



# Lecture #11 of 14

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

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# Chemical Kinetics

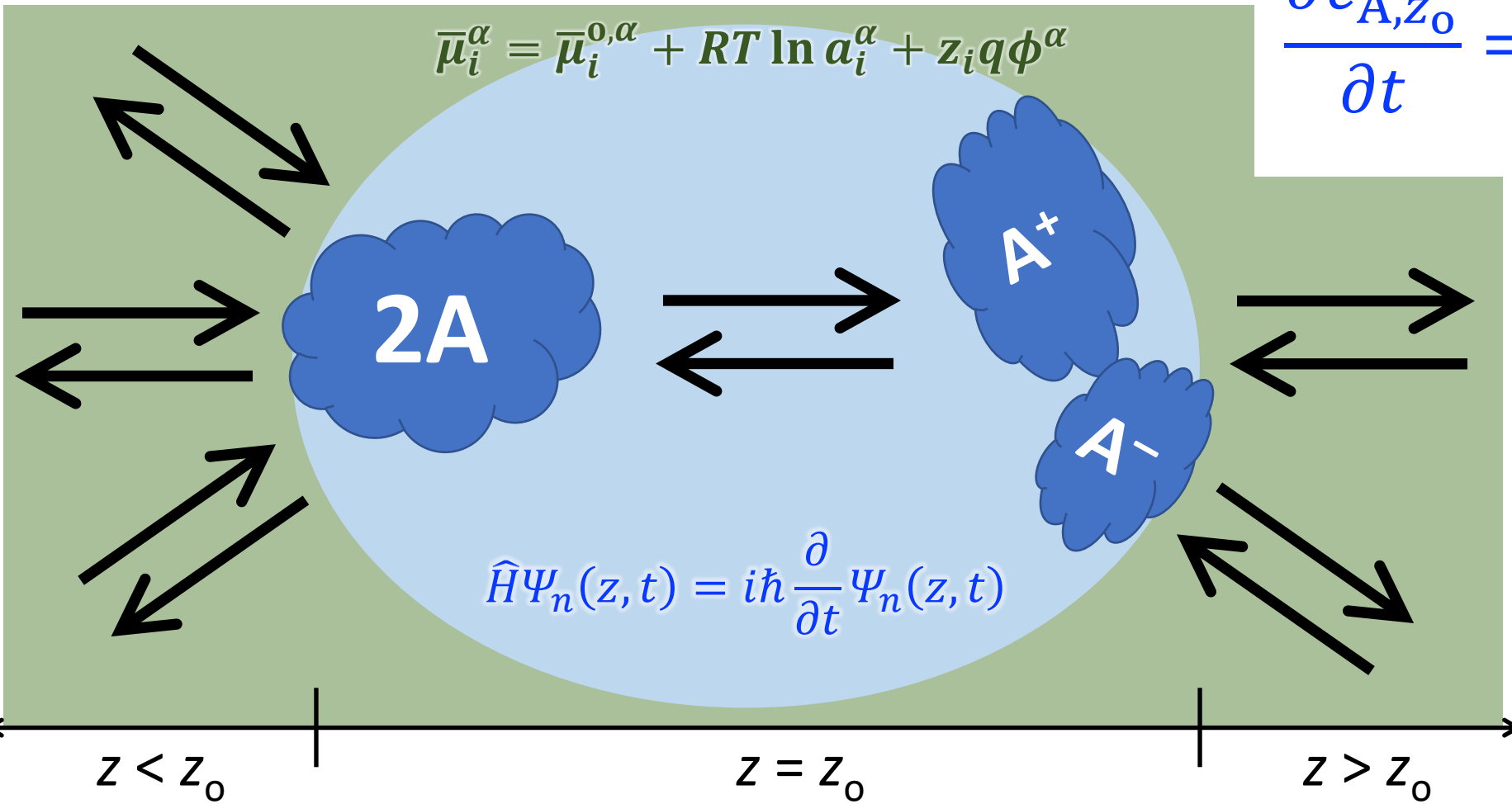
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**Quiz Time!**

# 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

# Continuity of Mass



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

*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

# Thermodynamics *versus* Kinetics

**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...

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

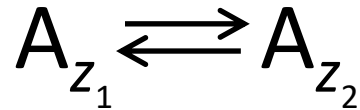
rate of change of the (c)oncentration of species A with respect to (t)ime, in units of  $M s^{-1} (mol dm^{-3} s^{-1})$

mass action (R)ate laws that effect species A, e.g.  $R_A = k_3 a_B a_D^2 \approx k_3 [B][D]^2$  (to a first order, this is driven by differences in chemical potential of various species,  $\mu_j$ )

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,  $\bar{\mu}_i$ )

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

# 1D Transport in Liquids (solids are simpler)



$$\frac{\partial c_{A,z_0}}{\partial t} = \frac{\partial N_A}{\partial z}$$

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

(MechEs should be yawning)

... 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)...

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

What are the directions for the dimensions of  $D_A$ ?

**BOLD**  $((\text{cm}^2/\text{s}) / \text{cm}) = \text{cm}/\text{s}$ ... a velocity!

... and with  $\frac{\partial}{\partial z}$ , units are  $\text{s}^{-1}$ ... an inverse time constant!

... and that equals zero at **steady state**

(Note that...  $R_{A,\text{total}} = -k'_f c_A + k'_b c_B$ ... with  $k'_j$  ( $\text{s}^{-1}$ ), an inverse time constant!)

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

Let's expand the total differential...

$$\text{Flux}_{z,e} = -\frac{\sigma_e}{F^2} \frac{d\bar{\mu}_e}{dz} - S_{e,T_e} \frac{dT_e}{dz} \quad \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_{j \neq i}} = \bar{\mu}_i = \mu_i + z_i q \phi$$

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

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

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

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

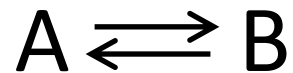
... assuming a species, e, with valency, z<sub>e</sub>, equal to -1

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

Drift-Diffusion equation

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

# Mass Action / Microscopic Reversibility



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

(Chemists should be yawning)

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

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

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

- Law of mass action
- Principle of microscopic reversibility

... and in solid-state physics...  $R_{e^-,total} = \sum_j \text{Gen}_{e^-,j} - \sum_j \text{Rec}_{e^-,j}$

$k_j$  (M/s)... a rate!

$k'_j$  ( $s^{-1}$ )... an inverse time constant!

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

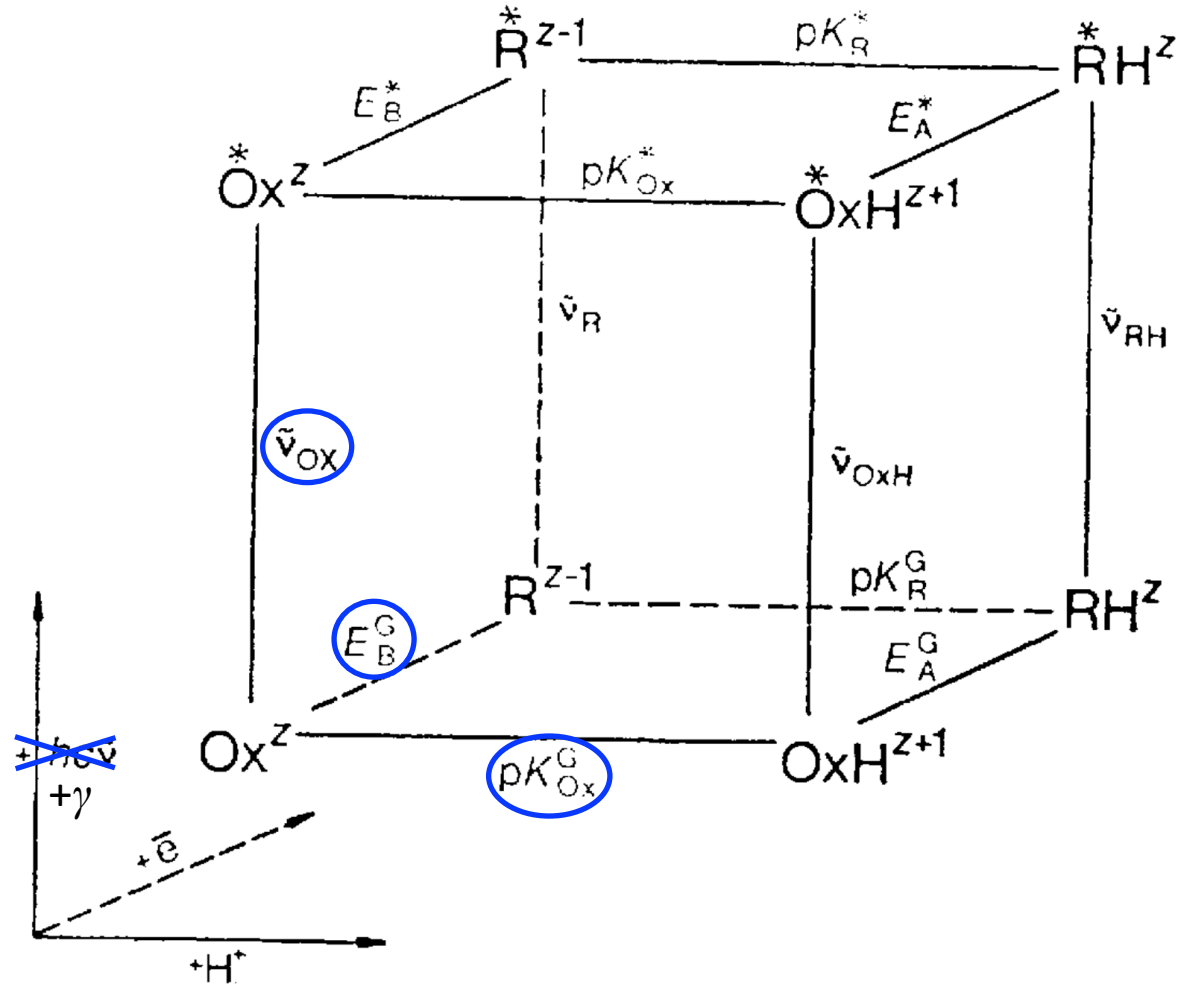
So,  $\Delta G^{0',\alpha} = -RT \ln K'$ , with  $K' = \frac{c_{B,eq}^\alpha / c_B^{0,\alpha}}{c_{A,eq}^\alpha / c_A^{0,\alpha}} \dots$  and, of course,  $K' = \exp\left(-\frac{\Delta G^{0',\alpha}}{RT}\right)$

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

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



# Förster Cube and Square Schemes



## Questions to ponder...

In this figure, what do the thermodynamic parameters  $E$ ,  $pK$ , and  $\bar{\nu}$  represent?

$E = E^0$  (standard-state reduction potential)

$pK = pK_a = -\log K_a$  (acid dissociation constant)

$\bar{\nu} = \frac{1}{\lambda}$  (wavenumber)

How are they related?

