mathrm{AB}}{}^{\mathrm{o}}$ range



$$\boldsymbol{\beta} = \frac{\lambda_{\mathrm{AB}} + \Delta G_{\mathrm{AB}}{}^{\mathrm{o}}}{2\lambda_{\mathrm{AB}}}$$

Brønsted slope...
... most people use $\boldsymbol{\alpha}$...
... but I prefer $\boldsymbol{\beta}$
... like in EChem

... this is just Albery's Equation 8

J. Albery, *Ann. Rev. Phys. Chem.*, **1980**, *31*, 227–263
R. A. Marcus, *Farad. Discuss. Chem. Soc.*, **1982**, *74*, 7–15

Marcus Kinetic Behavior

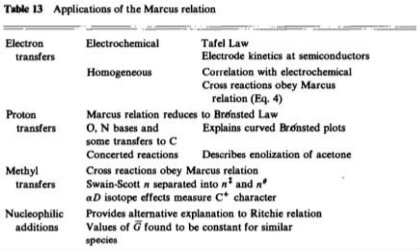


Table 13 Applications of the Marcus relation

Electron transfers	Electrochemical	Tafel Law Electrode kinetics at semiconductors
	Homogeneous	Correlation with electrochemical Cross reactions obey Marcus relation (Eq. 4)
Proton transfers	Marcus relation reduces to Brønsted Law	
	O, N bases and some transfers to C	Explains curved Brønsted plots
	Concerted reactions	Describes enolization of acetone
Methyl transfers	Cross reactions obey Marcus relation Swain-Scott n separated into $n^{\ddagger}$ and $n^{\#}$ αD isotope effects measure C^{+} character	
Nucleophilic additions	Provides alternative explanation to Ritchie relation Values of $\overline{G}$ found to be constant for similar species	

J. Albery, *Ann. Rev. Phys. Chem.*, **1980**, *31*, 227–263
R. A. Marcus, *Farad. Discuss. Chem. Soc.*, **1982**, *74*, 7–15

(REVIEW)

Schrödinger Equation

Poisson's Equation (from Gauss's law)

$$\frac{\partial^2 \phi(x)}{\partial x^2} = -\frac{\rho}{\varepsilon} \qquad \mathbf{E} = -\frac{\partial \phi(x)}{\partial x}$$

But you still didn't tell us why we need to recall this equation

$$\hat{H}\psi_n(x) = (\hat{T} + \hat{V})\psi_n(x) = \mathrm{E}_n \psi(x)$$

… we need to fill **internal energies**, E_n, with particles… okay.

for a point charge… look familiar?

$$\phi(r) = \frac{q}{4\pi\varepsilon r}$$

… and that under most chemical conditions, potential energy, $\hat{V}(x)$, is **electrostatic**, $\phi(x)$
… which is actually not so limiting because there are only 4-ish forces of Nature
… and while we're at it, let's (re)learn **overlap integral** (S_{nm}), **expectation value** ($\langle p_n \rangle$), **bra–ket notation** ($\langle \psi_n | \psi_m \rangle$), and exponential **tunneling** probability…

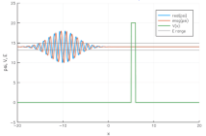
Probability Density$(x) = |\psi_n(x)|^2 = \psi_n^*(x)\psi_n(x)$

… with $\psi_n^*(x)$ (complex conjugate)

Overlap integral, $S_{nm} = \int_{-\infty}^{\infty} \psi_n^*(x)\psi_m(x)\,dx = \langle \psi_n | \psi_m \rangle$

… with $\langle \Psi_n |$ ("bra") and $| \Psi_m \rangle$ ("ket")

Mean Energy, $\langle \mathrm{E}_n \rangle = \frac{\int_{-\infty}^{\infty} \Psi_n^*(x,t)\hat{H}\Psi_n(x,t)dx}{\int_{-\infty}^{\infty} \Psi_n^*(x,t)\Psi_n(x,t)dx} = \langle \Psi_n | \hat{H} | \Psi_n \rangle = \langle \hat{H} \rangle$



https://en.wikipedia.org/wiki/Quantum_tunnelling#/media/File:E14-V20-B1.gif

Molecular Orbital Theory

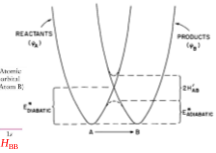
Marcus–Hush (1950s–1960s)
theoretical (semiclassical) rate constant equation

$$k_{\mathrm{ET}} = \underbrace{\frac{2\pi}{\hbar}|H_{\mathrm{DA}}|^2}_{\text{quantum adiabatic electronic coupling}} \underbrace{\frac{1}{\sqrt{4\pi\lambda_{\mathrm{AB}}kT}}\exp\left(-\frac{\Delta G_{\mathrm{AB}}{}^{\neq}}{kT}\right)}_{\text{classical nuclear free-energy dependence}}$$

Molecular Orbital Theory
linear combination of atomic orbitals

(50) The splitting at the intersection is only equal to $2H_{AB}$ when the overlap of the electronic wave functions can be neglected. More generally it is equal to $2(H_{AB} - S_{AB}H_{AA})/(1 - S_{AB}{}^2)$ where $S_{AB} = \langle \psi_A | \psi_B \rangle$.

