



## Lecture #11 of 14

(3: TThF, 5: MTWThF, 4: MTWTh, 2: TW)

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## Chemical Kinetics

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**Quiz Time!**

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## Chemical Kinetics

- Continuity of mass, Mass transfer, Nernst–Planck equation, Diffusion, Diffusion coefficient, Migration, Mobility, Convection, Boundary layer
- **Mass action, Microscopic reversibility, Förster cube, Square schemes, Rate constants, Activation energies, Transition-state theory, Marcus–Hush theory, Transition-state character, Reorganization energies (outer and inner)**
- **Linear free energy relationships**, Charge transfer across electrified interfaces, Butler–Volmer equation, Fermi’s golden rule, Solid-state physics, Marcus–Gerischer theory
- Rate-determining step, Steady-state & Pre-equilibrium approximations, Langmuir/Frumkin isotherms

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Continuity of Mass

(REVIEW) 296

$\bar{\mu}_i^\alpha = \bar{\mu}_i^\alpha + RT \ln a_i^\alpha + z_i q \phi^\alpha$

$\frac{\partial C_{A,z_0}}{\partial t} = \sum_j R_{A,j} - \frac{\partial N_A}{\partial z}$

$H \psi_n(z,t) = i \hbar \frac{\partial}{\partial t} \psi_n(z,t)$

$z < z_0$        $z = z_0$        $z > z_0$

*Note: Adjusting just one variable is difficult... but people, like us, can try*

"Jean Piaget, the Swiss psychologist who first studied object permanence in infants, argued that it is one of an infant's most important accomplishments, as, without this concept, objects would have no separate, permanent existence."  
- Wiki, Object permanence

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Thermodynamics versus Kinetics

(REVIEW) 297

Thermodynamics are only as important as their influence on kinetics...

... energetics from thermodynamics dictate **equilibrium concentrations**...

... but it is the **kinetic (and transport) properties** that influence how those conditions change upon perturbation...

rate of change of the (c)oncentration of species A with respect to (t)ime, in units of  $M s^{-1}$  (mol dm<sup>-3</sup> s<sup>-1</sup>)

$\frac{\partial C_{A,z_0}}{\partial t} = \sum_j R_{A,j} - \frac{\partial N_A}{\partial z}$

rate of change of the molar flux (N) of species A with respect to position (z), e.g.  $N_A = -D \frac{\partial a_A}{\partial z}$  (to a first order, this is driven by differences in electrochemical potential of a single species,  $\mu_i$ )

mass action (R)ate laws that effect species A, e.g.  $R_+ = k_1 a_A a_B^2 = k_1 [B][D]^2$  (to a first order, this is driven by differences in chemical potential of various species,  $\mu_j$ )

... this master equation describes all kinetic and transport processes for mass... more on this later...

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1D Transport in Liquids (solids are simpler)

(REVIEW) 298

$\frac{\partial C_{A,z_0}}{\partial t} = - \frac{\partial N_A}{\partial z}$  (MechEs should be yawning)

$A_1 \rightleftharpoons A_2$

$N_A = - \left( \frac{D_A c_A}{RT} \right) \frac{\partial \bar{\mu}_A}{\partial z} + v c_A$

... there are many driving forces for flux of species...  
... convection (vc) is just one (e.g., dT/dx)

Group terms... then mass transfer resembles mass action (assume v = 0 for simplicity)...

$N_A = -D_A \frac{\partial \left( \frac{\bar{\mu}_A}{RT} \right)}{\partial z} c_A$

What are the directions for the dimensions of  $D_A$ ?  
**BOLD** ((cm<sup>2</sup>/s) / cm) = cm/s... a velocity!  
... and with  $\frac{\partial}{\partial z}$ , units are s<sup>-1</sup>... an inverse time constant!  
... and that equals zero at steady state

(Note that...  $R_{A,total} = -k_f c_A + k_b c_B$ ... with  $k_j$  (s<sup>-1</sup>), an inverse time constant!)

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### 1D Transport in Solids (liquids are "harder")

Let's expand the total differential...

