Lecture #12 of 14

(3: TThF, 5: MT*W*ThF, 4: MT*W*<u>**Th**</u>, 2: TW)

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Summary of Key Equations and Equilibrium

$$A \rightleftharpoons B$$

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

(Chemists should be yawning)

$$\bar{\mu}_B^\alpha - \bar{\mu}_A^\alpha = \Delta G^\alpha = \Delta G^{o,\alpha} + RT \ln Q \text{... where } Q = \frac{a_B^\alpha}{a_A^\alpha} = \frac{\gamma_B^\alpha (c_B^\alpha / c_B^{o,\alpha})}{\gamma_A^\alpha (c_A^\alpha / c_A^{o,\alpha})}$$

$R_{A,f} = -k_f a_A$ $\quad R_{B,f} = +k_f a_A$ $\quad k_j$ (M/s)... a rate!

$R_{A,b} = +k_b a_B$ $\quad R_{B,b} = -k_b a_B$ $\quad k'_j$ (s^{-1})... an inverse time constant!

$$\bar{\mu}_i^\alpha = \left(\frac{\partial G^\alpha}{\partial n_i^\alpha}\right)_{T,p,n_{j\neq i}^\alpha}$$

$$\frac{\partial c_{A,z_o}^\alpha}{\partial t} = -k_f a_A^\alpha + k_b a_B^\alpha = -k'_f c_A^\alpha + k'_b c_B^\alpha = -\frac{\partial c_{B,z_o}^\alpha}{\partial t}$$

Now, consider the reaction to be at equilibrium (3 ways)... $\Delta G^\alpha = 0 = \Delta G^{o,\alpha} + RT \ln Q$

... and so, $\Delta G^{o,\alpha} = -RT \ln K$, with $K = \frac{a_{B,eq}^\alpha}{a_{A,eq}^\alpha} = \frac{\gamma_B^\alpha (c_{B,eq}^\alpha / c_B^{o,\alpha})}{\gamma_A^\alpha (c_{A,eq}^\alpha / c_A^{o,\alpha})}$

And also, $\bar{\mu}_B^\alpha - \bar{\mu}_A^\alpha = 0$... and so, $\bar{\mu}_A^\alpha = \bar{\mu}_B^\alpha$... if that is even helpful

And also, $\frac{\partial c_{A,z_o}^\alpha}{\partial t} = 0 = -\frac{\partial c_{B,z_o}^\alpha}{\partial t} = -k_f a_{A,eq}^\alpha + k_b a_{B,eq}^\alpha$... and so $\frac{k_f}{k_b} = \frac{a_{B,eq}^\alpha}{a_{A,eq}^\alpha} = \frac{\gamma_B^\alpha (c_{B,eq}^\alpha / c_B^{o,\alpha})}{\gamma_A^\alpha (c_{A,eq}^\alpha / c_A^{o,\alpha})} = K$

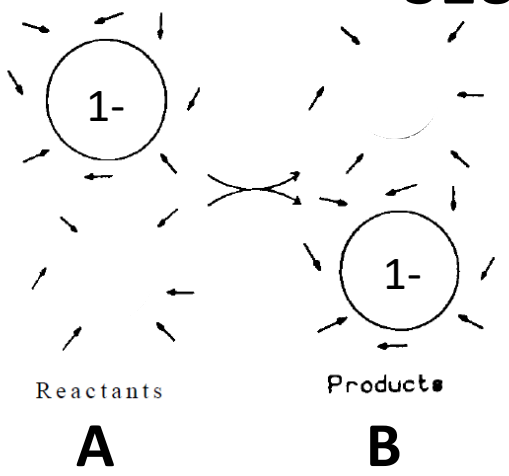
Transport as a Chemical Reaction

$$\frac{\partial c_{A,z_o}}{\partial t} = \sum_j R_{A,j} - \frac{\partial \mathbf{N}_A}{\partial z}$$

… in a reaction "volume" z_o…

… that encompasses z_1 and z_2

$$A^-_{z_1} \rightleftharpoons A^-_{z_2}$$

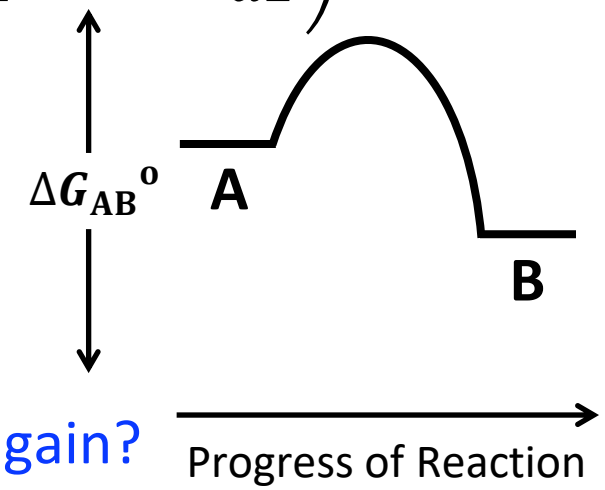


$$\boldsymbol{R_A} = -k_f \boldsymbol{c_{A_{z_1}}} + k_b \boldsymbol{c_{A_{z_2}}} = (\boldsymbol{k_b} - \boldsymbol{k_f})\boldsymbol{c_{A_{z_1}}} + \boldsymbol{k_b}\Delta \boldsymbol{c_A}$$ … where $\boldsymbol{c_{A_{z_2}}} = \boldsymbol{c_{A_{z_1}}} + \Delta \boldsymbol{c_A}$

$$\mathbf{N_A} = \left(-\frac{D_A}{RT}\frac{\partial \bar{\mu}_A}{\partial z}\right)\boldsymbol{c_A} = -\frac{D_A}{RT}\left(\frac{RT}{\boldsymbol{c_A}}\frac{d\boldsymbol{c_A}}{dz} + \frac{d\mu_A^o}{dz} - RT\frac{d(\ln\gamma)}{dz} - RT\frac{d(\ln c_A^o)}{dz} - F\frac{d\phi}{dz}\right)\boldsymbol{c_A}$$

$$= -D_A\frac{d\boldsymbol{c_A}}{dz} + \frac{-D_A F\mathbf{E}'}{RT}\boldsymbol{c_A} \approx -\frac{D_A}{l}\Delta \boldsymbol{c_A} + \frac{-D_A F\mathbf{E}'}{RT}\boldsymbol{c_A}$$

… where $\mathbf{E}'$ is an **effective force field**



$$-\frac{\partial \mathbf{N_A}}{\partial z} \approx \frac{D_A}{l^2}\Delta \boldsymbol{c_A} + \frac{D_A F\mathbf{E}'}{RTl}\boldsymbol{c_A} = \underbrace{"\boldsymbol{k_b}"\Delta \boldsymbol{c_A}}_{(diffusion)} + \underbrace{"(\boldsymbol{k_b} - \boldsymbol{k_f})"\boldsymbol{c_A}}_{(drift)}$$

… what is $\boldsymbol{D_A}$ again?