**Redox:**  $E^0 = -\Delta G^0/nF$

**Acidity:**  $pK_a = -\log K_a = \Delta G^0/(2.303RT)$

**Light:**  $hc\bar{\nu} = \frac{hc}{\lambda} = h\nu = E_{\text{photon}}$

In 10

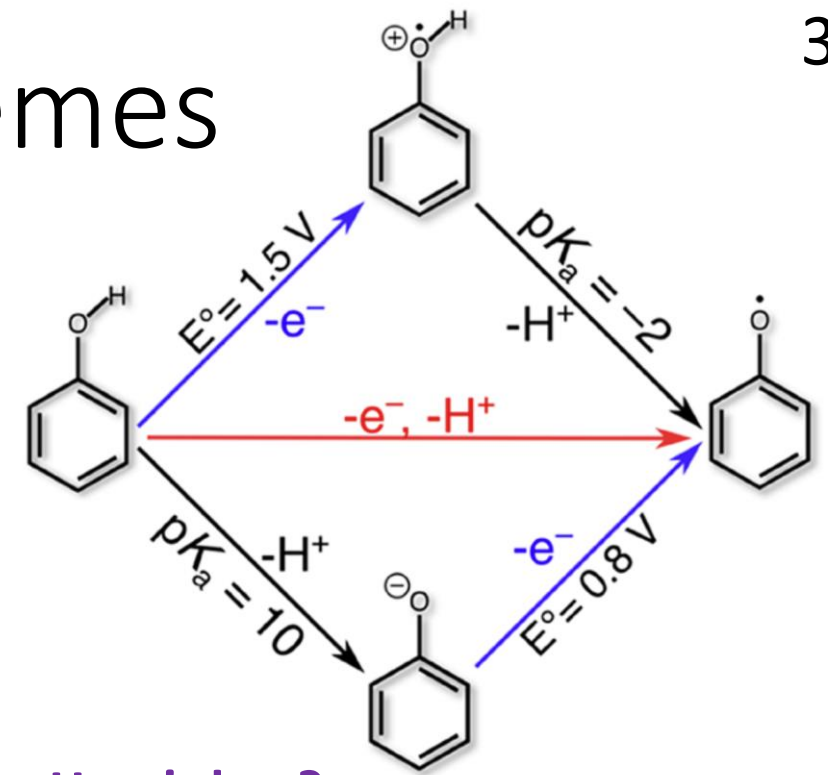
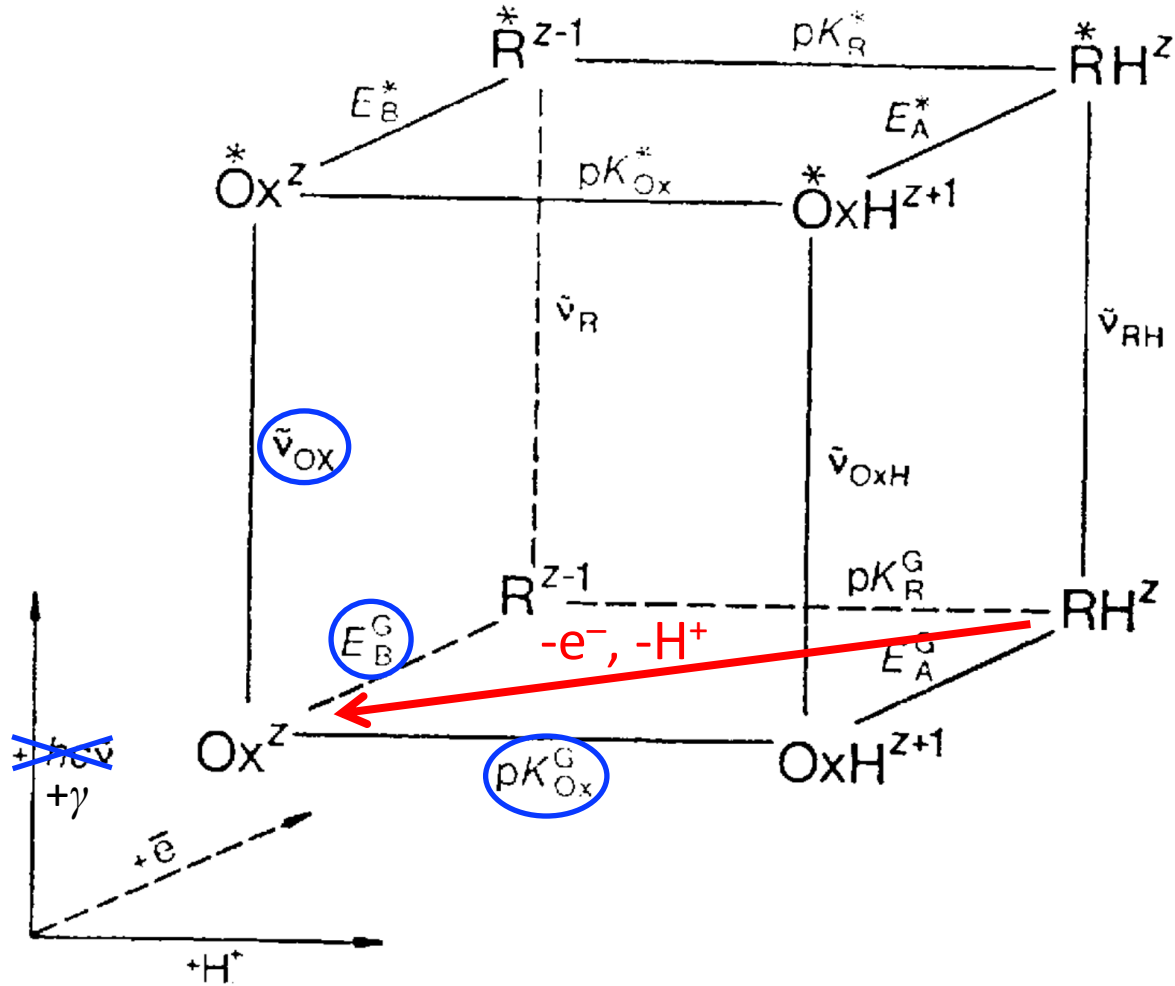
What is the reference state for each?

$E^0(\text{H}^+(\text{aq})/\text{H}_2) = 0$ ;  $pK_a(\text{H}^+(\text{aq})) = 0$ ; 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



Does this obey Hess's law?

Redox:  $E^0 = -\Delta G^0/nF$

Acidity:  $pK_a = -\log K_a = \Delta G^0/(2.303RT)$

Thus,  $E^0 = -pK_a \times (2.303RT/nF) = -59.2mV \times pK_a$

Does Bottom Route = Top Route?

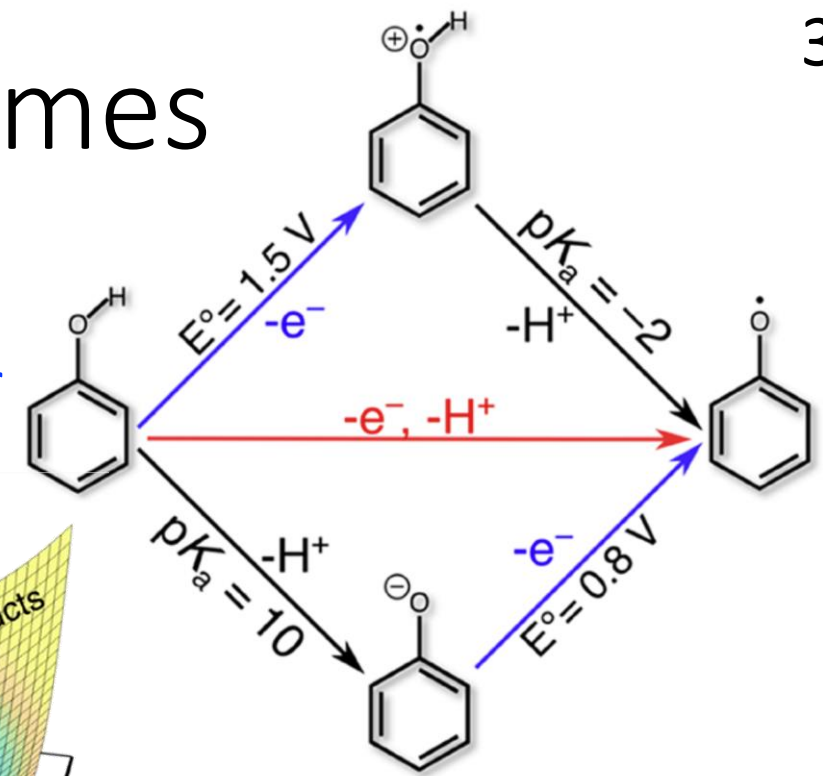
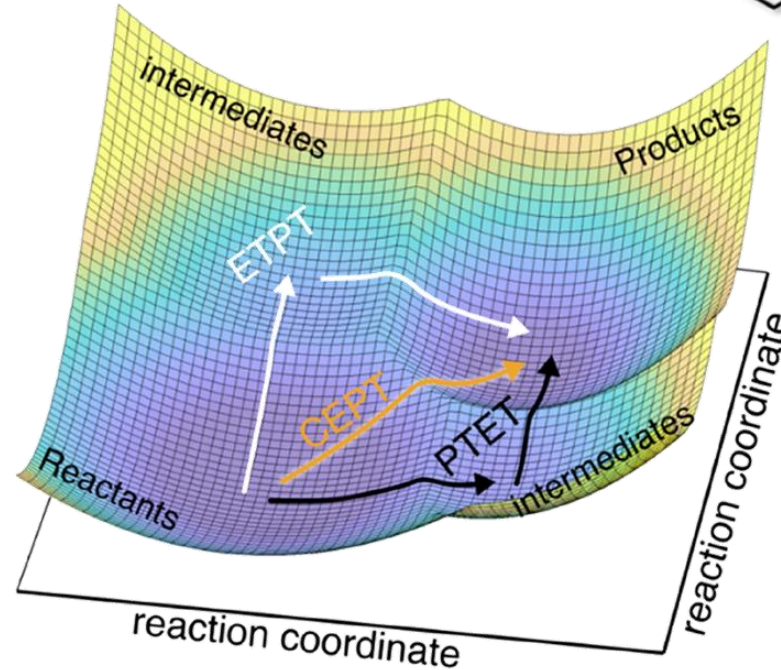
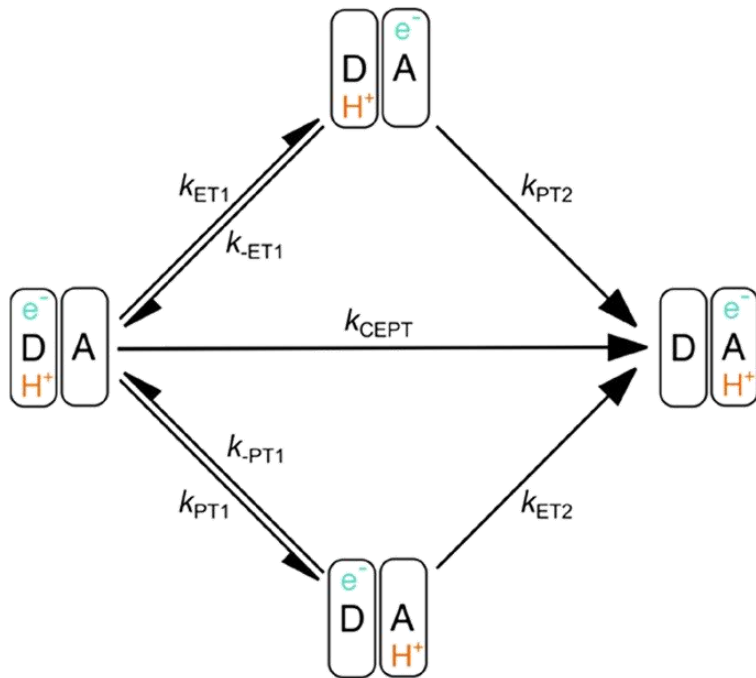
$10(-0.0592V) + -0.8V = -1.5V + -2(-0.0592V)$

$-0.59V + -0.8V \approx -1.5V + 0.12V$ ... so, ~yes!