... assuming a species, e, with valency, z<sub>e</sub>, equal to -1

... other species may have different values for every term, except φ

Drift-Diffusion equation

$$\text{Flux}_{z,e} = -\frac{\sigma_e d\mu_e}{F^2 dz} - S_e T_e \frac{dT_e}{dz} \quad \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} = \mu_i = \mu_i^0 + z_i q \phi$$

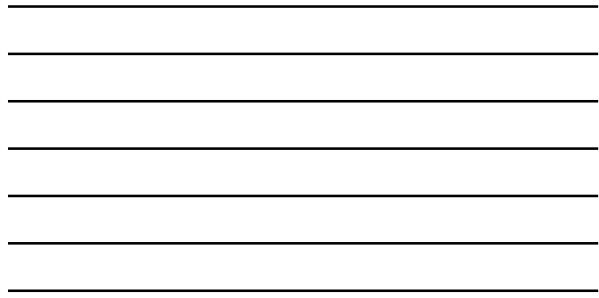
$$\text{Flux}_{z,e} = -\frac{D_e n_e}{kT_e} \left(\frac{d\mu_e}{dz} + q \frac{d\phi}{dz}\right) - S_e T_e \frac{dT_e}{dz} \quad \mu_i = \mu_i^0 + kT_i \ln a_i = \mu_i^0 + kT_i \ln \left(\frac{\gamma_i n_i}{n_i^0}\right)$$

$$\text{Flux}_{z,e} = -\frac{D_e n_e}{kT_e} \left(\frac{d\mu_e^0}{dz} + \frac{kT_e}{\gamma_e} \frac{d\gamma_e}{dz} + \frac{kT_e}{n_e} \frac{dn_e}{dz} - \frac{kT_e}{n_e^0} \frac{dn_e^0}{dz} + k \left(\ln \frac{\gamma_e n_e}{n_e^0}\right) \frac{dT_e}{dz} + q \frac{d\phi}{dz}\right) - S_e T_e \frac{dT_e}{dz}$$

$$\text{Flux}_{z,e} = -D_e \left(\frac{n_e}{kT_e} \frac{d\mu_e^0}{dz} + \frac{n_e}{\gamma_e} \frac{d\gamma_e}{dz} + \frac{dn_e}{dz} - \frac{n_e}{n_e^0} \frac{dn_e^0}{dz} + \frac{n_e}{T_e} \left(\ln \frac{\gamma_e n_e}{n_e^0}\right) \frac{dT_e}{dz} + \frac{q n_e}{kT_e} \frac{d\phi}{dz}\right) - S_e T_e \frac{dT_e}{dz}$$

$$\text{Flux}_{z,e} = -D_e \frac{dn_e}{dz} + \frac{q D_e n_e}{kT_e} \frac{d\phi}{dz} \quad \dots \text{assuming spatially invariant } \mu_e^0, \gamma_e, n_e^0, T_e$$

$$\text{Flux}_{z,e} = -D_e n_e \left(\frac{d\mu_e^0}{kT_e dz} + \frac{d(\ln \gamma_e)}{dz} + \frac{d(\ln n_e)}{dz} - \frac{d(\ln n_e^0)}{dz} - \frac{d(q\phi)}{kT_e dz}\right) - D_{n_e, \sigma_e, n_e^0, T_e} \frac{dT_e}{dz}$$



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### Mass Action / Microscopic Reversibility

$$\frac{\partial C_{A,z_0}}{\partial t} = \sum_j R_{A,j}$$

(Chemists should be yawning)

$$A \rightleftharpoons B$$

$$\Delta G^\alpha = \Delta G^{0,\alpha} + RT \ln Q \dots \text{ where } Q = \frac{a_B^\alpha}{a_A^\alpha} = \frac{\gamma_B^\alpha (c_B^\alpha/c_B^{0,\alpha})}{\gamma_A^\alpha (c_A^\alpha/c_A^{0,\alpha})}$$

$$R_{A,f} = -k_f a_A \quad R_{B,f} = +k_f a_A$$

$$R_{A,b} = +k_b a_B \quad R_{B,b} = -k_b a_B$$

- Law of mass action
- Principle of microscopic reversibility

... and in solid-state physics...  $R_{e^- \text{ total}} = \sum_j \text{Gen}_{e^-,j} - \sum_j \text{Rec}_{e^-,j}$   $k_j$  (M/s)... a rate!  $K_j$  (s<sup>-1</sup>)... an inverse time constant!