… since the reaction volume is >1 Å^3 , l > 1 Å… and D(aq) < 10^{-4} cm^2/s… $\boldsymbol{k_{D(aq)}}$ **< 10^{12} s^{-1} = (>1 ps)$^{-1}$**

Chemical Kinetics

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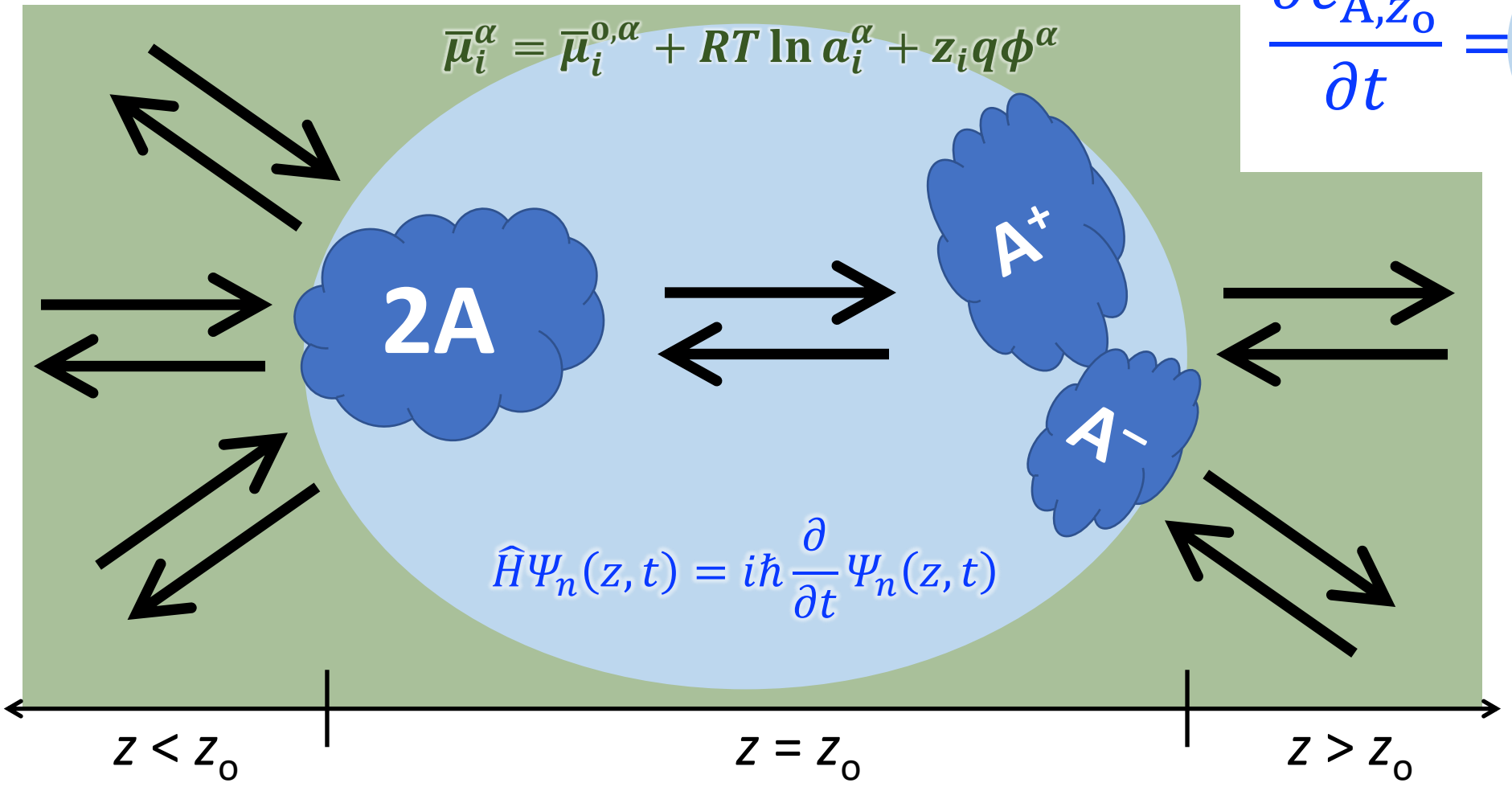
Quiz Time!

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

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



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…

$$\frac{\partial c_{\mathrm{A},z_\mathrm{o}}}{\partial t} = \sum_j R_{\mathrm{A},j} - \frac{\partial \mathbf{N}_\mathrm{A}}{\partial z}$$

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. $R_\mathrm{A} = k_3 a_\mathrm{B} a_\mathrm{D}^2 \approx k_3[\mathrm{B}][\mathrm{D}]^2$
(to a first order, this is driven by differences in chemical potential of various species, μ_j)

rate of change of the molar flux (**N**) of species A with respect to position (*z*),
e.g. $\mathbf{N}_\mathrm{A} = -D\frac{\partial a_\mathrm{A}}{\partial z}$
(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)

$$A_{z_1} \rightleftharpoons A_{z_2}$$

$$\frac{\partial c_{A,z_o}}{\partial t} = \boxed{-\frac{\partial \mathbf{N}_A}{\partial z}}$$

(MechEs should be yawning)

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

… 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)…

$$\mathbf{N}_A = -\boldsymbol{D}_A \frac{\partial\left(\bar{\mu}_A/_{RT}\right)}{\partial z} c_A$$

What are the directions for the dimensions of $\boldsymbol{D}_A$?

BOLD ((cm^2/s) / cm) = cm/s… a velocity!

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

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

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

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

Let's expand the total differential…

… assuming a species, e, with valency, z_e, equal to –1

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

$$\text{Flux}_{z,e} = -\frac{\sigma_e}{F^2}\frac{d\bar{\mu}_e}{dz} - S_{e,T_e}\frac{dT_e}{dz}$$

$$\left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_{j\neq i}} = \bar{\mu}_i = \mu_i + z_i q\phi$$

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

$$\mu_i = \mu_i^0 + kT_i \ln a_i = \mu_i^0 + kT_i \ln\left(\frac{\gamma_i n_i}{n_i^0}\right)$$

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

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

$$\text{Flux}_{z,e} = -D_e\frac{dn_e}{dz} + \frac{qD_e n_e}{kT_e}\frac{d\phi}{dz}$$

… assuming spatially invariant μ_e^0, γ_e, n_e^0, T_e

Drift–Diffusion equation

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

Outer Reorganization Energy

Marcus–Hush (1950s–1960s)

theoretical (semiclassical) rate constant equation

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

$$\Delta G_{\mathrm{AB}}^{\neq} = \frac{\left(\lambda_{\mathrm{AB}} + \Delta G_{\mathrm{AB}}^{\circ}\right)^2}{4\lambda_{\mathrm{AB}}}$$