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

# Förster Cube and Square Schemes

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



... and this can constitute a ground-state, or excited-state, free energy landscape (N-dimensional potential energy surface)

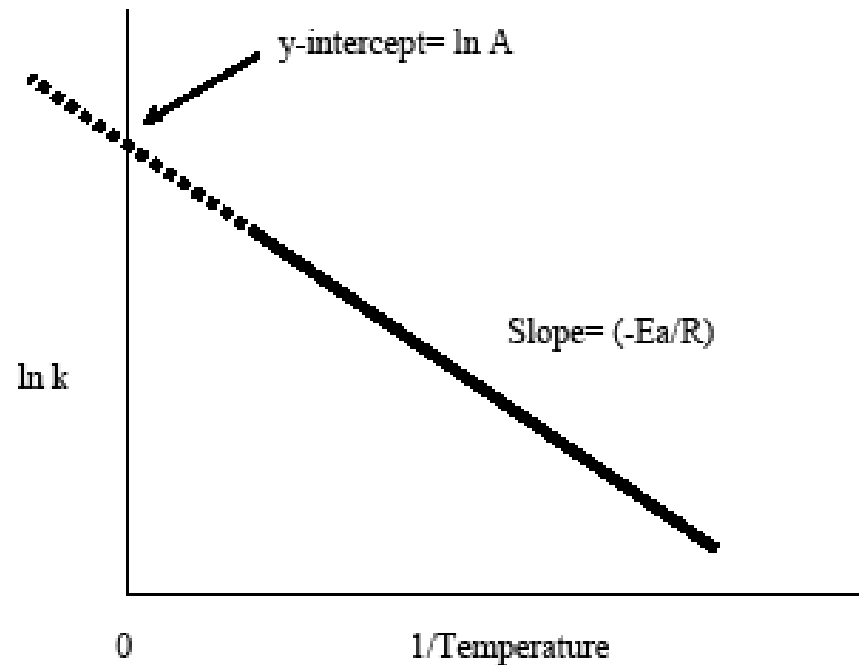
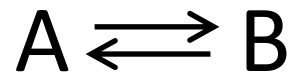
**Figure 2.** (Left) Square scheme that summarizes the mechanisms by which proton-coupled electron transfer can proceed. The edges of the square show the sequential mechanisms with ETPT and PTET on the top and bottom, respectively. The pathway bisecting the square is concerted, where  $e^-$  and  $H^+$  are transferred without the formation of an intermediate species. Note that the donor and acceptor units 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.

# Activation Energies

Arrhenius (1889)

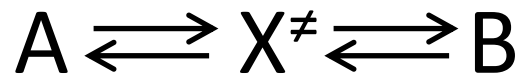
empirical rate constant equation

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



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  $R = N_A k_B \dots$  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?  **$(161 \text{ fs})^{-1} = (1.61 \times 10^{-13} \text{ s})^{-1}$**

# Marcus–Hush Theory



Marcus–Hush (1950s–1960s)

theoretical (semiclassical) rate constant equation

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



Eyring–Polanyi–Evans (1930s)

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

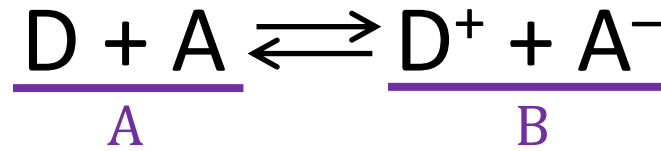
$$k_f = \kappa \nu K^\ddagger = \frac{\kappa k_{\text{B}}T}{h} K^\ddagger \dots \text{ with } \mathbf{transmission\ coefficient, } \kappa, \text{ and } \mathbf{vibrational\ frequency, } \nu \text{ (s}^{-1}\text{)}$$

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

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

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quantum adiabatic  
electronic coupling

classical nuclear free-  
energy dependence

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

proportional to  $\frac{d\bar{\mu}_A}{dz}$

proportional to  $\exp\left((\lambda_{\text{AB}} + \Delta G_{\text{AB}}^0)^2\right)$

... 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?

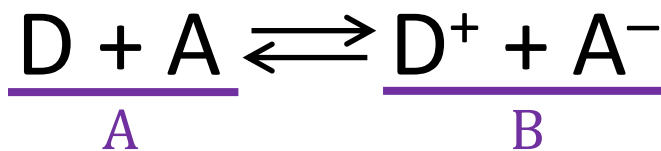
$$\Delta G_{\text{AB}}^\ddagger = \frac{(\lambda_{\text{AB}} + \Delta G_{\text{AB}}^0)^2}{4\lambda_{\text{AB}}}$$

... wait... there is a direct relation between thermodynamics ( $\Delta G_{\text{AB}}^0$ ) and kinetics ( $\Delta G_{\text{AB}}^\ddagger$ )?

... this makes sense since  $\frac{d\bar{\mu}_A}{dz}$  drives transport... *which can be written as a chemical reaction*

... but that key relationship is quadratic... meaning a parabola? Huh?!?!?!?

# Marcus–Hush Theory



Marcus–Hush (1950s–1960s)

theoretical (semiclassical) rate constant equation

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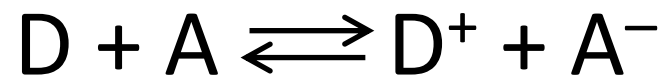
classical nuclear free-  
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$$k_{\text{ET}} = \frac{2\pi}{\hbar} |H_{\text{DA}}|^2 \frac{1}{\sqrt{4\pi\lambda_{\text{AB}}kT}} \exp\left(-\frac{(\lambda_{\text{AB}} + \Delta G_{\text{AB}}^0)^2}{4\lambda_{\text{AB}}kT}\right) \dots \text{what kind of function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

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

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

# Marcus–Hush Theory



Marcus–Hush (1950s–1960s)

Standard Normal Distribution

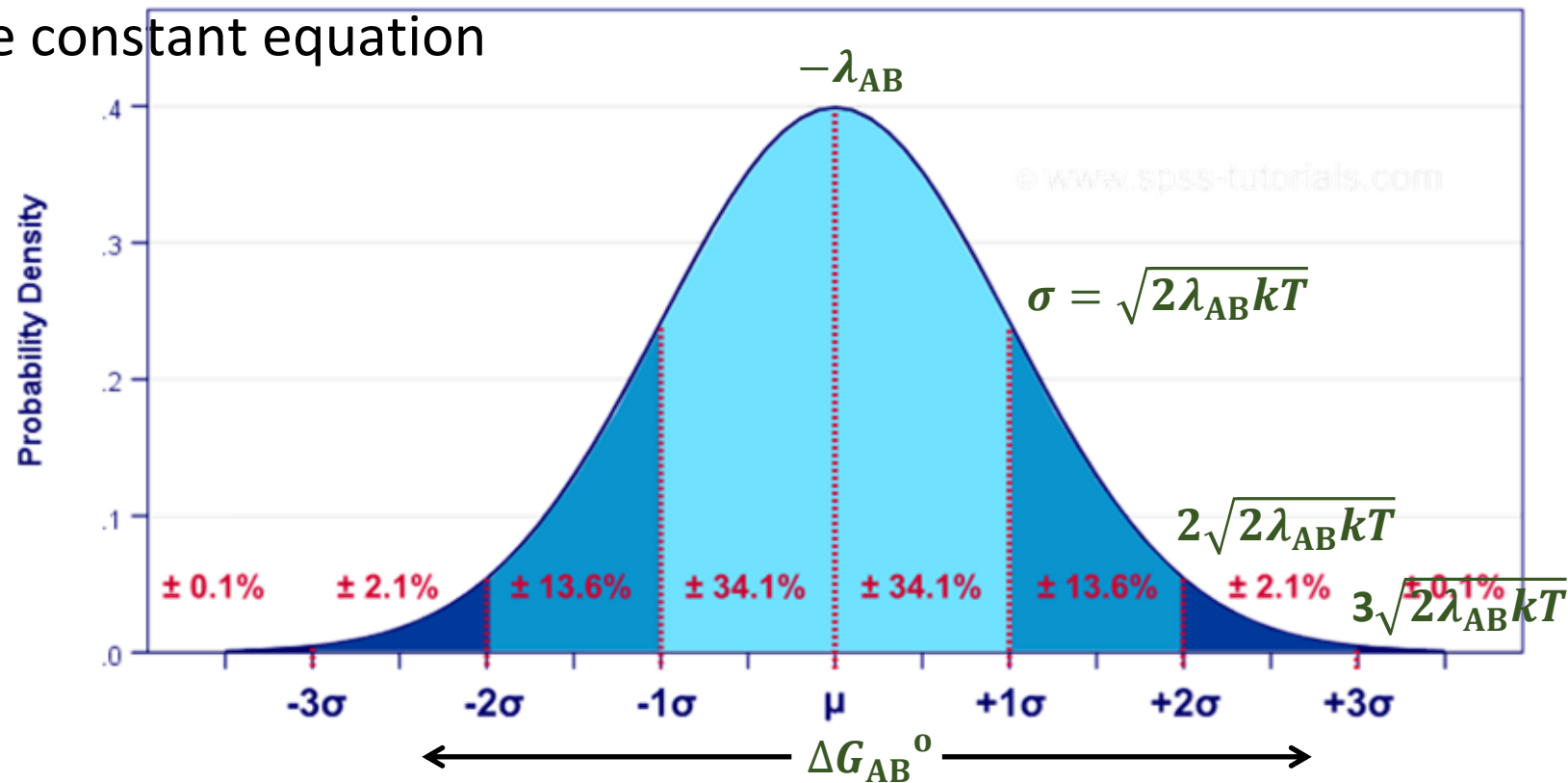
A

B

$\mu = 0 | \sigma = 1$

theoretical (semiclassical) rate constant equation

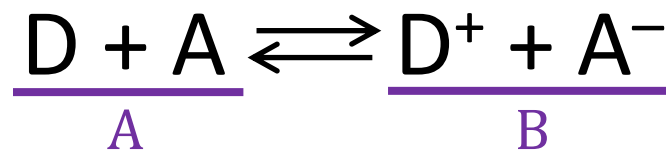
... wait... the classical component in Marcus electron-transfer theory is a **normal distribution** as a function of standard-state thermodynamic driving force ( $\Delta G_{AB}^0$ )?... **Yep!**



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



# Marcus–Hush Theory



Marcus–Hush (1950s–1960s)

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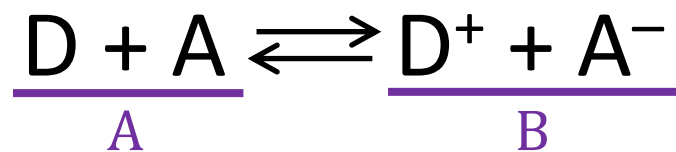
$$k_{\text{ET}} = \frac{2\pi}{\hbar} |H_{\text{DA}}|^2 \frac{1}{\sqrt{4\pi\lambda_{\text{AB}}kT}} \exp\left(-\frac{(\lambda_{\text{AB}} + \Delta G_{\text{AB}}^0)^2}{4\lambda_{\text{AB}}kT}\right)$$