Now, consider the reaction to be at equilibrium...  $\Delta G^\alpha = 0 = \Delta G^{0,\alpha} + RT \ln Q' = \bar{\mu}_B^\alpha - \bar{\mu}_A^\alpha$

So,  $\Delta G^{0,\alpha} = -RT \ln K'$ , with  $K' = \frac{c_B^{0,\alpha}/c_B^{0,\alpha}}{c_A^{0,\alpha}/c_A^{0,\alpha}}$ ... and, of course,  $K' = \exp\left(-\frac{\Delta G^{0,\alpha}}{RT}\right)$

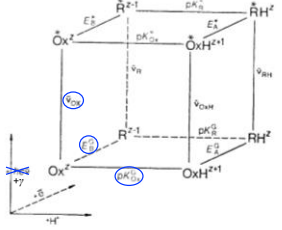
But also,  $\frac{\partial c_A}{\partial t} = 0 = -k_f a_{A,eq}^\alpha + k_b a_{B,eq}^\alpha \dots \frac{k_f}{k_b} = \frac{a_{B,eq}^\alpha}{a_{A,eq}^\alpha} = K = K' \frac{\gamma_B^\alpha}{\gamma_A^\alpha}$  ... it can get messy

Or equivalently,  $\frac{\partial c_A}{\partial t} = 0 = -k_f' c_{A,eq}^\alpha + k_b' c_{B,eq}^\alpha \dots \frac{k_f'}{k_b'} = \frac{c_{B,eq}^\alpha}{c_{A,eq}^\alpha} = K' = \frac{c_B^{0,\alpha}}{c_A^{0,\alpha}} = K \frac{\gamma_B^\alpha c_B^{0,\alpha}}{\gamma_A^\alpha c_A^{0,\alpha}}$



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### Förster Cube and Square Schemes



Questions to ponder... In this figure, what do the thermodynamic parameters E, pK, and v represent?

$E = E^0$  (standard-state reduction potential)  
 $pK = pK_a = -\log K_a$  (acid dissociation constant)  
 $v = \frac{1}{\lambda}$  (wavenumber)

How are they related?  
**Redox:**  $E^0 = -\Delta G^0/nF$   
**Acidity:**  $pK_a = -\log K_a = \Delta G^0/(2.303RT)$   
**Light:**  $hc\tilde{\nu} = \frac{hc}{\lambda} = h\nu = E_{\text{photon}}$

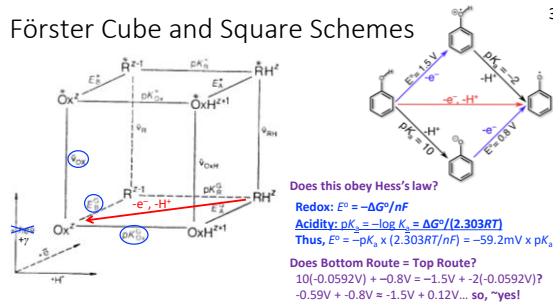
What is the reference state for each?  
 $E^0(\text{H}^+(\text{aq})/\text{H}_2) = 0; pK_a(\text{H}^+(\text{aq})) = 0; 0$

... before we add light... let's backtrack a bit...  
 ... first we must understand dark thermal processes... Z. R. Grabowski & W. Rubaszewska, J. Chem. Soc. Faraday Trans. 1, 1977, 73, 11-28



### Förster Cube and Square Schemes

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... anyway... but is the concerted path possible? R. Tyburski, T. Liu, S. D. Glover & L. Hammarström, *J. Am. Chem. Soc.*, 2021, 143, 560-576

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### Förster Cube and Square Schemes

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... oh, I see... by moving oppositely charged species in a concerted fashion, electrostatic (Born solvation) energy will be much smaller