… but what causes this parabolic relationship?…

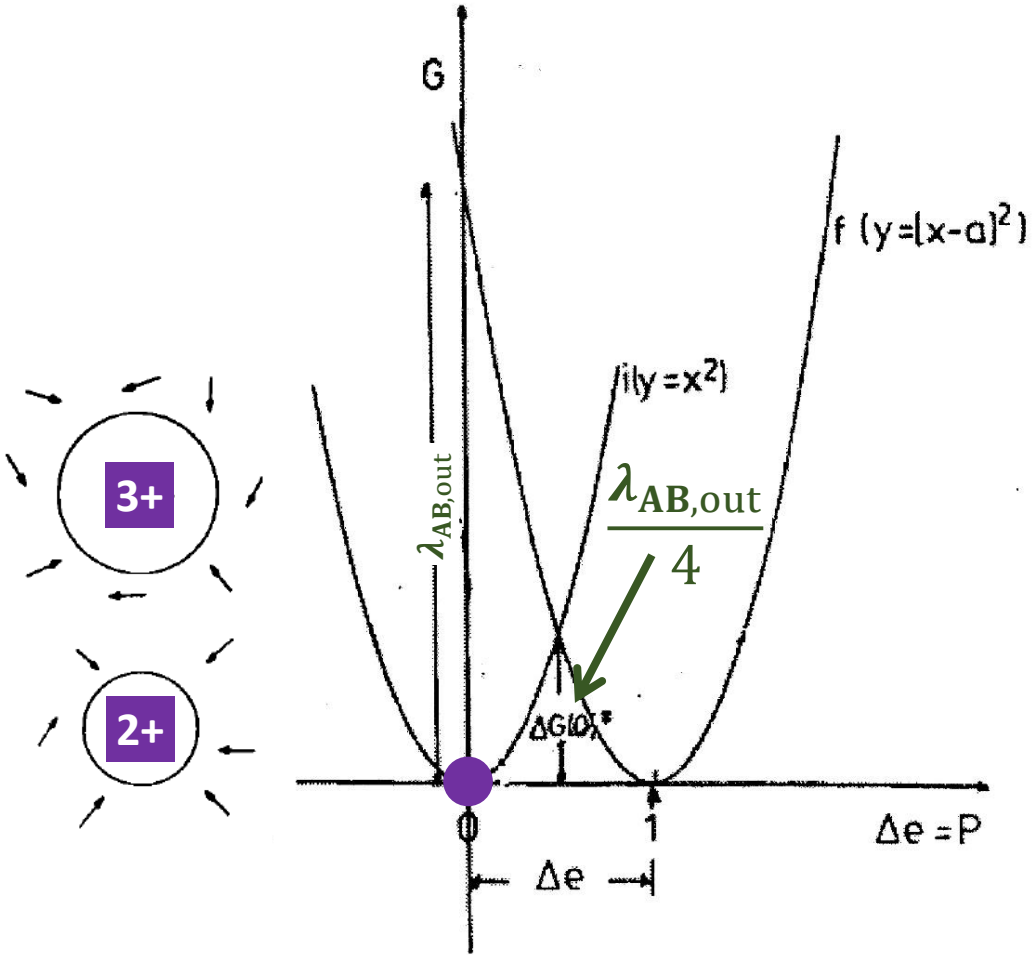
… what physical expression results in a quadratic dependence on **charge**?

… classical electrostatics… of the solvent!

… dielectric continuum model…

… $G_{\mathrm{out}} \approx 1$ eV in water

… G_{out} decreases as permittivity decreases



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

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

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

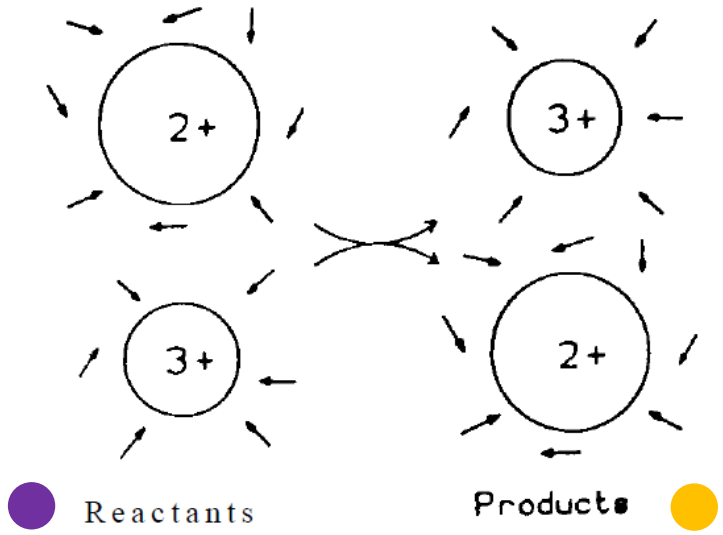
… this is for a harmonic oscillator

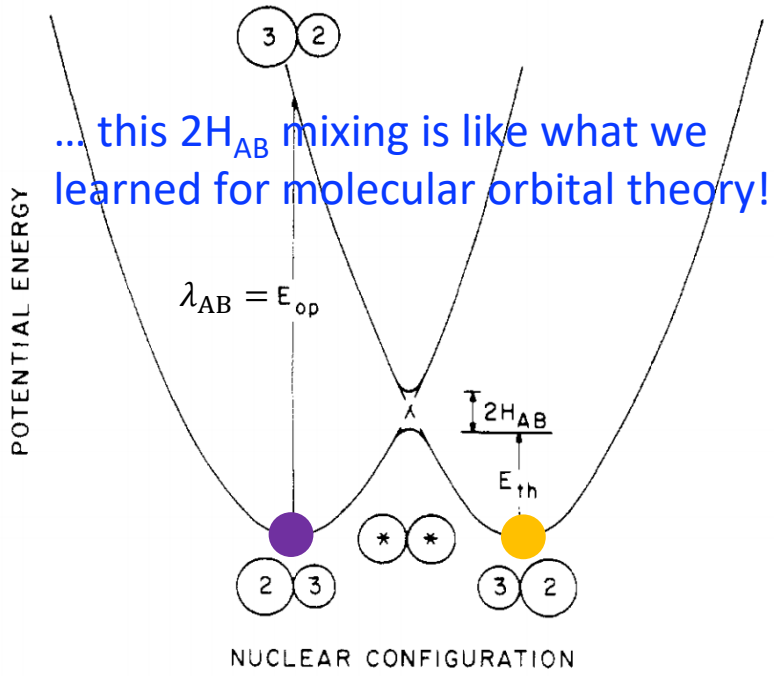
… with force constants, f_l…

… and yes, it's another parabola!

Electron Transfer in Solution

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





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

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

More Quantum Mechanics

Poisson's Equation (from Gauss's law)

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

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

for a point charge… look familiar?

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

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

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

… 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…

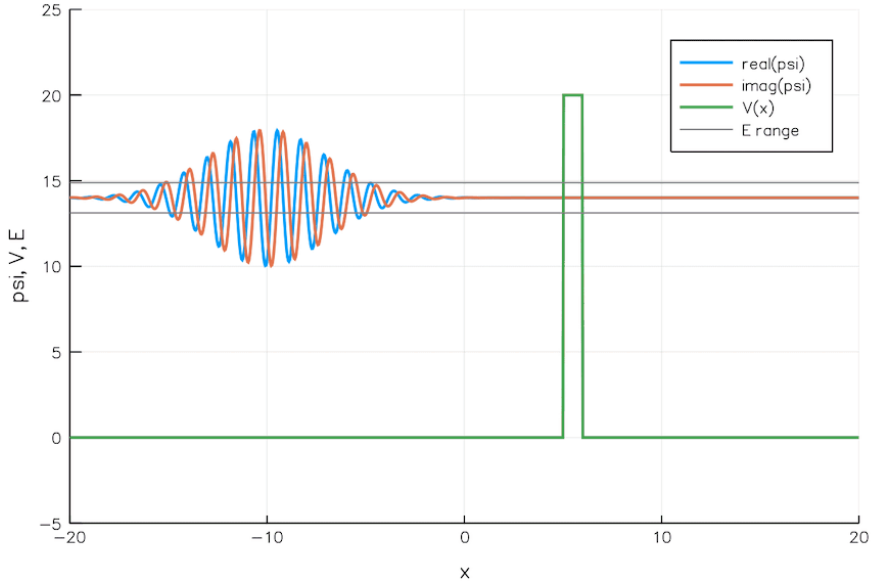
Probability Density$(x) = |\psi_n(x)|^2 = \psi_n^*(x)\psi_n(x)$