$\ln k_{\text{ET}}$

0  $-\Delta G_{\text{AB}}^0$



# Marcus–Hush Theory



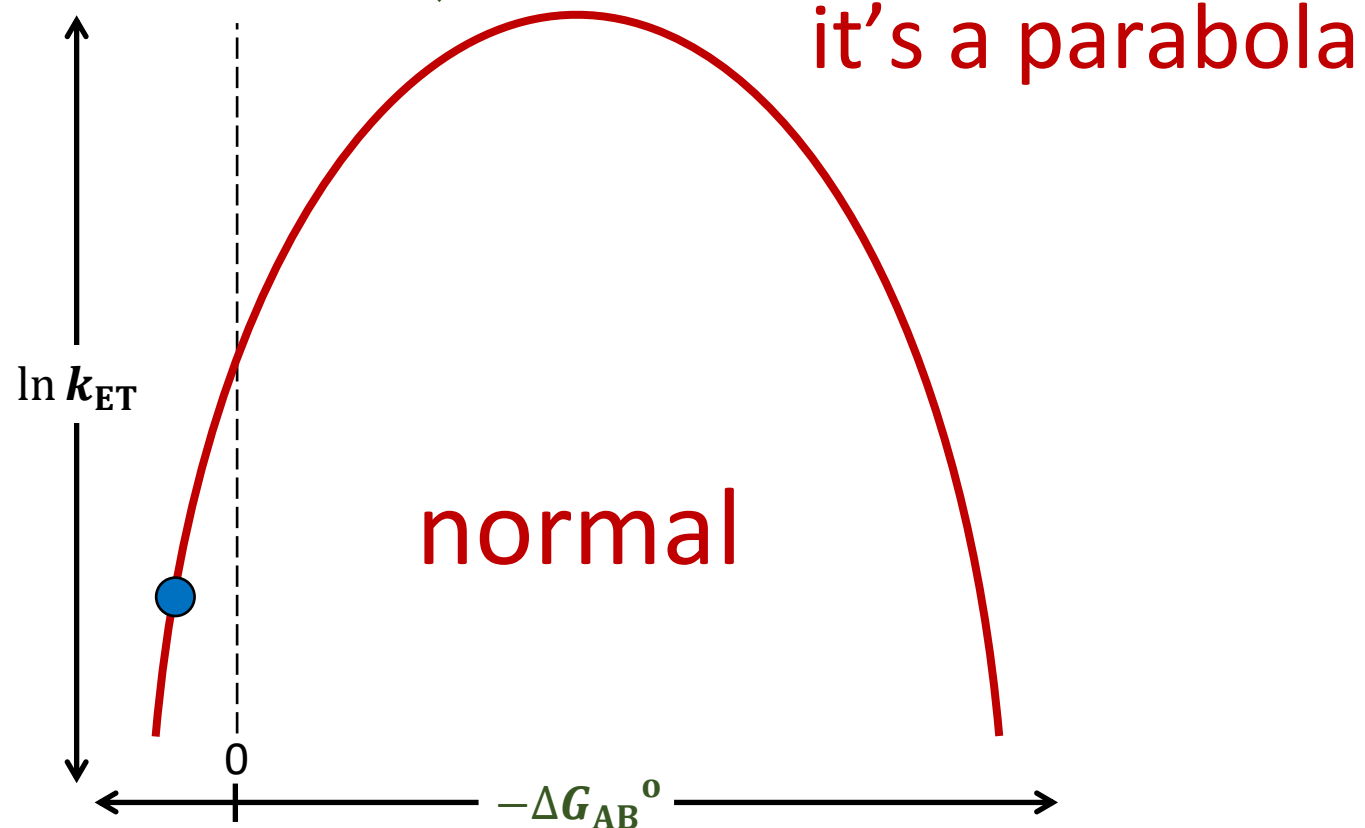
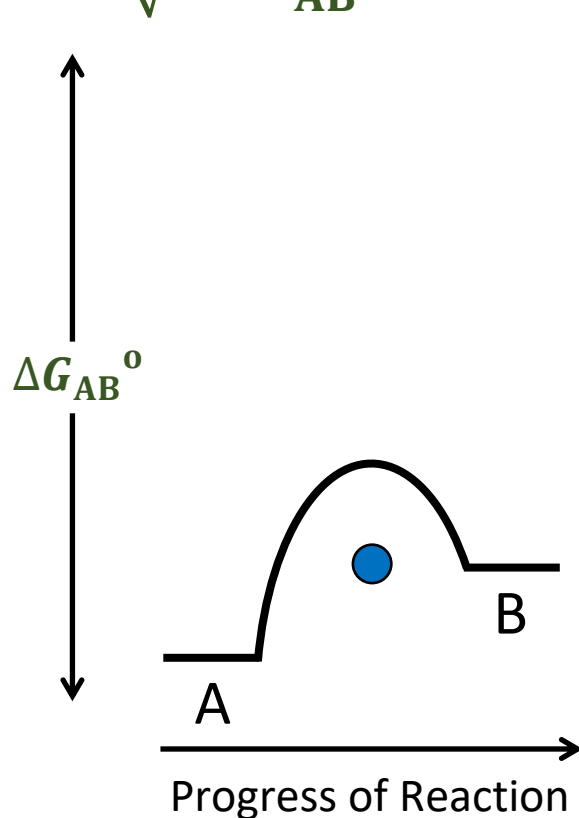
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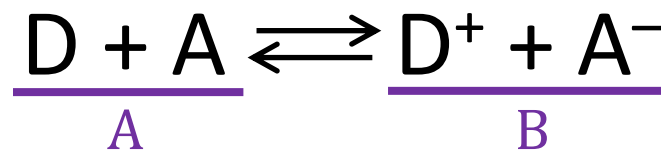
$$k_{\text{ET}} = \frac{2\pi}{\hbar} |H_{\text{DA}}|^2 \frac{1}{\sqrt{4\pi\lambda_{\text{AB}}kT}} \exp\left(-\frac{(\lambda_{\text{AB}} + \Delta G_{\text{AB}}^0)^2}{4\lambda_{\text{AB}}kT}\right)$$

How can a thermodynamically unfavorable reaction proceed?

Mass Action!