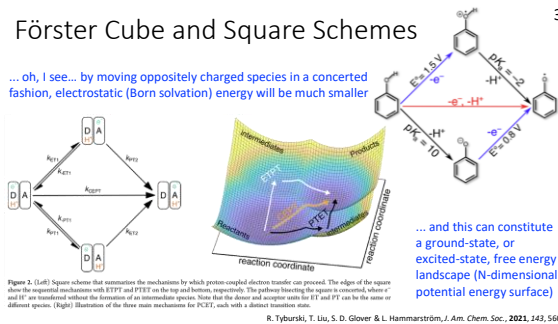


Figure 2. (Left) Square scheme that summarizes the mechanisms by which proton-coupled electron transfer can proceed. The edges of the square show the sequential mechanisms with EPT and PET on the top and bottom, respectively. The paths between the square is concerted, where e<sup>-</sup> and H<sup>+</sup> are transferred without the formation of an intermediate species. Note that the donor and acceptor sites for ET and PT can be the same or different species. (Right) Illustration of the three main mechanisms for PCET, each with a distinct transition state.

R. Tyburski, T. Liu, S. D. Glover & L. Hammarström, *J. Am. Chem. Soc.*, 2021, 143, 560-576

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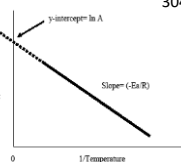
### Activation Energies

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Arrhenius (1889)

empirical rate constant equation

$$k_f = A e^{-\frac{E_a}{RT}} \dots \text{pre-exponential factor, } A, \text{ has units of } s^{-1} \ln k$$

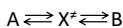


Eyring-Polanyi-Evans (1930s)

theoretical rate constant equation (from transition-state theory / activated complex theory)

$$k_f = \kappa \nu K^\ddagger = \frac{\kappa k_B T}{h} K^\ddagger \dots \text{with transmission coefficient, } \kappa, \text{ and vibrational frequency, } \nu \text{ (s}^{-1}\text{)}$$

... and  $R = N_A k_B$  ... and  $\frac{\kappa k_B T}{h}$  has units of  $s^{-1}$



$$k_f = \frac{\kappa k_B T}{h} \exp\left(-\frac{\Delta G^\ddagger}{RT}\right) = \frac{\kappa k_B T}{h} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \exp\left(-\frac{\Delta H^\ddagger}{RT}\right) \dots \text{and so } A \text{ contains } \Delta S^\ddagger$$

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

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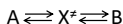
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### Marcus–Hush Theory 305

**Marcus–Hush (1950s–1960s)**  $D + A \rightleftharpoons D^+ + A^-$  ... but how is this a first-order reaction (s<sup>-1</sup>)?

theoretical (semiclassical) rate constant equation

$$k_{ET} = \frac{2\pi}{\hbar} |H_{DA}|^2 \frac{1}{\sqrt{4\pi\lambda_{AB}kT}} \exp\left(-\frac{\Delta G_{AB}^\ddagger}{kT}\right) \dots \frac{2\pi |H_{DA}|^2}{\hbar^2 \sqrt{4\pi\lambda_{AB}kT}} \text{ has units of } s^{-1}$$



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

$$k_f = \kappa k_B T \exp\left(-\frac{\Delta G^\ddagger}{RT}\right) \dots \text{ with transmission coefficient, } \kappa, \text{ and vibrational frequency, } \nu, \text{ (s}^{-1}\text{)}$$

... and  $R = N_A k_B$  ... and  $\frac{\kappa k_B T}{h}$  has units of s<sup>-1</sup>

$$k_f = \frac{\kappa k_B T}{h} \exp\left(-\frac{\Delta G^\ddagger}{RT}\right) = \frac{\kappa k_B T}{h} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \exp\left(-\frac{\Delta H^\ddagger}{RT}\right) \dots \text{ and so } A \text{ contains } \Delta S^\ddagger$$

... what is the largest predicted pre-exponential factor at 25 °C? (161 fs)<sup>-1</sup> = (1.61 x 10<sup>-13</sup> s)<sup>-1</sup>