… 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

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

quantum adiabatic electronic coupling

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

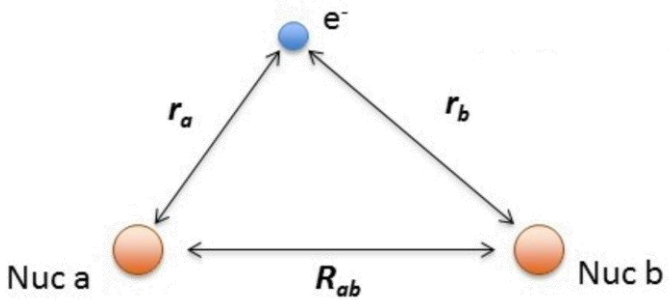
… remember the simplicity of H_2^+… which resembles λ_{out} math

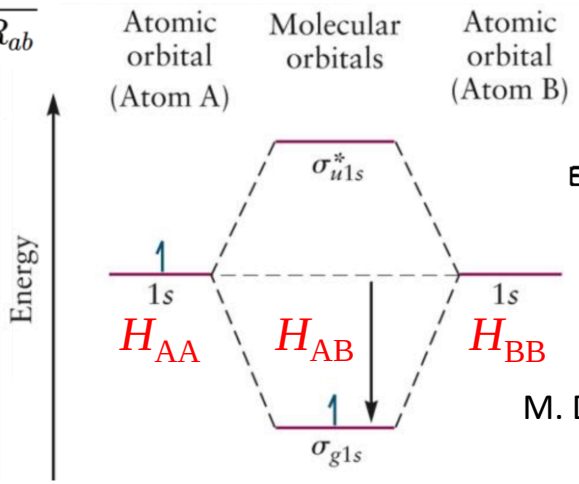
$$\hat{H}(r, R_{ab}) = -\frac{\hbar^2}{2m}\nabla_a^2 - \frac{\hbar^2}{2m}\nabla_b^2 - \frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_a} - \frac{e^2}{4\pi\epsilon_0 r_b} + \frac{e^2}{4\pi\epsilon_0 R_{ab}}$$

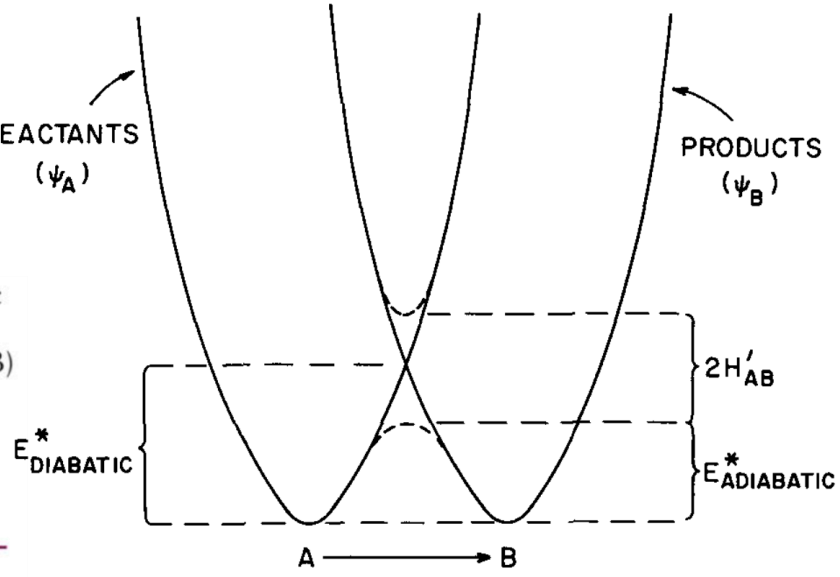
matrix

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

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







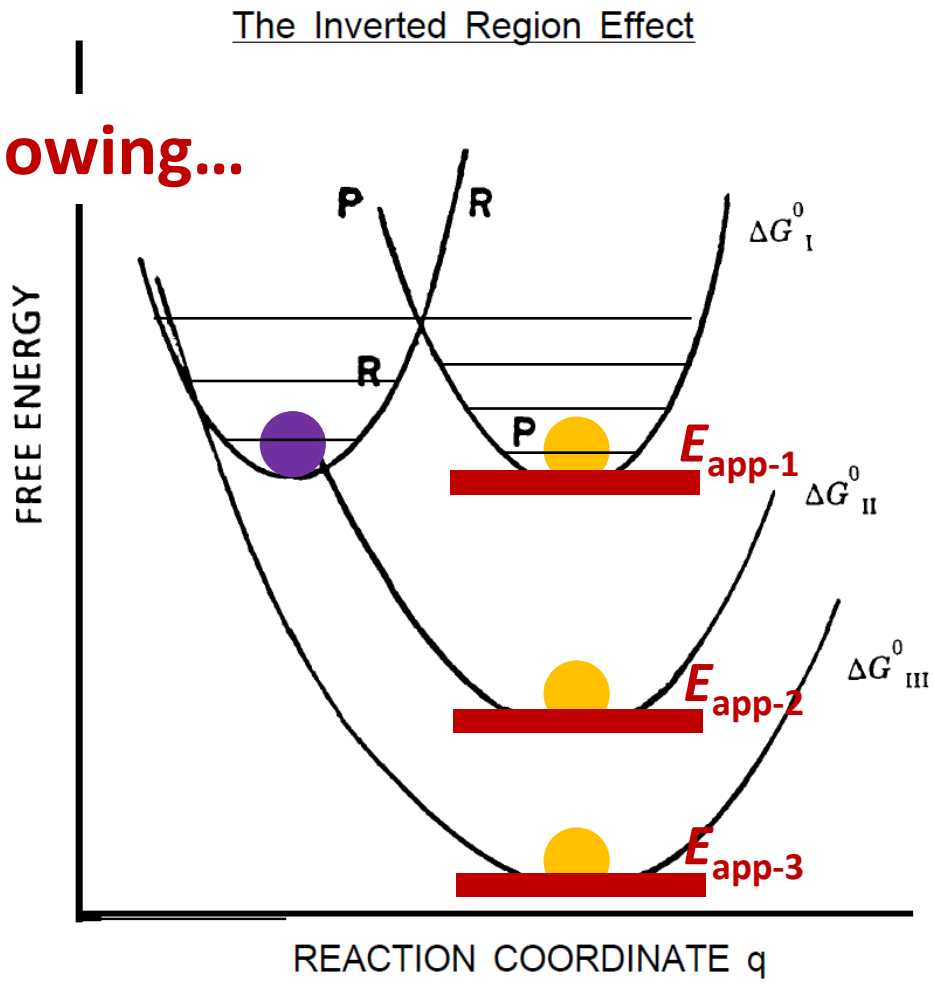
M. D. Newton, *Int. J. Quantum. Chem.*, **1980**, *18*, 363–391
N. Sutin, *Acc. Chem. Res.*, **1982**, *15*, 275–282

Observation of Inverted Region Behavior

Marcus–Hush (1950s–1960s)