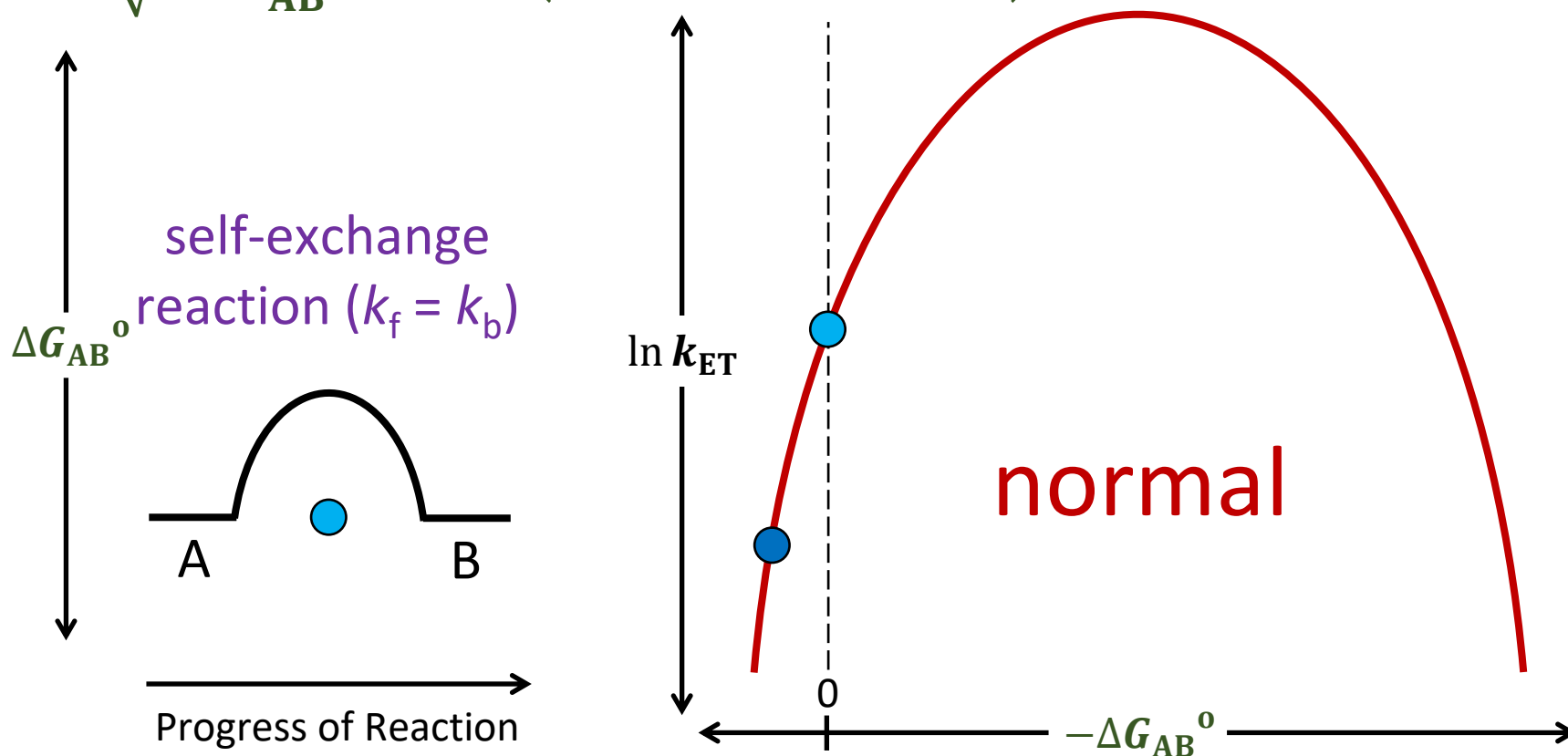
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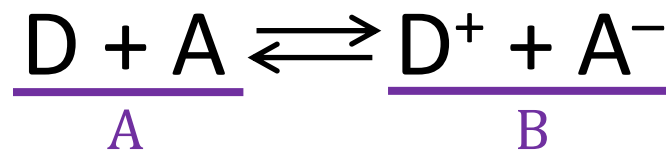
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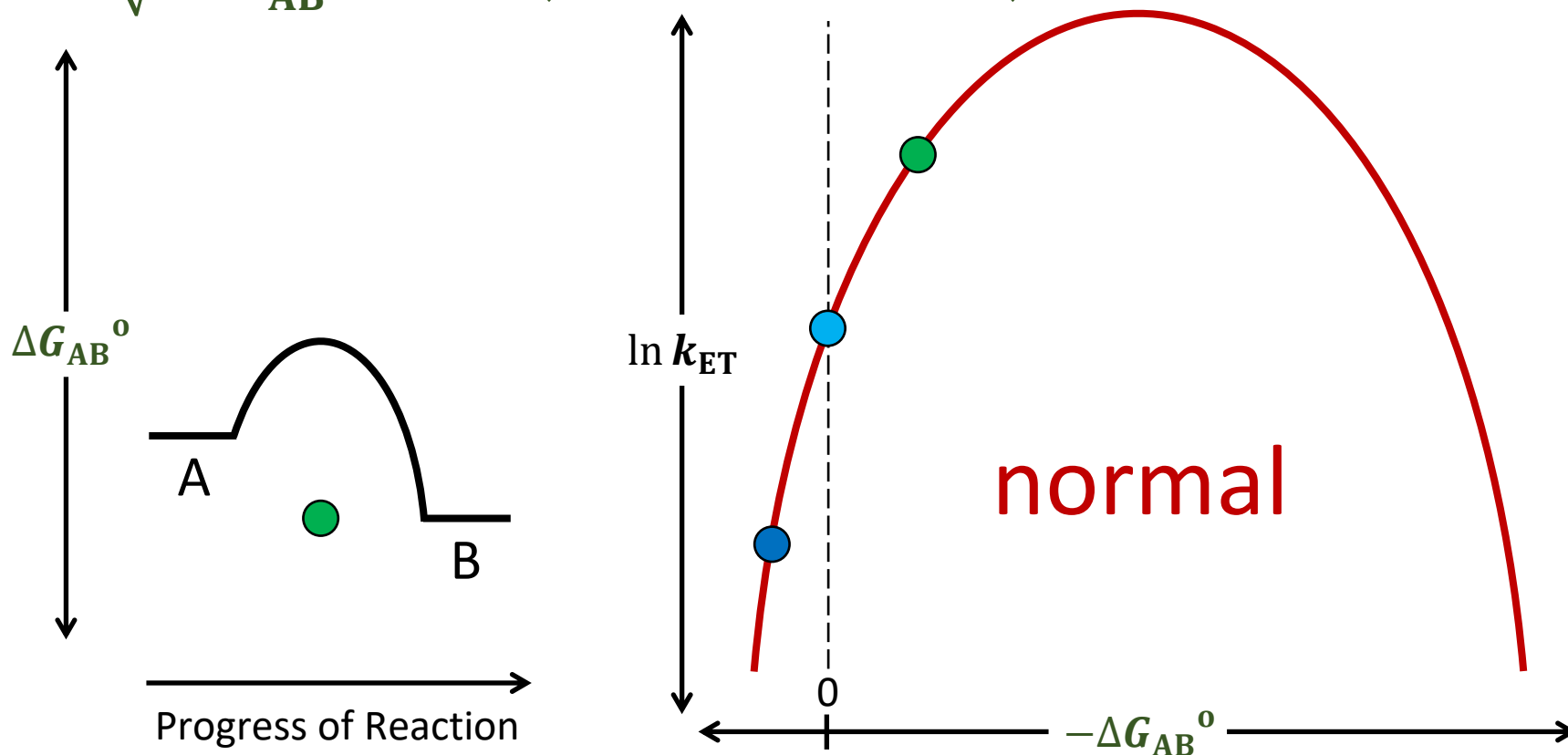
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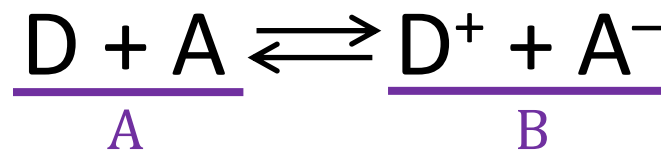
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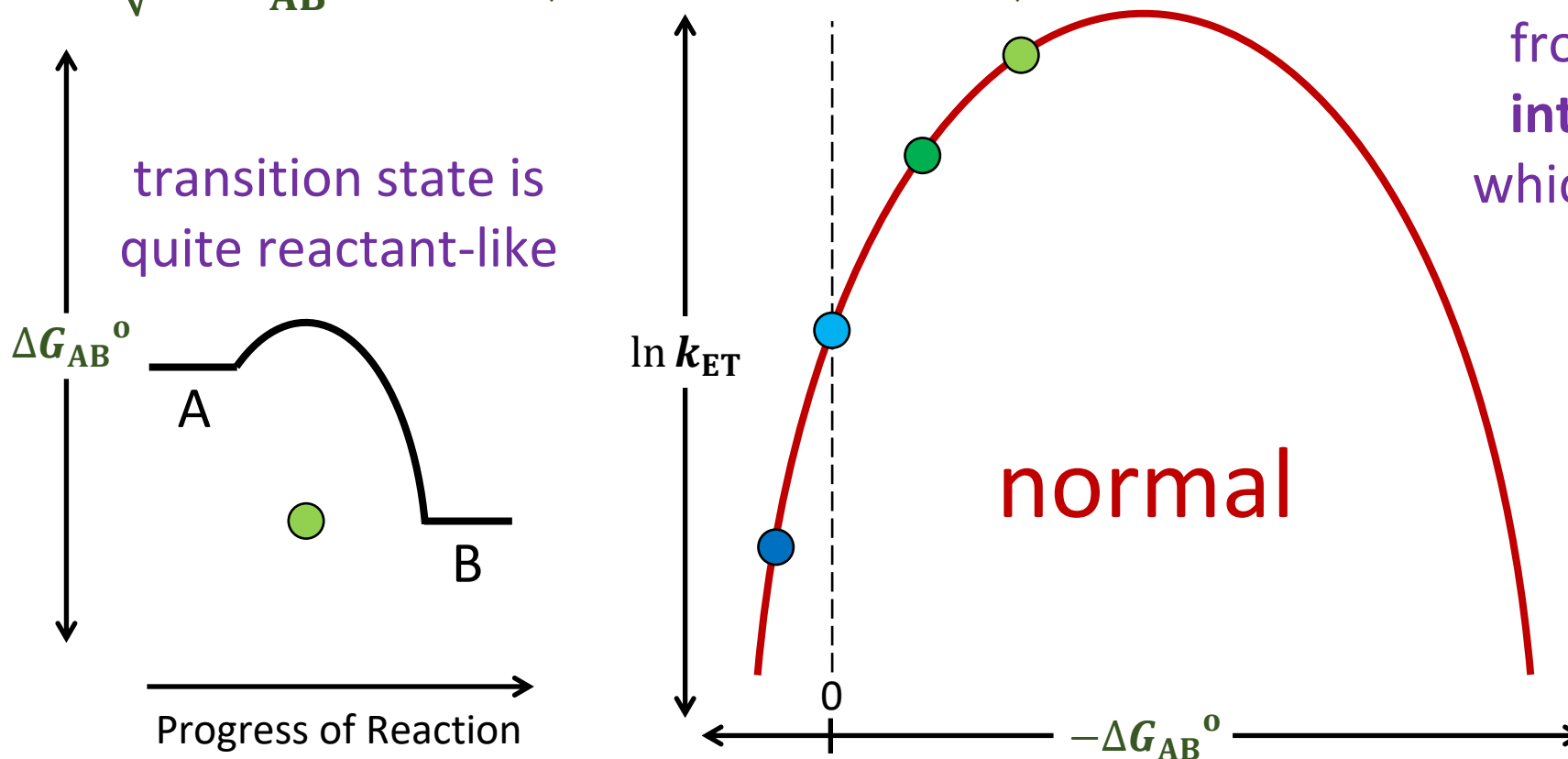
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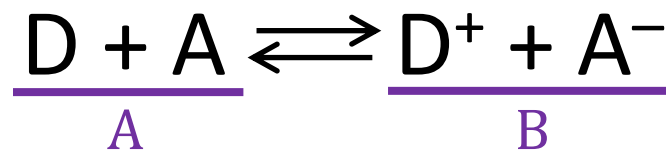
theoretical (semiclassical) rate constant equation

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



Note that a **transition state** only lasts on the order of a bond vibration ( $h/k_{\text{B}}T \approx 160$  fs) and differs from a proper **intermediate**, which lasts much longer

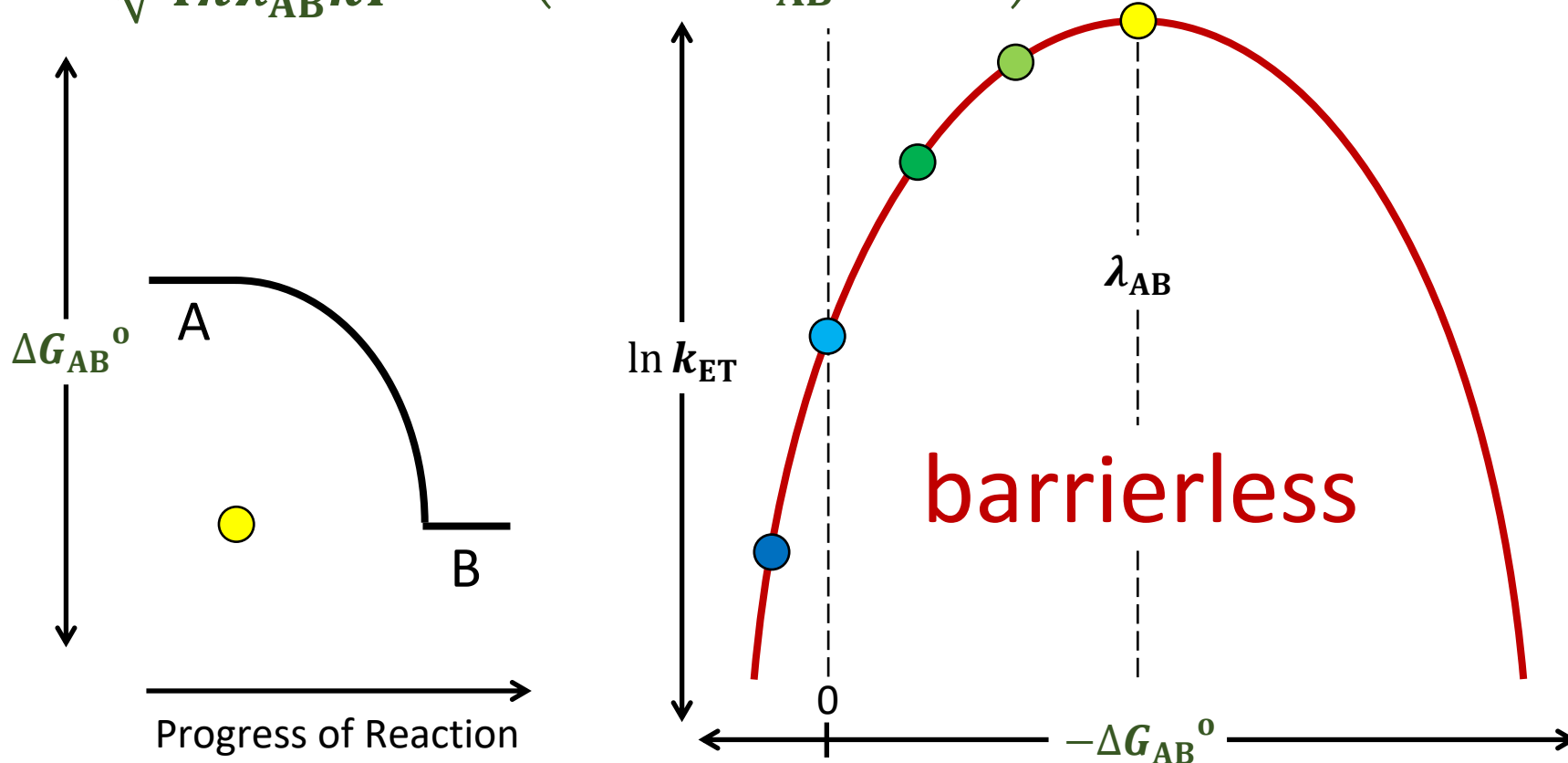
# Marcus–Hush Theory



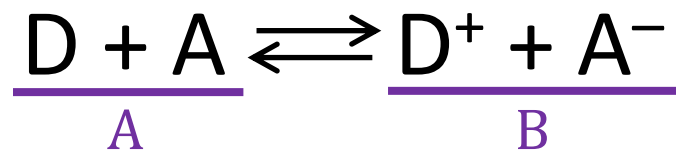
Marcus–Hush (1950s–1960s)