### Marcus–Hush Theory 306

**Marcus–Hush (1950s–1960s)**  $D + A \rightleftharpoons D^+ + A^-$

theoretical (semiclassical) rate constant equation

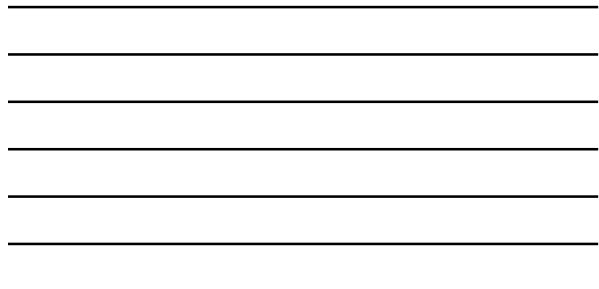
$$k_{ET} = \frac{2\pi}{\hbar} |H_{DA}|^2 \frac{1}{\sqrt{4\pi\lambda_{AB}kT}} \exp\left(-\frac{\Delta G_{AB}^\ddagger}{kT}\right) \quad \frac{\partial c_{A,z_0}}{\partial t} = \sum_j R_{A,j} \left[ -\frac{\partial N_A}{\partial z} \right]$$

quantum adiabatic electronic coupling
classical nuclear free-energy dependence
proportional to  $\frac{d\mu_A}{dz}$

... which term shall we discuss first?  
 ... I don't know about you, but when given a choice between classical and quantum mechanical  
 ... I go with classical... OK?

$$\Delta G_{AB}^\ddagger = \frac{(\lambda_{AB} + \Delta G_{AB}^0)^2}{4\lambda_{AB}}$$

... wait... there is a direct relation between thermodynamics ( $\Delta G_{AB}^0$ ) and kinetics ( $\Delta G_{AB}^\ddagger$ )?  
 ... this makes sense since  $\frac{d\mu_A}{dz}$  drives transport... which can be written as a chemical reaction  
 ... but that key relationship is quadratic... meaning a parabola? Huh?!?!?!?



### Marcus–Hush Theory 307

**Marcus–Hush (1950s–1960s)**  $D + A \rightleftharpoons D^+ + A^-$

theoretical (semiclassical) rate constant equation

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

quantum adiabatic electronic coupling
classical nuclear free-energy dependence

$$k_{ET} = \frac{2\pi}{\hbar} |H_{DA}|^2 \frac{1}{\sqrt{4\pi\lambda_{AB}kT}} \exp\left(-\frac{(\lambda_{AB} + \Delta G_{AB}^0)^2}{4\lambda_{AB}kT}\right) \dots \text{ what kind of function is this?}$$

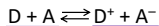
$\Delta G_{AB}^\ddagger = \frac{(\lambda_{AB} + \Delta G_{AB}^0)^2}{4\lambda_{AB}}$

$$k_{ET} = \frac{2\pi}{\hbar} |H_{DA}|^2 \frac{1}{\sqrt{2\pi} \sqrt{2\lambda_{AB}kT}} \exp\left(-\frac{1}{2} \left(\frac{\Delta G_{AB}^0 - (-\lambda_{AB})}{\sqrt{2\lambda_{AB}kT}}\right)^2\right) \dots \text{ does this help at all?}$$



## Marcus–Hush Theory

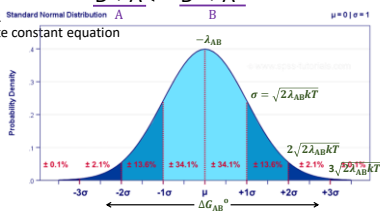
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Marcus–Hush (1950s–1960s)

theoretical (semiclassical) rate constant equation

... wait... the classical component in Marcus electron-transfer theory is a normal distribution as a function of standard-state thermodynamic driving force ( $\Delta G_{AB}^0$ )?... Yep!



$$k_{ET} = \frac{2\pi}{\hbar} |H_{DA}|^2 \frac{1}{\sqrt{2\pi} \sqrt{2\lambda_{AB} kT}} \exp\left(-\frac{1}{2} \left(\frac{\Delta G_{AB}^0 - (-\lambda_{AB})}{\sqrt{2\lambda_{AB} kT}}\right)^2\right) \dots \text{does this help at all?}$$

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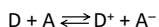
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## Marcus–Hush Theory

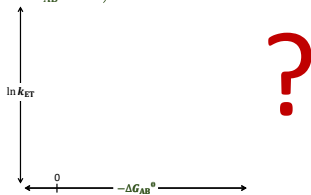
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Marcus–Hush (1950s–1960s)

theoretical (semiclassical) rate constant equation

$$k_{ET} = \frac{2\pi}{\hbar} |H_{DA}|^2 \frac{1}{\sqrt{4\pi\lambda_{AB} kT}} \exp\left(-\frac{(\lambda_{AB} + \Delta G_{AB}^0)^2}{4\lambda_{AB} kT}\right)$$