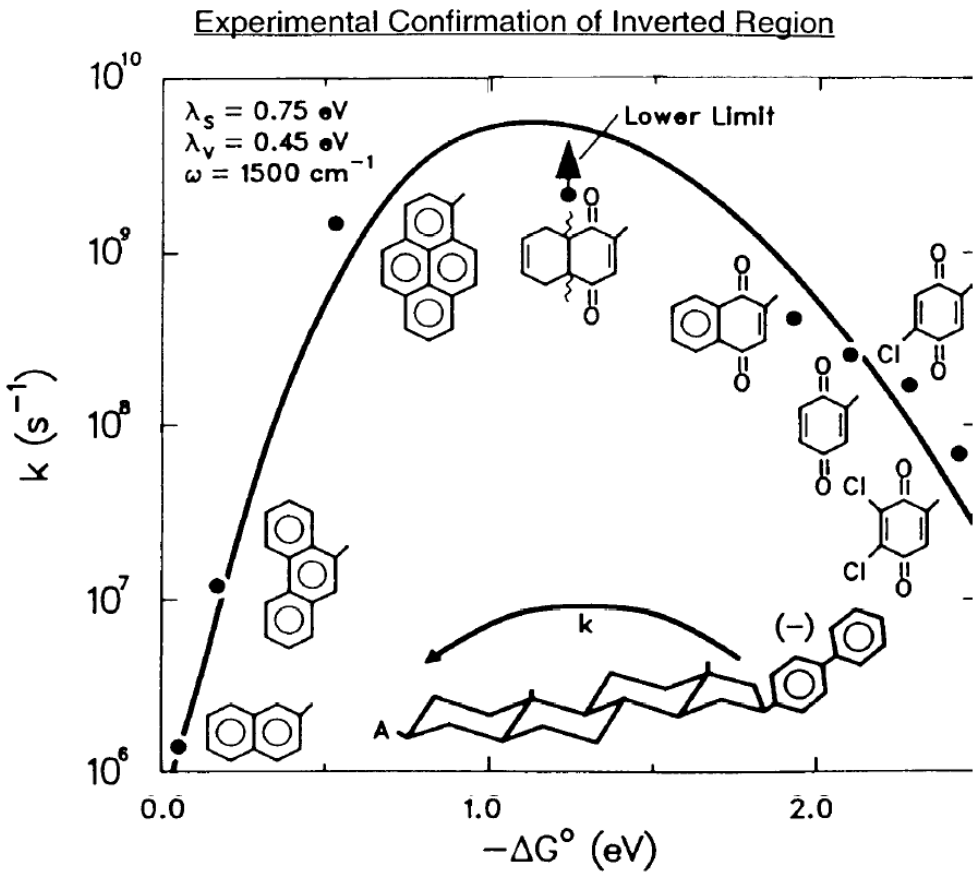
theoretical (semiclassical) rate constant equation

Foreshadowing…



Closs–Miller (1984)

observation 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

Linear Free Energy Relationships (LFERs)

Marcus–Hush (1950s–1960s)

theoretical (semiclassical) rate constant equation

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.*

Div. III PDF Text JSON History Feedback Last revised: February 24, 2014

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

J. Albery, *Ann. Rev. Phys. Chem.*, **1980**, *31*, 227–263

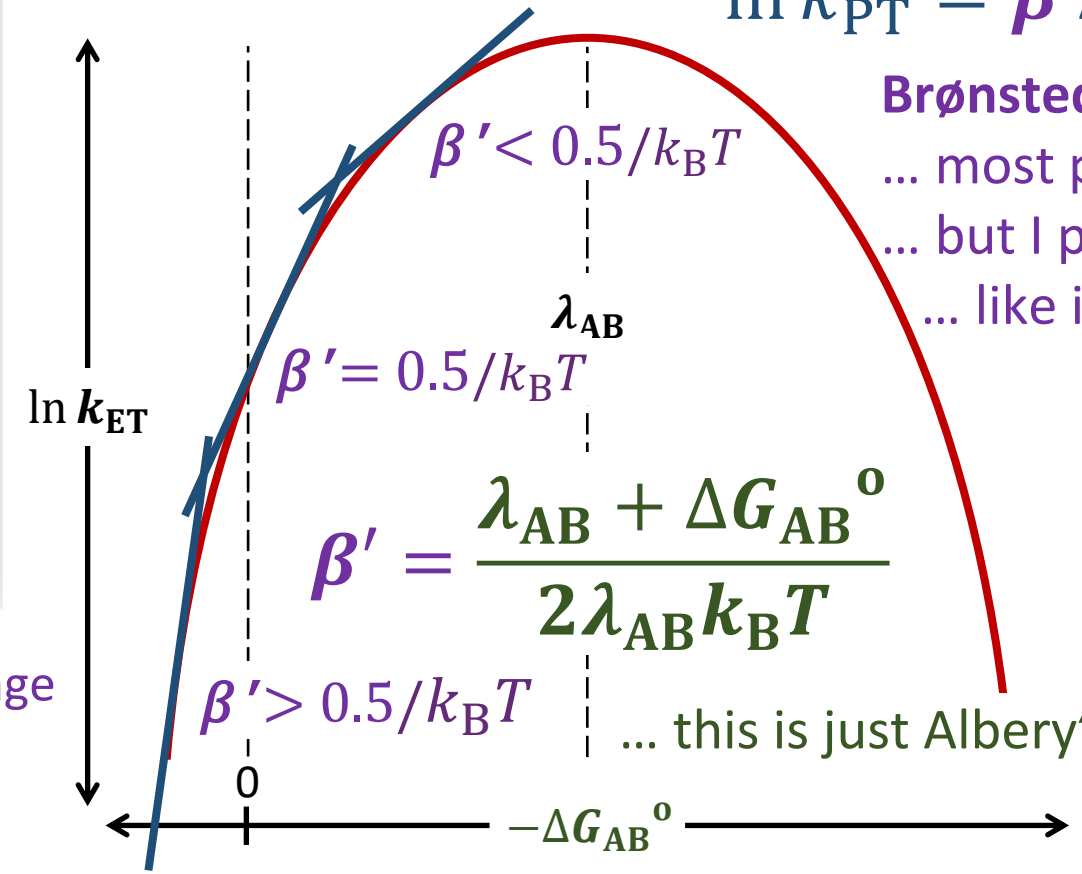
R. A. Marcus, *Farad. Discuss. Chem. Soc.*, **1982**, *74*, 7–15

Brønsted–Pedersen (1924)

empirical LFER for proton transfer

$$\ln k_{PT} = -\boldsymbol{\beta}\, pK_a + C$$

$$\ln k_{PT} = \boldsymbol{\beta}\, \Delta pK_a + C'$$



$$\boldsymbol{\beta'} = \frac{\boldsymbol{\lambda_{AB} + \Delta G_{AB}{}^{o}}}{\boldsymbol{2\lambda_{AB} k_B T}}$$

Brønsted slope...

... most people use $\boldsymbol{\alpha}$...

... but I prefer $\boldsymbol{\beta}$

... like in EChem

... this is just Albery's Equation 8

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^{θ}	
	αD isotope effects measure C^{+} character	
Nucleophilic additions	Provides alternative explanation to Ritchie relation	
	Values of $\bar{G}$ 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

Charge Transfer across Electrified Interfaces

… aren't these so-called "heterogeneous electron-transfer reactions"?… Sure.

$$e^{-,M} + O \rightleftharpoons R$$

FYI: For each c_O and c_R, electrochemical equilibrium ($j = 0$) is attained via interfacial charge transfer to alter $\Delta\phi^{M|s}$

$$R_O = \frac{\partial c_{O,z_o}}{\partial t} = -\boldsymbol{k_f} c_O + \boldsymbol{k_b} c_R$$

… R_O is a rate… with units of M/s (= mol dm^{-3} s^{-1})

… $\boldsymbol{k_j}$ (s^{-1}) is an inverse time constant!

$$j_E = nF\left(-\boldsymbol{k'}_{f,E} c_{O,z_o} + \boldsymbol{k'}_{b,E} c_{R,z_o}\right)$$

… j_E is a current density… with units of A/cm^2 (= C cm^{-2} s^{-1})

… $\boldsymbol{k'}_{j,E}$ (cm s^{-1}) is a velocity!