theoretical (semiclassical) rate constant equation

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



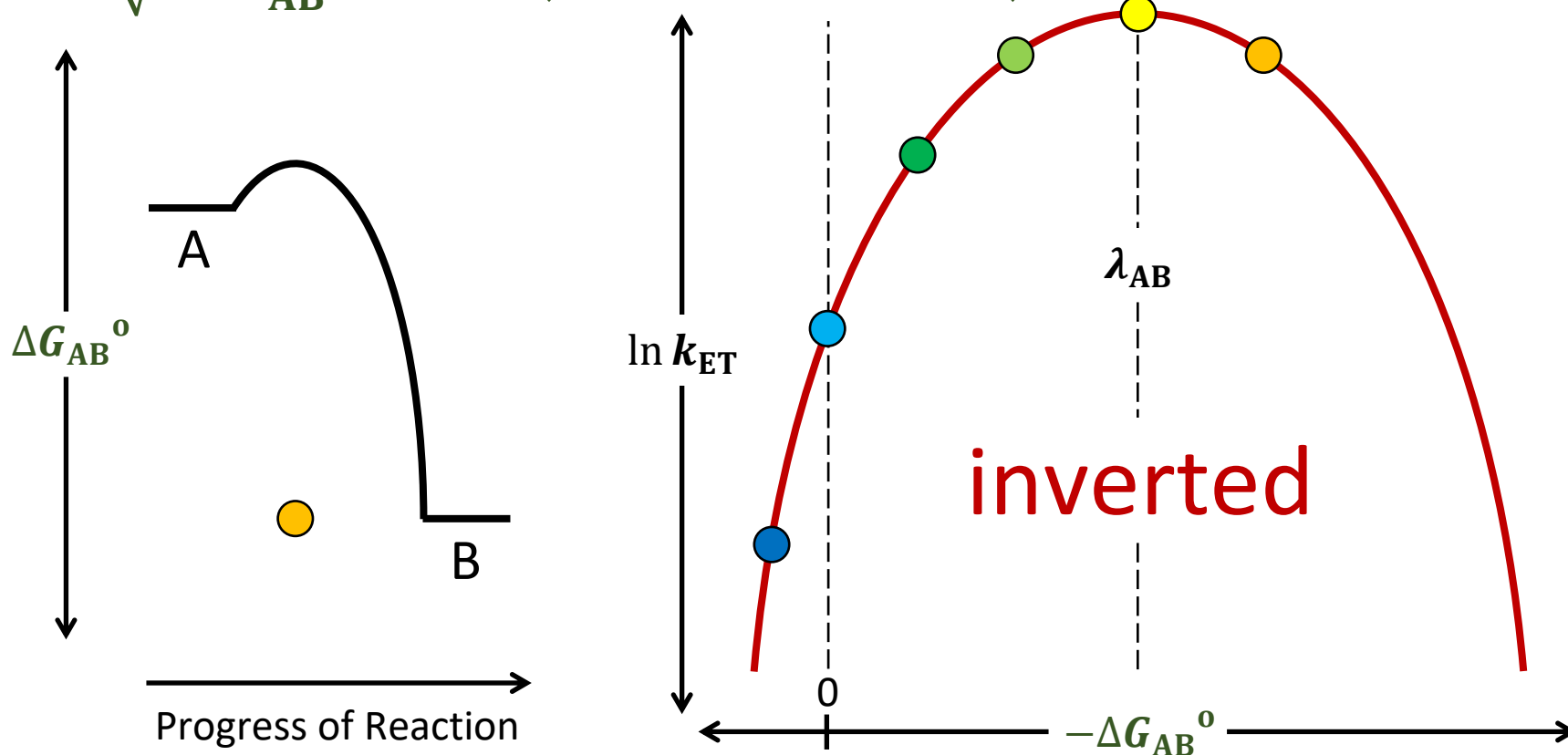
# Marcus–Hush Theory



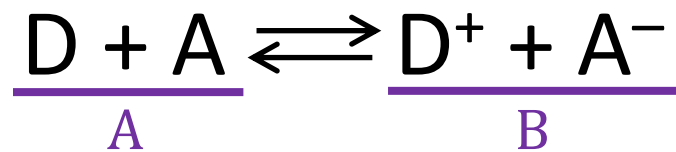
Marcus–Hush (1950s–1960s)

theoretical (semiclassical) rate constant equation

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



# Marcus–Hush Theory



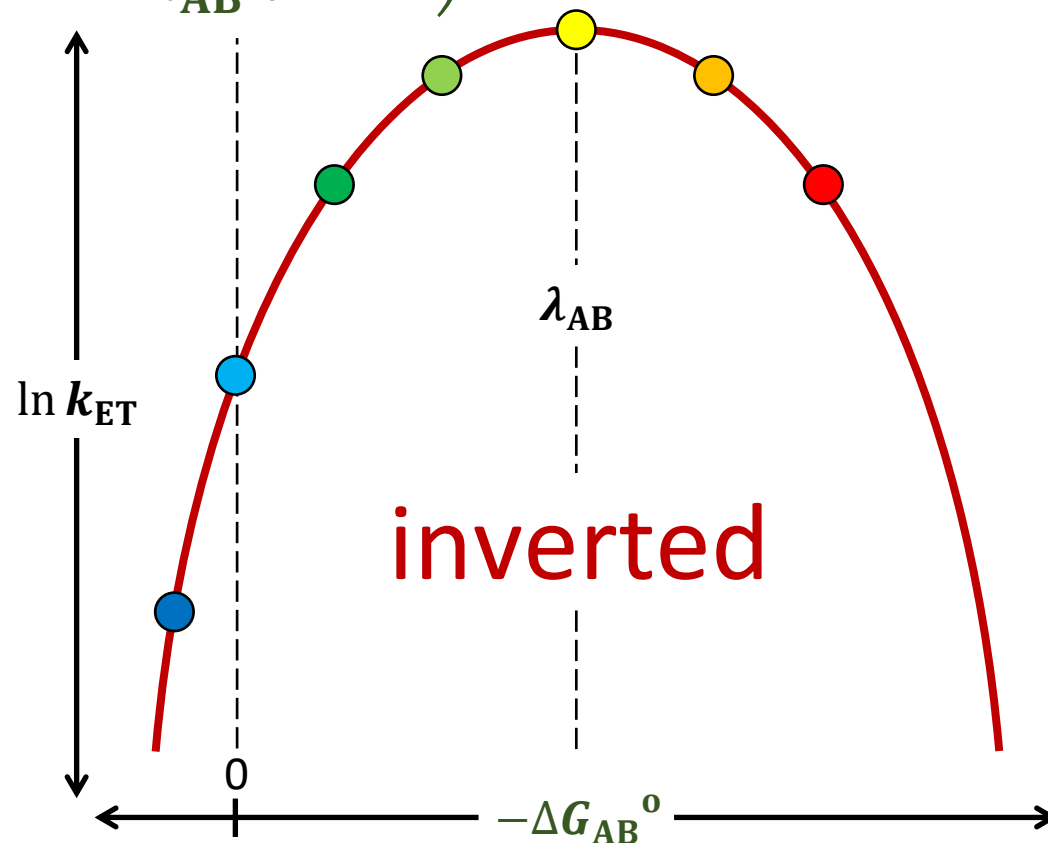
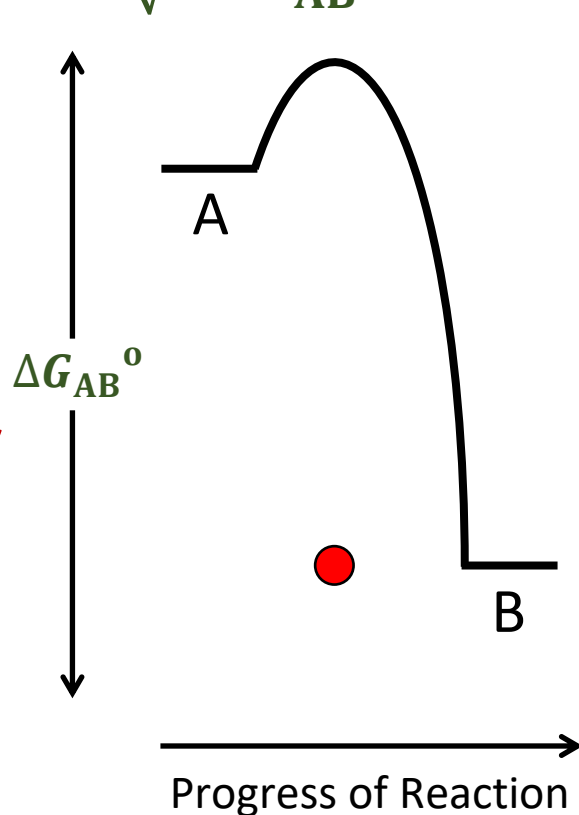
Marcus–Hush (1950s–1960s)

theoretical (semiclassical) rate constant equation

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

... this looks odd...