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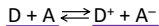
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## Marcus–Hush Theory

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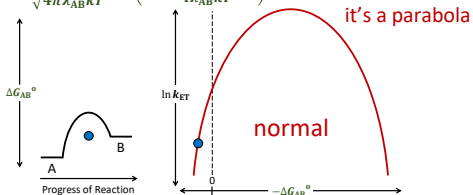
Marcus–Hush (1950s–1960s)

theoretical (semiclassical) rate constant equation

$$k_{ET} = \frac{2\pi}{\hbar} |H_{DA}|^2 \frac{1}{\sqrt{4\pi\lambda_{AB} kT}} \exp\left(-\frac{(\lambda_{AB} + \Delta G_{AB}^0)^2}{4\lambda_{AB} kT}\right)$$

How can a thermodynamically unfavorable reaction proceed?

Mass Action!




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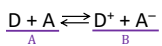
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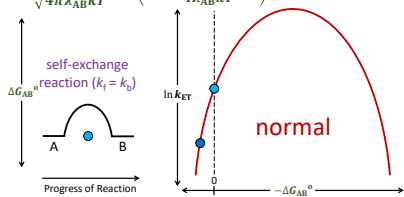
## Marcus–Hush Theory



Marcus–Hush (1950s–1960s)

theoretical (semiclassical) rate constant equation

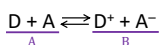
$$k_{ET} = \frac{2\pi}{\hbar} |H_{DA}|^2 \frac{1}{\sqrt{4\pi\lambda_{AB}kT}} \exp\left(-\frac{(\lambda_{AB} + \Delta G_{AB}^0)^2}{4\lambda_{AB}kT}\right)$$



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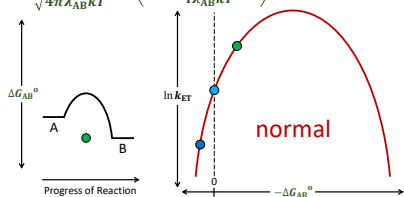
## Marcus–Hush Theory



Marcus–Hush (1950s–1960s)

theoretical (semiclassical) rate constant equation

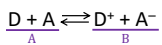
$$k_{ET} = \frac{2\pi}{\hbar} |H_{DA}|^2 \frac{1}{\sqrt{4\pi\lambda_{AB}kT}} \exp\left(-\frac{(\lambda_{AB} + \Delta G_{AB}^0)^2}{4\lambda_{AB}kT}\right)$$



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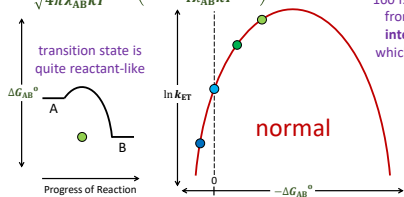
## Marcus–Hush Theory



Marcus–Hush (1950s–1960s)

theoretical (semiclassical) rate constant equation

$$k_{ET} = \frac{2\pi}{\hbar} |H_{DA}|^2 \frac{1}{\sqrt{4\pi\lambda_{AB}kT}} \exp\left(-\frac{(\lambda_{AB} + \Delta G_{AB}^0)^2}{4\lambda_{AB}kT}\right)$$

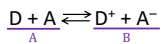


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Note that a transition state only lasts on the order of a bond vibration ( $\hbar/k_B T \approx 160$  fs) and differs from a proper intermediate, which lasts much longer



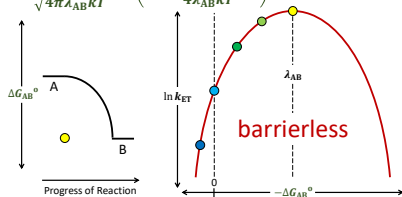
## Marcus–Hush Theory



Marcus–Hush (1950s–1960s)

theoretical (semiclassical) rate constant equation

$$k_{ET} = \frac{2\pi}{\hbar} |H_{DA}|^2 \frac{1}{\sqrt{4\pi\lambda_{AB}kT}} \exp\left(-\frac{(\lambda_{AB} + \Delta G_{AB}^0)^2}{4\lambda_{AB}kT}\right)$$