… as a specific case choose $\boldsymbol{E^{o\prime}}$… and thus, $j_{E^{o\prime}} = nF\left(-\boldsymbol{k'}_{f,E^{o\prime}} c_{O,z_o} + \boldsymbol{k'}_{b,E^{o\prime}} c_{R,z_o}\right)$

But how does this lead to the Butler–Volmer eqn?…

$$0 = j_{E^{o\prime}} = nF\left(-\boldsymbol{k'}_{f,E^{o\prime}} + \boldsymbol{k'}_{b,E^{o\prime}}\right)$$

$$j_E = \boldsymbol{j_o}\left\{\exp\left(\frac{(1-\boldsymbol{\beta})F\boldsymbol{\eta}}{RT}\right) - \exp\left(\frac{-\boldsymbol{\beta}F\boldsymbol{\eta}}{RT}\right)\right\}$$

$$\boldsymbol{k'}_{f,E^{o\prime}} = \boldsymbol{k'}_{b,E^{o\prime}} = \boldsymbol{k^0}$$

$$\boldsymbol{\eta} = \left(\boldsymbol{E} - \boldsymbol{E_{eq}}\right) = \boldsymbol{E_{app}} = \frac{\Delta G^o}{-nF}$$

… where $\boldsymbol{\eta}$ (V) is overpotential

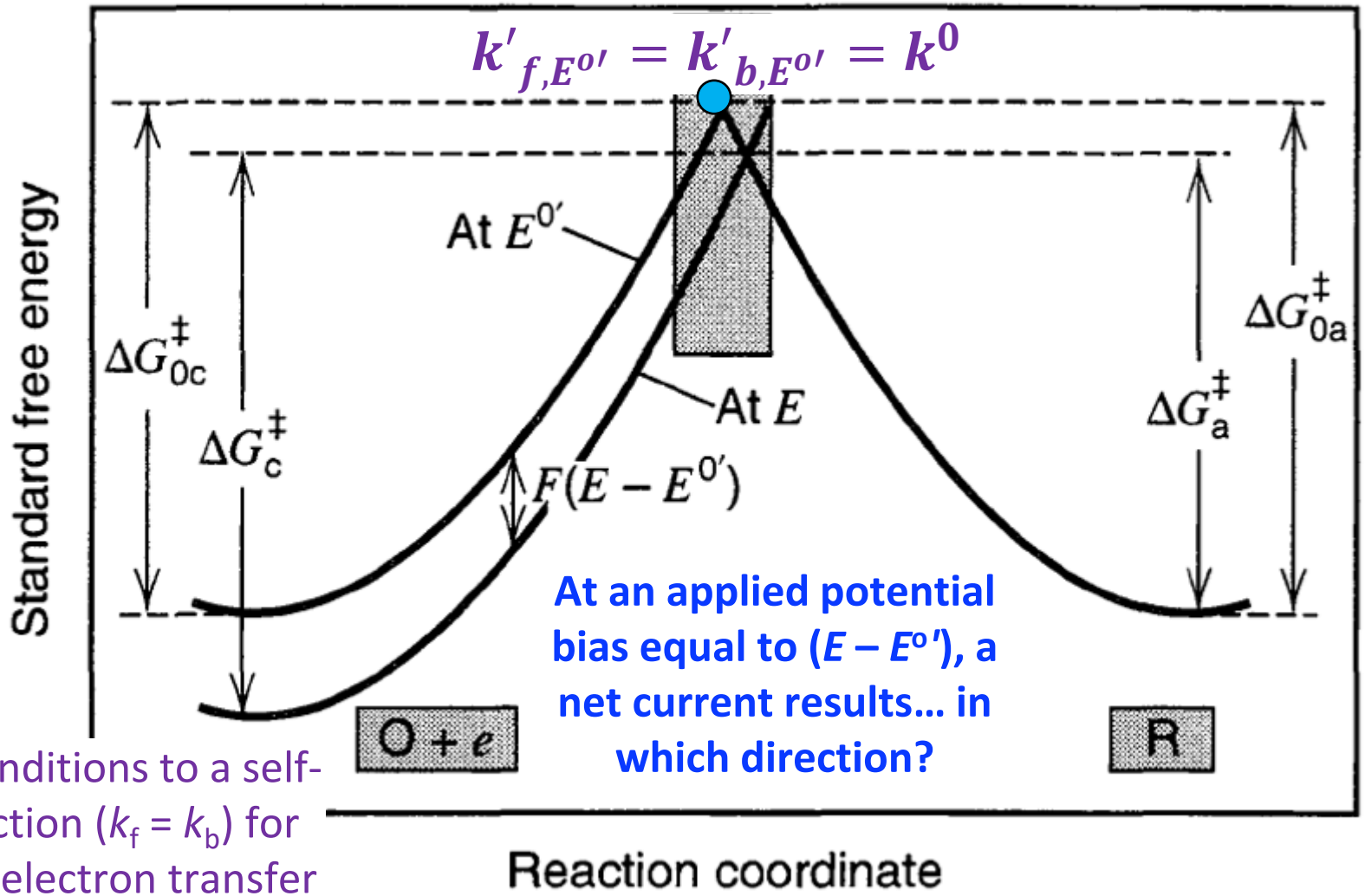
… this suggests that we will replace $\boldsymbol{k'}_{j,E}$ velocity rate constants…

… with thermodynamic driving force terms!… But how?… **M–H!**

Charge Transfer across Electrified Interfaces

$$e^{-,M} + O \rightleftharpoons R$$

Bard & Faulkner, Chapter 3, Figure 3.3.2, Page 95



At an applied potential bias equal to ($E - E^{o\prime}$), a net current results… in which direction?

Key Electrochemical Information

- In electrochemistry, application of a potential, E_{app}, varies the electro-chemical potential of electrons (e^-) in the (M)etal working electrode, $\bar{\mu}_e^{\text{M}}$
- Based on thermodynamics, when written as a reduction reaction, changing $\bar{\mu}_e^{\text{M}}$ alters the free energy **(and one assumes also the standard-state free energy)** of the reactants, as $\Delta G_{\text{A}} = \bar{\mu}_e^{\text{M}} + \bar{\mu}_{\text{O}}$ **(and $\Delta G^{\text{o}}_{\text{A}} = \bar{\mu}_e^{\text{M}} + \bar{\mu}^{\text{o}}_{\text{O}}$)**
- *The derivation here assumes that the electrode is inert, e.g. not like battery electrodes*

* analogous conditions to a self-exchange reaction ($k_f = k_b$) for homogeneous electron transfer