… which equals $(E_+ - E_-)$ from MO Theory

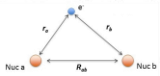


… remember the simplicity of $H_2{}^+$… which resembles λ_{out} math

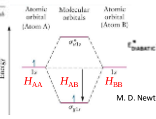
$$\hat{H}(r, R_{ab}) = -\frac{\hbar^2}{2m}\nabla_a^2 - \frac{\hbar^2}{2m}\nabla_b^2 - \frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_a} - \frac{e^2}{4\pi\epsilon_0 r_b} + \frac{e^2}{4\pi\epsilon_0 R_{ab}}$$

matrix

$$\hat{H} = \begin{pmatrix} H_{AA} & H_{AB} \\ H_{BA} & H_{BB} \end{pmatrix}$$



$$E_{\pm}(R) = \frac{1}{1 \pm S(R)}(H_{AA}(R) \pm H_{AB}(R))$$



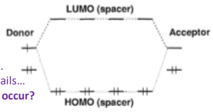
M. D. Newton, *Int. J. Quantum. Chem.*, **1980**, *18*, 363–391
N. Sutin, *Acc. Chem. Res.*, **1982**, *15*, 275–282

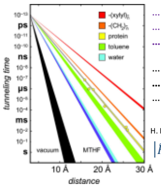
Quantum Mechanical Tunneling / Superexchange

Marcus–Hush (1950s–1960s)
theoretical (semiclassical) rate constant equation

$$k_{\mathrm{ET}} = \frac{2\pi}{\hbar}|H_{\mathrm{DA}}|^2 \frac{1}{\sqrt{4\pi\lambda_{\mathrm{AB}}kT}}\exp\left(-\frac{\Delta G_{\mathrm{AB}}{}^{\neq}}{kT}\right)$$

Superexchange *(not hopping!)*
long-distance through-bond transport





… although through-space tunneling is legit…
… it requires overlap of small wavefunction tails…
… how does long-distance electron transfer occur?

… incoherent multi-step hopping…
… or coherent superexchange…
… where $\beta_{\mathrm{eff,hop}} \ll \beta_{\mathrm{super}} < \beta_{\mathrm{tunnel}}$

$$|\hat{H}_{\mathrm{DA}}| = |\hat{H}^{\mathrm{o}}_{\mathrm{DA}}| \exp\left(-\frac{\beta_{\mathrm{super}}(N-1)}{2}\right)$$

… where N is the number of bonds

H. B. Gray & J. R. Winkler, *PNAS*, **2005**, *102*, 3534–3539

$$|\hat{H}_{\mathrm{DA}}| = |\langle \Psi_{\mathrm{D}} | \hat{H}_{\mathrm{DA}} | \Psi_{\mathrm{A}} \rangle| = |\hat{H}^{\mathrm{o}}_{\mathrm{DA}}| \exp\left(-\frac{\beta_{\mathrm{tunnel}}(z_{\mathrm{DA}} - z_{\mathrm{DA}}{}^{\mathrm{o}})}{2}\right)$$

… where β_{tunnel} has units of Å^{-1}

G. L. Closs & J. R. Miller, *Science*, **1988**, *240*, 440–447

Inner *versus* Outer Sphere Reactions

Marcus–Hush (1950s–1960s)
theoretical (semiclassical) rate constant equation

$$k_{\mathrm{ET}} = \frac{2\pi}{\hbar}|H_{\mathrm{DA}}|^2 \frac{1}{\sqrt{4\pi\lambda_{\mathrm{AB}}kT}} \exp\left(-\frac{\Delta G_{\mathrm{AB}}^{\neq}}{kT}\right)$$

Creutz–Taube ion (1969)

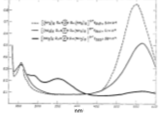
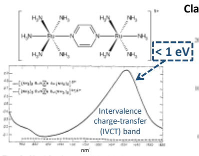


Figure 1. Visible–ultraviolet spectra of [2,2], [2,3], and [3,3] in 0.05 N HClO$_4$. (Absorbance around 560 mμ for [3,3] is probably due to residual [2,3] in the solution; photoreduction of [3,3] takes place readily.) $\epsilon_{2,2}$ and $\epsilon_{2,3}$ are measured in the range 2–3 × 10^{-4} M, path length 1 cm. $\epsilon_{3,3}$ is measured at 8 × 10^{-4} M, 1-cm path length.