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





# Outer Reorganization Energy

Marcus–Hush (1950s–1960s)

theoretical (semiclassical) rate constant equation

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

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

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

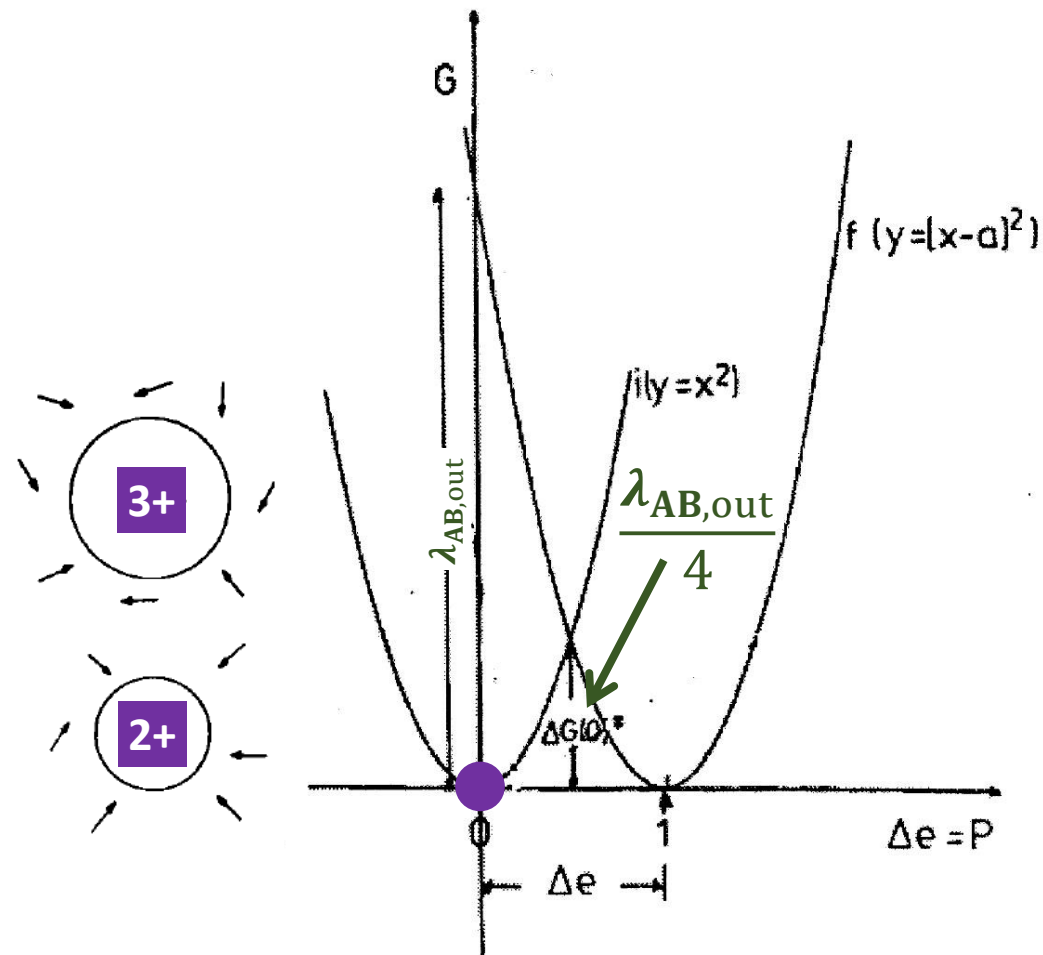
... what physical expression results in a quadratic dependence on **charge**?

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

... dielectric continuum model...

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

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



$$\lambda_{\text{out}} = \left( \frac{1}{2r_{\text{D}}} + \frac{1}{2r_{\text{A}}} - \frac{1}{R_{\text{DA}}} \right) \left( \frac{1}{\epsilon_{\infty}} - \frac{1}{\epsilon_{\text{s}}} \right) (\Delta e)^2$$

# Outer + Inner Reorganization Energy

## 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

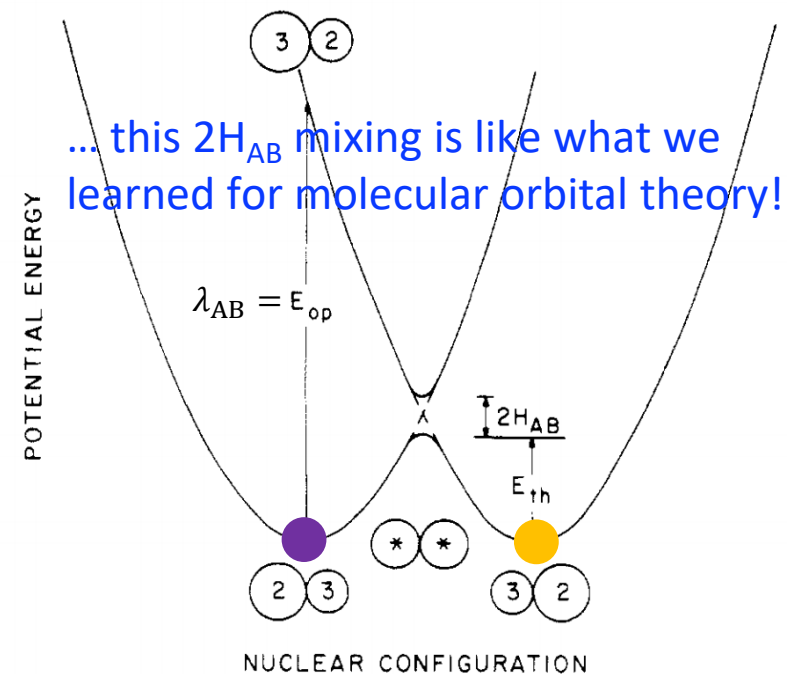
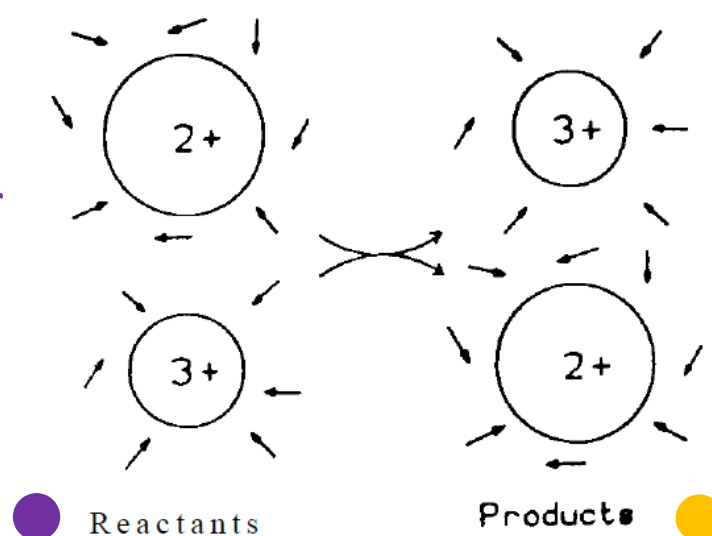
$$\lambda_i = \sum_l \lambda_{i,l} = \frac{1}{2} \sum_l f_l (\Delta q_{e,l})^2$$

... this is for a harmonic oscillator  
... with force constants,  $f_l$ ...

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

## Electron Transfer in Solution

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



# More Quantum Mechanics

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

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

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

Poisson's Equation (from Gauss's law)

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

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

for a point charge...  
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**...

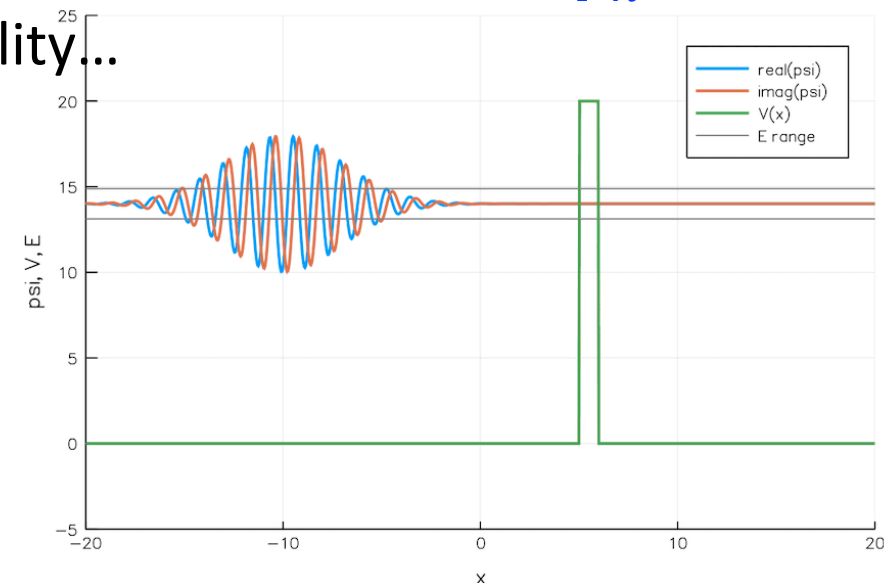
$$\text{Probability Density}(x) = |\psi_n(x)|^2 = \psi_n^*(x)\psi_n(x)$$

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

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

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

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



# Molecular Orbital Theory

## Marcus–Hush (1950s–1960s)

theoretical (semiclassical) rate constant equation

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

quantum adiabatic  
electronic coupling

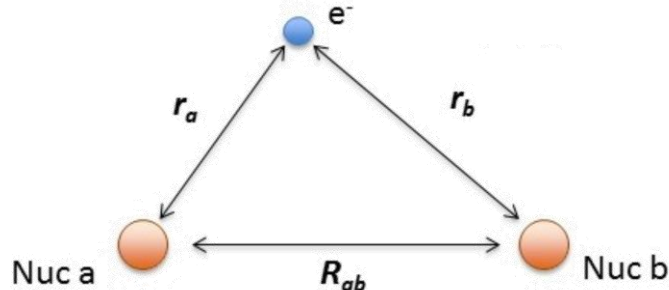
classical nuclear free-  
energy dependence

... remember the simplicity of  $\text{H}_2^+$ ... which resembles  $\lambda_{\text{out}}$  math

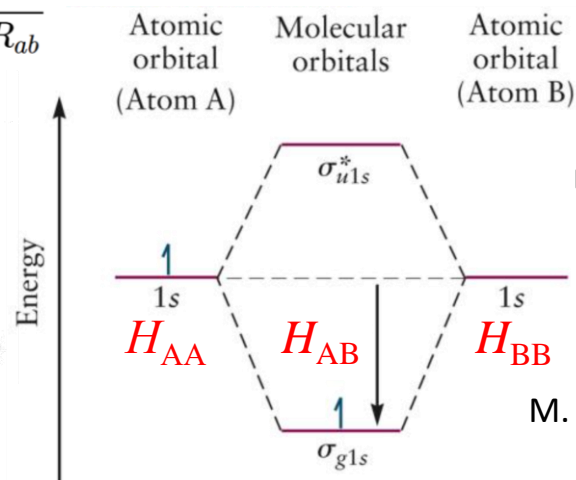
$$\hat{H}(r, R_{ab}) = -\frac{\hbar^2}{2m} \nabla_a^2 - \frac{\hbar^2}{2m} \nabla_b^2 - \frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_a} - \frac{e^2}{4\pi\epsilon_0 r_b} + \frac{e^2}{4\pi\epsilon_0 R_{ab}}$$