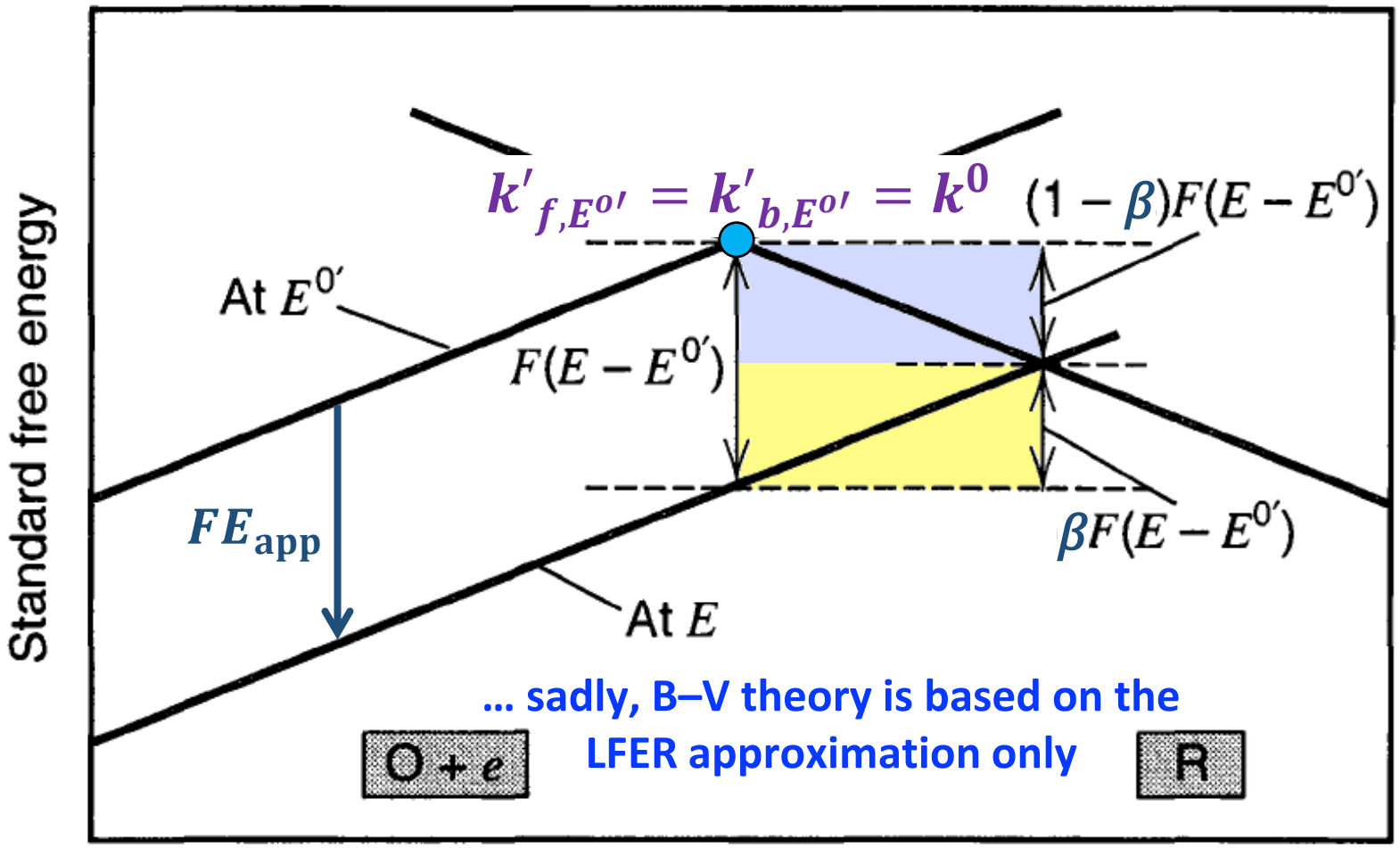
Charge Transfer across Electrified Interfaces

$$e^{-,M} + O \rightleftharpoons R$$

Bard & Faulkner, Chapter 3, Figure 3.3.2, Page 95

Key Electrochemical Information

- In electrochemistry, application of a potential, E_{app}, varies the electro-chemical potential of electrons (e^-) in the (M)etal working electrode, $\bar{\mu}_e^{\text{M}}$
- Based on thermodynamics, when written as a reduction reaction, changing $\bar{\mu}_e^{\text{M}}$ alters the free energy **(and one assumes also the standard-state free energy)** of the reactants, as $\Delta G_{\text{A}} = \bar{\mu}_e^{\text{M}} + \bar{\mu}_{\text{O}}$ **(and $\Delta G_{\text{A}}^{\text{o}} = \bar{\mu}_e^{\text{M}} + \bar{\mu}_{\text{O}}^{\text{o}}$)**
- Based on approximations, altering ΔG_{A} changes all ΔG values on the reaction coordinate relative to ΔG_{A}, and not the parabolic/linear shape of the reactant "surface"… **Should it?**



$\beta + (1-\beta) = 1$

Butler–Volmer equation

$$e^{-,M} + O \rightleftharpoons R$$

$$j_E = nF\left(\boldsymbol{k'}_{\boldsymbol{b},\boldsymbol{E}} c_{\mathrm{R},z_\mathrm{o}} - \boldsymbol{k'}_{\boldsymbol{f},\boldsymbol{E}} c_{\mathrm{O},z_\mathrm{o}}\right)$$

… for this example, let's assume that $n = 1$…

$$j_E = F\boldsymbol{k^0}\left\{c_{\mathrm{R},z_\mathrm{o}} \exp\left(\frac{(1-\boldsymbol{\beta})F(E-E^{\mathrm{o}\prime})}{RT}\right) - c_{\mathrm{O},z_\mathrm{o}} \exp\left(\frac{-\boldsymbol{\beta}F(E-E^{\mathrm{o}\prime})}{RT}\right)\right\}$$

Current–Potential Characteristic

$$j_E = \boldsymbol{j_\mathrm{o}}\left\{\frac{c_{\mathrm{R},z_\mathrm{o}}}{c_\mathrm{R}^*} \exp\left(\frac{(1-\boldsymbol{\beta})F\boldsymbol{\eta}}{RT}\right) - \frac{c_{\mathrm{O},z_\mathrm{o}}}{c_\mathrm{O}^*} \exp\left(\frac{-\boldsymbol{\beta}F\boldsymbol{\eta}}{RT}\right)\right\}$$

$$\boldsymbol{\eta} = \left(\boldsymbol{E} - \boldsymbol{E_\mathrm{eq}}\right) = \boldsymbol{E_\mathrm{app}}$$

$$\boldsymbol{j_\mathrm{o}} = F\boldsymbol{k^0} c_\mathrm{R}^{*\,\beta} c_\mathrm{O}^{*\,(1-\beta)}$$

Current–Overpotential Equation

… c^* means bulk concentration… conversion is trivial using $\boldsymbol{E_\mathrm{eq}} = E^{\mathrm{o}\prime} - \frac{RT}{nF}\ln\frac{c_\mathrm{R}^*}{c_\mathrm{O}^*}$

$$j_E = \boldsymbol{j_\mathrm{o}}\left\{\exp\left(\frac{(1-\beta)F\boldsymbol{\eta}}{RT}\right) - \exp\left(\frac{-\beta F\boldsymbol{\eta}}{RT}\right)\right\}$$