Intervalence charge-transfer (IVCT) band

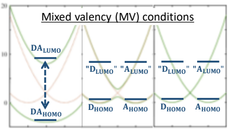
Figure 2. Near-infrared spectrum of [2,3] in D$_2$O: concentration of [2,3] = 1.5 × 10^{-4} M; 1-cm path length. (Dashed line is actually the blank, but accurately indicates the spectra of [2,2] and [2,3] in this range above 750 mμ at this concentration level.)

Taube (1950s–1970s)
inner sphere electron transfer

Robin–Day MV classification… **label each below!**

Class I: nonadiabatic ($H_{\mathrm{DA}} \approx 0$)
Class II: adiabatic, localized ($0 < 2H_{\mathrm{DA}} < \lambda_{\mathrm{AB}}$)
Class III: adiabatic, delocalized ($2H_{\mathrm{DA}} > \lambda_{\mathrm{AB}}$)

… so what is $2H_{\mathrm{DA}}$ for Class III [C–T]$^{5+}$?


Mixed valency (MV) conditions

C. Creutz & H. Taube, *J. Am. Chem. Soc.*, **1969**, *91*, 3988–3989
B. S. Brunschwig, C. Creutz & N. Sutin, *Chem. Soc. Rev.*, **2002**, *31*, 168–184

Huang–Rhys Factor

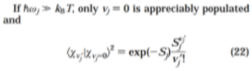
Marcus–Hush (1950s–1960s)
theoretical (semiclassical) rate constant equation

$$k_{\mathrm{ET}} = \frac{2\pi}{\hbar}|H_{\mathrm{DA}}|^2 \frac{1}{\sqrt{4\pi\lambda_{\mathrm{AB}}kT}} \exp\left(-\frac{\Delta G_{\mathrm{AB}}^{\neq}}{kT}\right)$$

$$= \nu_{\mathrm{n}}(r)\kappa_{\mathrm{el}}(r)\kappa_{\mathrm{n}}(r)$$

$$= \frac{2\pi}{\hbar}\langle\psi'_{\mathrm{el}}|\hat{H}'|\psi_{\mathrm{el}}\rangle^2\langle\psi'_{\mathrm{vib}}|\psi_{\mathrm{vib}}\rangle^2\delta(E' - E)$$

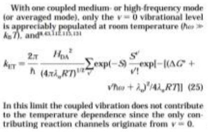
… separable due to the Born–Oppenheimer approximation


If $\hbar\omega_j \gg k_{\mathrm{B}}T$, only $v_j = 0$ is appreciably populated and

$$\langle\chi_{v_j'}|\chi_{v_j=0}\rangle^2 = \exp(-S_j)\frac{S_j^{v_j'}}{v_j'!} \qquad (22)$$

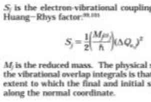
P. Chen & T. J. Meyer, *Chem. Rev.*, **1998**, *98*, 1439–1477

Fermi's Golden Rule
time-dependent perturbation theory


With one coupled medium- or high-frequency mode (or averaged mode), only the $v = 0$ vibrational level is appreciably populated at room temperature ($\hbar\omega \gg k_{\mathrm{B}}T$), and[8,43,112,115,131]

$$k_{\mathrm{ET}} = \frac{2\pi}{\hbar}\frac{{H_{\mathrm{DA}}}^2}{(4\pi\lambda_o RT)^{1/2}}\sum_{v'}\exp(-S)\frac{S^{v'}}{v'!}\exp[-[(\Delta G^\circ + v'\hbar\omega + \lambda_o)^2/4\lambda_o RT]] \quad (25)$$

In this limit the coupled vibration does not contribute to the temperature dependence since the only contributing reaction channels originate from $v = 0$.


S_j is the electron-vibrational coupling constant, or Huang–Rhys factor:[99,101]

$$S_j = \frac{1}{2}\left(\frac{M_j\omega_j}{\hbar}\right)(\Delta Q_e)^2 \qquad (19)$$

M_j is the reduced mass. The physical significance of the vibrational overlap integrals is that they give the extent to which the final and initial states coincide along the normal coordinate.

… we'll stop here, but it can get even messier, of course…

N. Sutin, *Acc. Chem. Res.*, **1982**, *15*, 275–282

Today's Critical Guiding Question

What thermodynamic term indicates whether a processes will net occur, or not, for a chemical reaction, and a single species… and uniquely for today, how does it allow us to quantitatively predict kinetic information… <u>for real this time: Part 2</u>?