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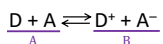
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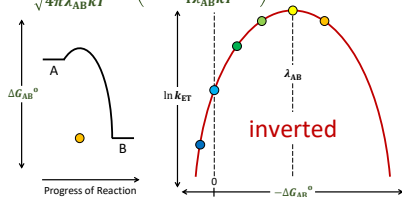
## Marcus–Hush Theory



Marcus–Hush (1950s–1960s)

theoretical (semiclassical) rate constant equation

$$k_{ET} = \frac{2\pi}{\hbar} |H_{DA}|^2 \frac{1}{\sqrt{4\pi\lambda_{AB}kT}} \exp\left(-\frac{(\lambda_{AB} + \Delta G_{AB}^0)^2}{4\lambda_{AB}kT}\right)$$



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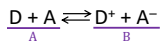
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## Marcus–Hush Theory



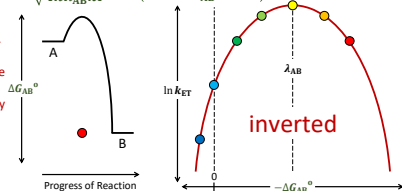
Marcus–Hush (1950s–1960s)

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... this looks odd...

... but what did we expect from a General Chemistry cartoon



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## Outer Reorganization Energy

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Marcus-Hush (1950s-1960s)

theoretical (semiclassical) rate constant equation

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

$$\Delta G_{AB}^{\ddagger} = \frac{(\lambda_{AB} + \Delta G_{AB}^0)^2}{4\lambda_{AB}}$$

... but what causes this parabolic relationship?...

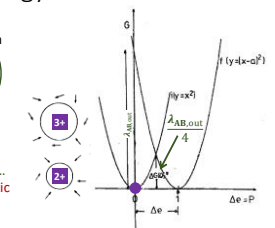
... what physical expression results in a quadratic dependence on charge?

... classical electrostatics... of the solvent!

... dielectric continuum model...

...  $G_{out} = 1 \text{ eV}$  in water

...  $G_{out}$  decreases as permittivity decreases



$$\lambda_{out} = \left(\frac{1}{2r_D} + \frac{1}{2r_A} - \frac{1}{R_{DA}}\right) \left(\frac{1}{\epsilon_{\infty}} - \frac{1}{\epsilon_s}\right) (\Delta e)^2$$



## Outer + Inner Reorganization Energy

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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

$$\lambda_i = \sum_j \lambda_{i,j} = \frac{1}{2} \sum_j f_j (\Delta q_{i,j})^2$$

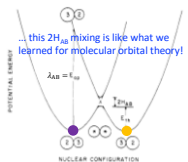
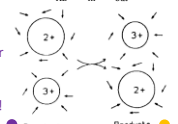
... this is for a harmonic oscillator

... with force constants,  $f_j$ ...

... and yes, it's another parabola!

Electron Transfer in Solution

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



... this 2H<sub>g</sub> mixing is like what we learned for molecular orbital theory!

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

N. Sutin, Acc. Chem. Res., 1982, 15, 275-282



## More Quantum Mechanics

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

$$\hat{H}\psi_n(x) = (\hat{T} + \hat{V})\psi_n(x) = E_n\psi_n(x)$$

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

Poisson's Equation (from Gauss's law)

$$\frac{\partial^2 \phi(x)}{\partial x^2} = -\frac{\rho}{\epsilon} \quad E = -\frac{\partial \phi(x)}{\partial x}$$

for a point charge...  $\phi(r) = \frac{q}{4\pi\epsilon r}$

look familiar?