matrix

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



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

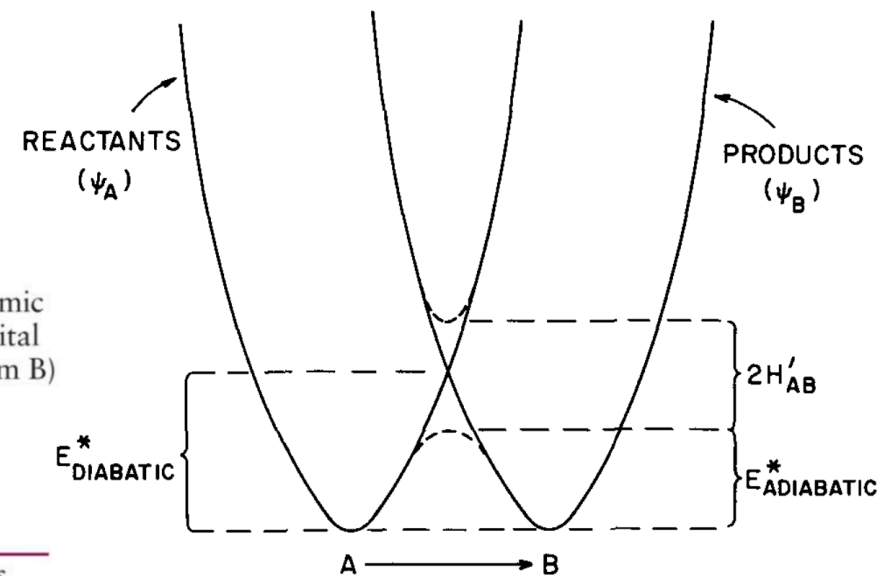


## Molecular Orbital Theory

linear combination of atomic orbitals

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

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



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

# Observation of Inverted Region Behavior

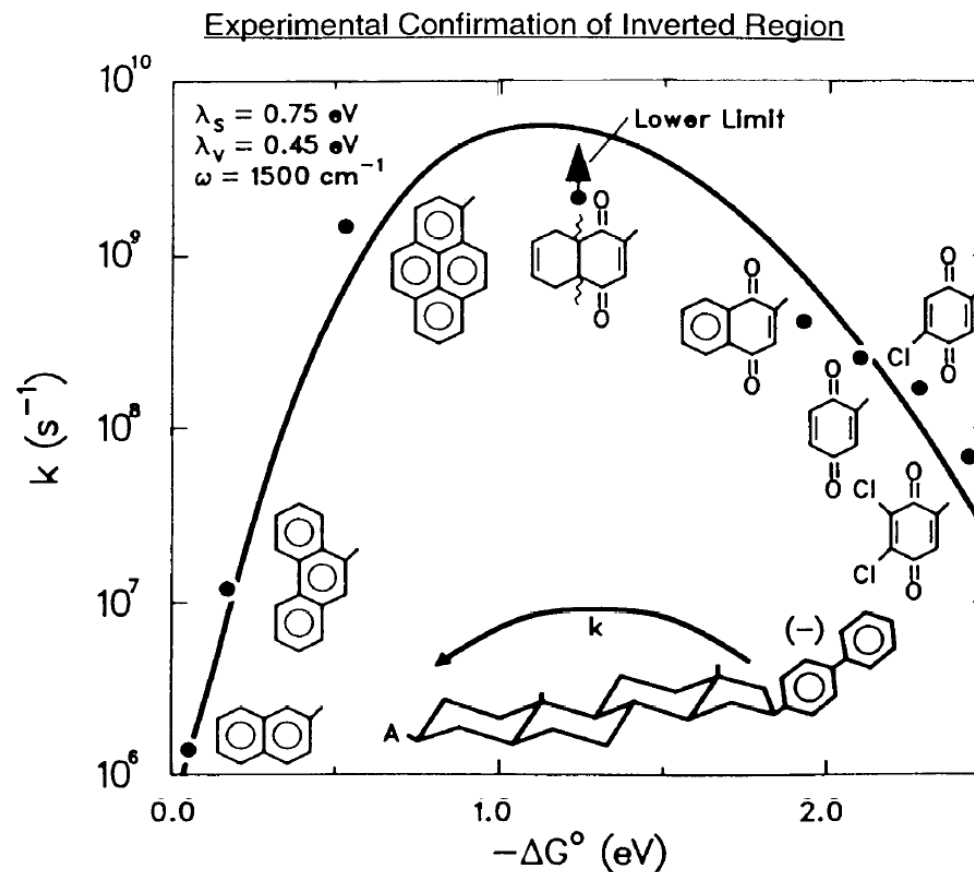
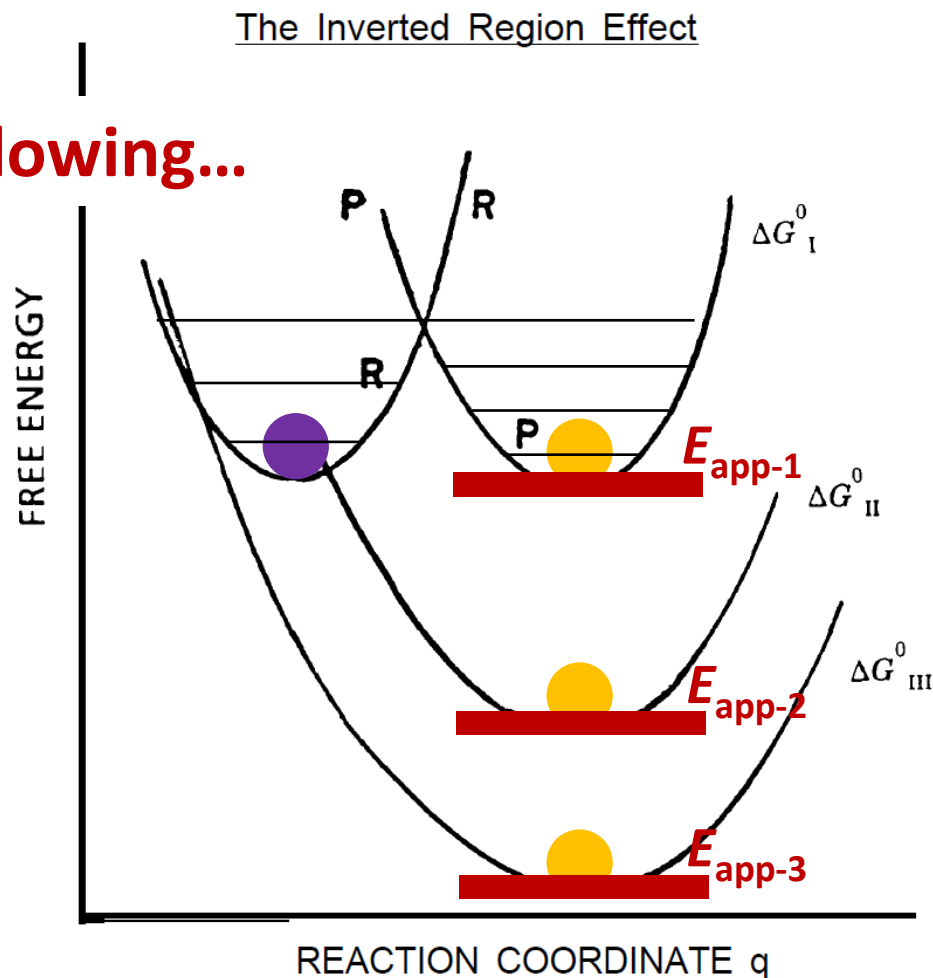
Marcus–Hush (1950s–1960s)

theoretical (semiclassical) rate constant equation

Cross–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)

Marcus–Hush (1950s–1960s)

theoretical (semiclassical) rate constant equation

Brønsted–Pedersen (1924)

empirical LFER for proton transfer

$$\ln k_{\text{PT}} = -\beta \text{p}K_{\text{a}} + C$$

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

Brønsted slope...

... most people use  $\alpha$ ...

... but I prefer  $\beta$

... like in EChem

**linear free-energy relation** Online use... < >

Also contains definition of: [linear Gibbs energy relation](#)

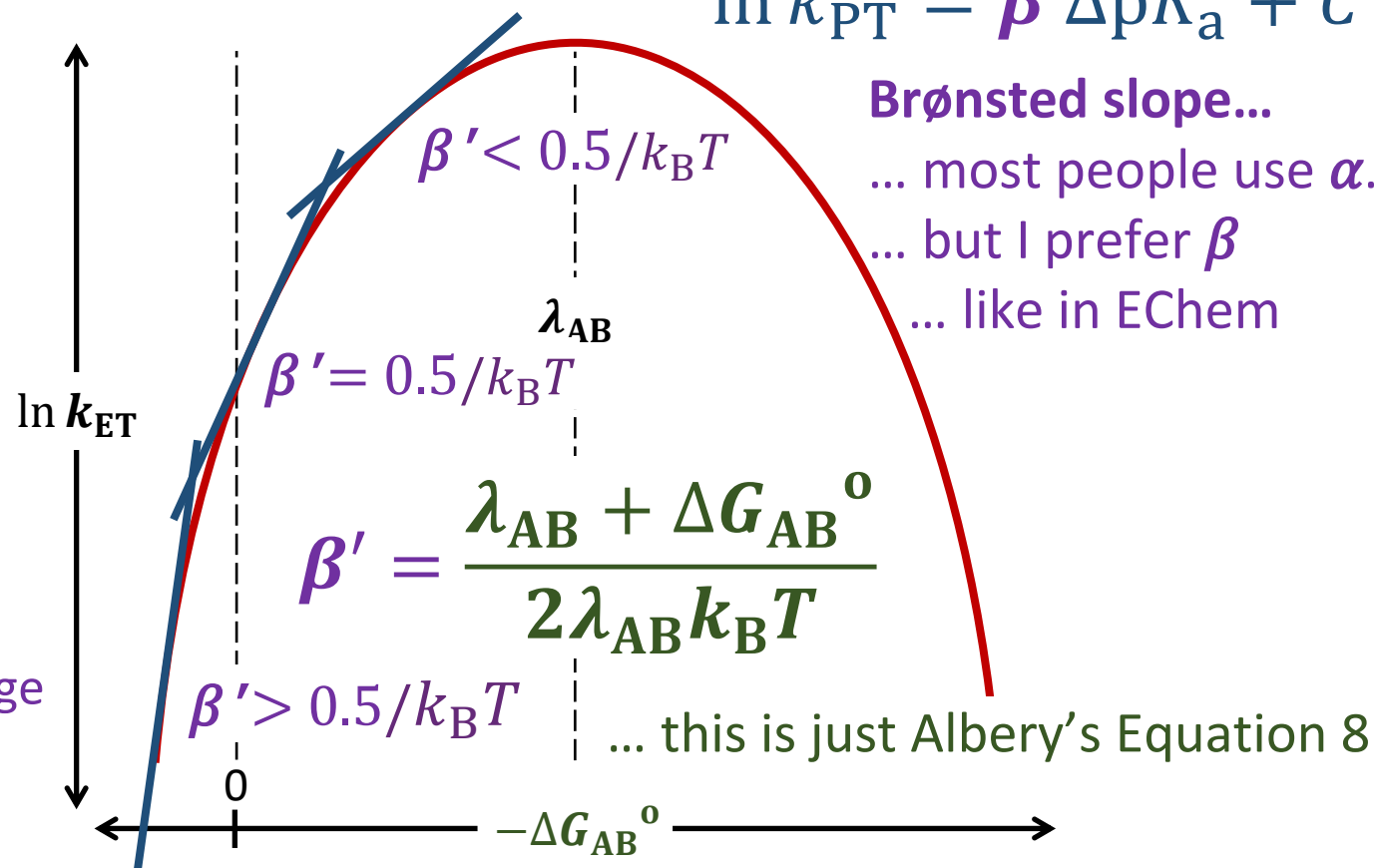
A linear correlation between the logarithm of a [rate constant](#) or [equilibrium constant](#) for one series of reactions and the logarithm of the [rate constant](#) or [equilibrium constant](#) for a related series of reactions. Typical examples of such relations (also known as linear Gibbs energy 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

Cite as: IUPAC. Compendium of Chemical Terminology, 2nd ed. (the "Gold Book"). Compiled by A. D. McNaught and A. Wilkinson. Blackwell Scientific Publications, Oxford (1997). Online version (2019-) created by S. J. Chalk. ISBN 0-9678550-9-8. <https://doi.org/10.1351/goldbook>.

Last revised: February 24, 2014



... trend looks linear over a small enough  $\Delta G_{\text{AB}}^{\circ}$  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

**Table 13** Applications of the Marcus relation

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

# Chemical Kinetics (*summary for today*)

- 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