... 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  $\rho(x) = |\psi_n(x)|^2 = \psi_n^*(x)\psi_n(x)$

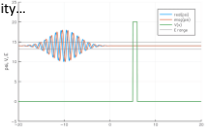
... with  $\psi_n^*(x)$  (complex conjugate)

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,  $\langle E_n \rangle = \int_{-\infty}^{\infty} \psi_n^*(x)\hat{H}\psi_n(x) dx = \langle \psi_n | \hat{H} | \psi_n \rangle = \langle \hat{H} \rangle$

[https://en.wikipedia.org/wiki/Quantum\\_tunneling#/media/File:E14-V20-81.gif](https://en.wikipedia.org/wiki/Quantum_tunneling#/media/File:E14-V20-81.gif)



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### Molecular Orbital Theory

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

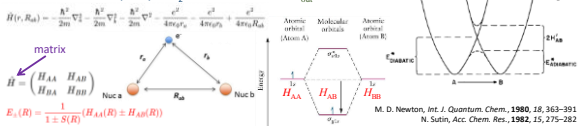
$$k_{ET} = \frac{2\pi}{\hbar} |H_{DA}|^2 \frac{1}{\sqrt{4\pi\lambda_{AB}kT}} \exp\left(-\frac{\Delta G_{AB}^{\ddagger}}{kT}\right)$$

quantum adiabatic  
electronic coupling
classical nuclear free-  
energy dependence

Molecular Orbital Theory  
linear combination of atomic orbitals

(30) 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  $2H_{AB}\sqrt{1+|S_{AB}|^2}$  where  $S_{AB} = \langle \psi_A | \psi_B \rangle$  ... which equals  $(E_+ - E_-)$  from MO Theory

... remember the simplicity of  $H_2^+$  ... which resembles  $\lambda_{\text{good}}$  math



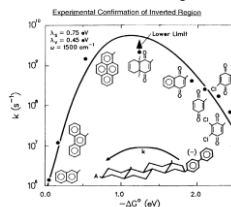
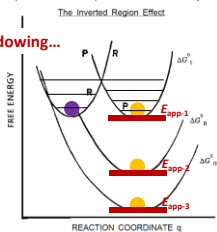
### Observation of Inverted Region Behavior

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

Closs-Miller (1984)  
observation of inverted region

Foreshadowing...



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

### Linear Free Energy Relationships (LFERs)

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

Brønsted-Pedersen (1924)  
empirical LFER for proton transfer

**Linear free-energy relation**

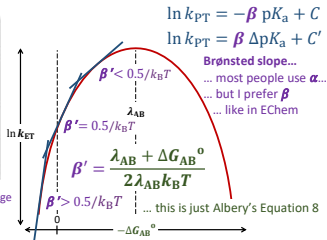
Also contains definition of linear Gibbs energy relation.

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 constant times energy (relative energy) change, and the logarithm of a rate constant is a linear function of the free energy (relative 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 sense of physical organic chemists (physical organic chemists) cannot change their names easily, so it is a case of a name that is hard to change.

Last modified February 20, 2014



... trend looks linear over a small enough  $\Delta G_{AB}^0$  range  
J. Albery, Ann. Rev. Phys. Chem., 1980, 31, 227-263  
R. A. Marcus, Farad. Discuss. Chem. Soc., 1982, 74, 7-15

## Marcus Kinetic Behavior

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**Table 13** Applications of the Marcus relation

Electron transfers	Electrochemical	Tafel Law
	Homogeneous	Electrode kinetics at semiconductors 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 Describes enolization of acetone
Methyl transfers	Cross reactions obey Marcus relation Swain-Scott $\rho$ separated into $\rho^+$ and $\rho^-$ $\alpha D$ isotope effects measure C <sup>+</sup> character	
Nucleophilic additions	Provides alternative explanation to Ritchie relation Values of $G$ found to be constant for similar species	

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

## Chemical Kinetics (*summary for today*)

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- Continuity of mass, Mass transfer, Nernst–Planck equation, Diffusion, Diffusion coefficient, Migration, Mobility, Convection, Boundary layer
- **Mass action, Microscopic reversibility, Förster cube, Square schemes, Rate constants, Activation energies, Transition-state theory, Marcus–Hush theory, Transition-state character, Reorganization energies (outer and inner)**
- **Linear free energy relationships**, Charge transfer across electrified interfaces, Butler–Volmer equation, Fermi’s golden rule, Solid-state physics, Marcus–Gerischer theory
- Rate-determining step, Steady-state & Pre-equilibrium approximations, Langmuir/Frumkin isotherms