Butler–Volmer Equation

… assuming one rapidly stirs

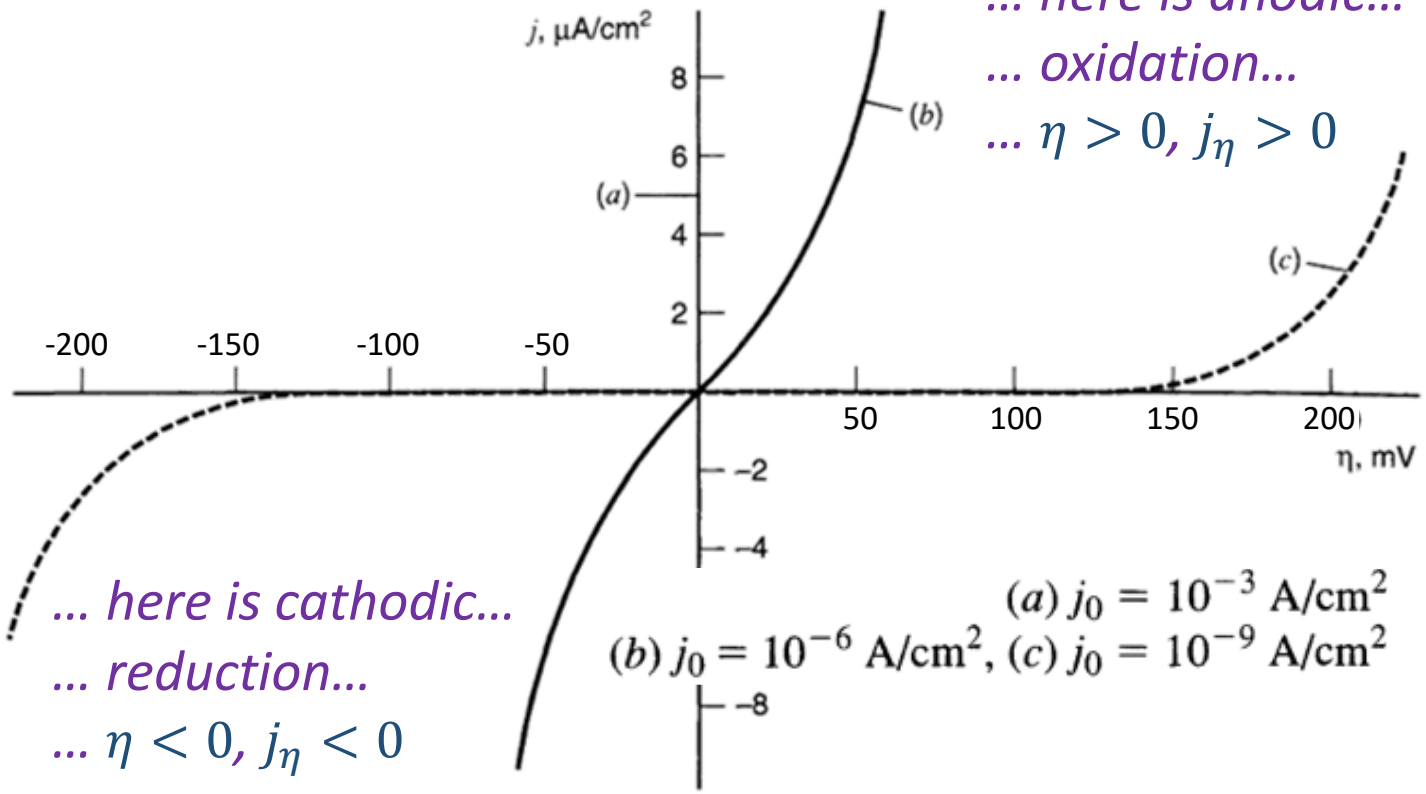
Tafel Slopes

$$\mathrm{TS_{cath}}^{-1} = \left(\frac{d(\log|j_E|)}{d|\boldsymbol{\eta}|}\right)_\mathrm{cath} = \frac{-\boldsymbol{\beta}F}{2.303RT}$$

$$\mathrm{TS_{an}}^{-1} = \left(\frac{d(\log j_E)}{d\boldsymbol{\eta}}\right)_\mathrm{an} = \frac{(1-\boldsymbol{\beta})F}{2.303RT}$$

Butler–Volmer equation

… let's examine effects of j_o (or k^0)…

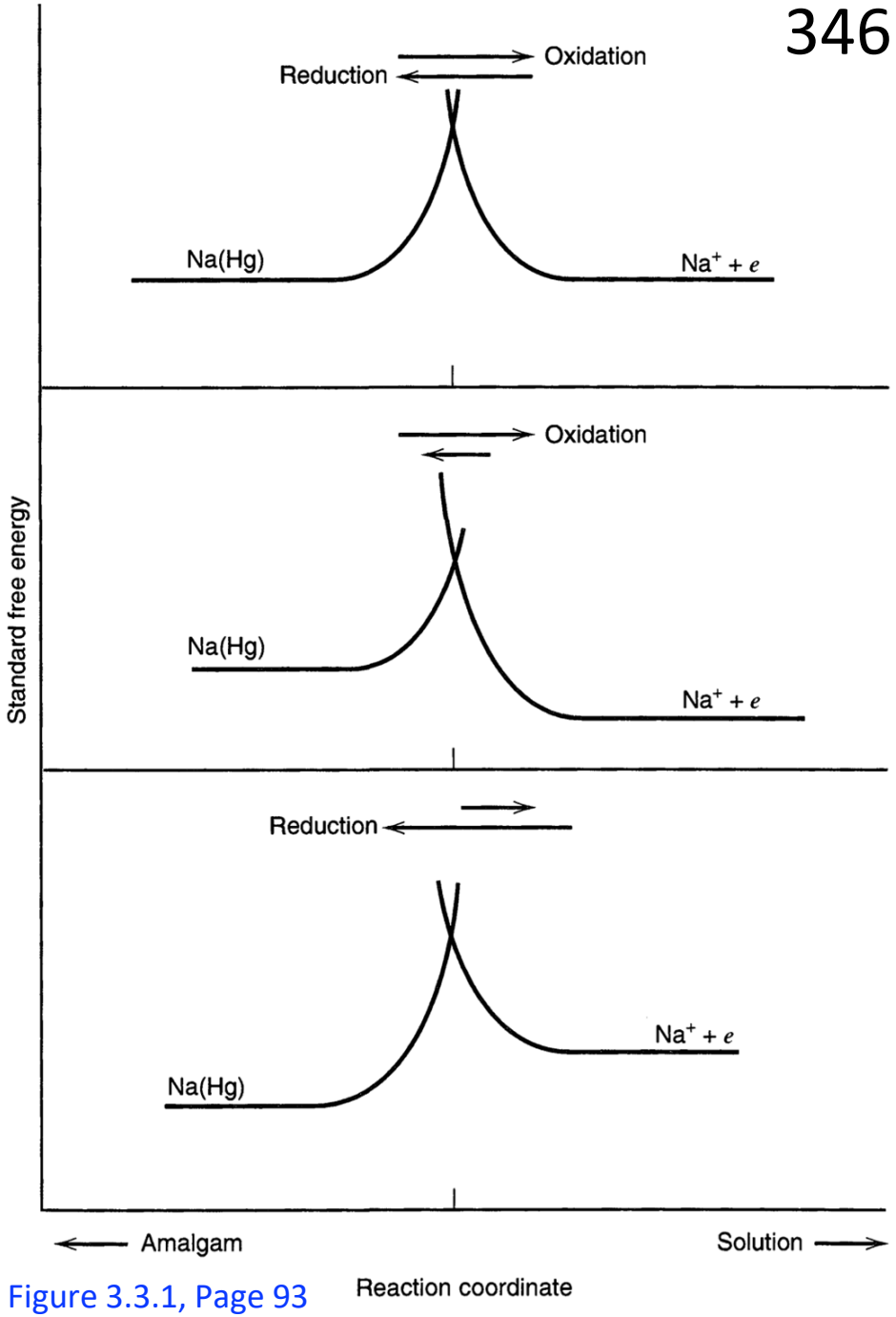


… here is anodic…
… oxidation…
… $\eta > 0$, $j_\eta > 0$

… here is cathodic…
… reduction…
… $\eta < 0$, $j_\eta < 0$

Bard & Faulkner, Chapter 3, Figure 3.4.2, Page 101

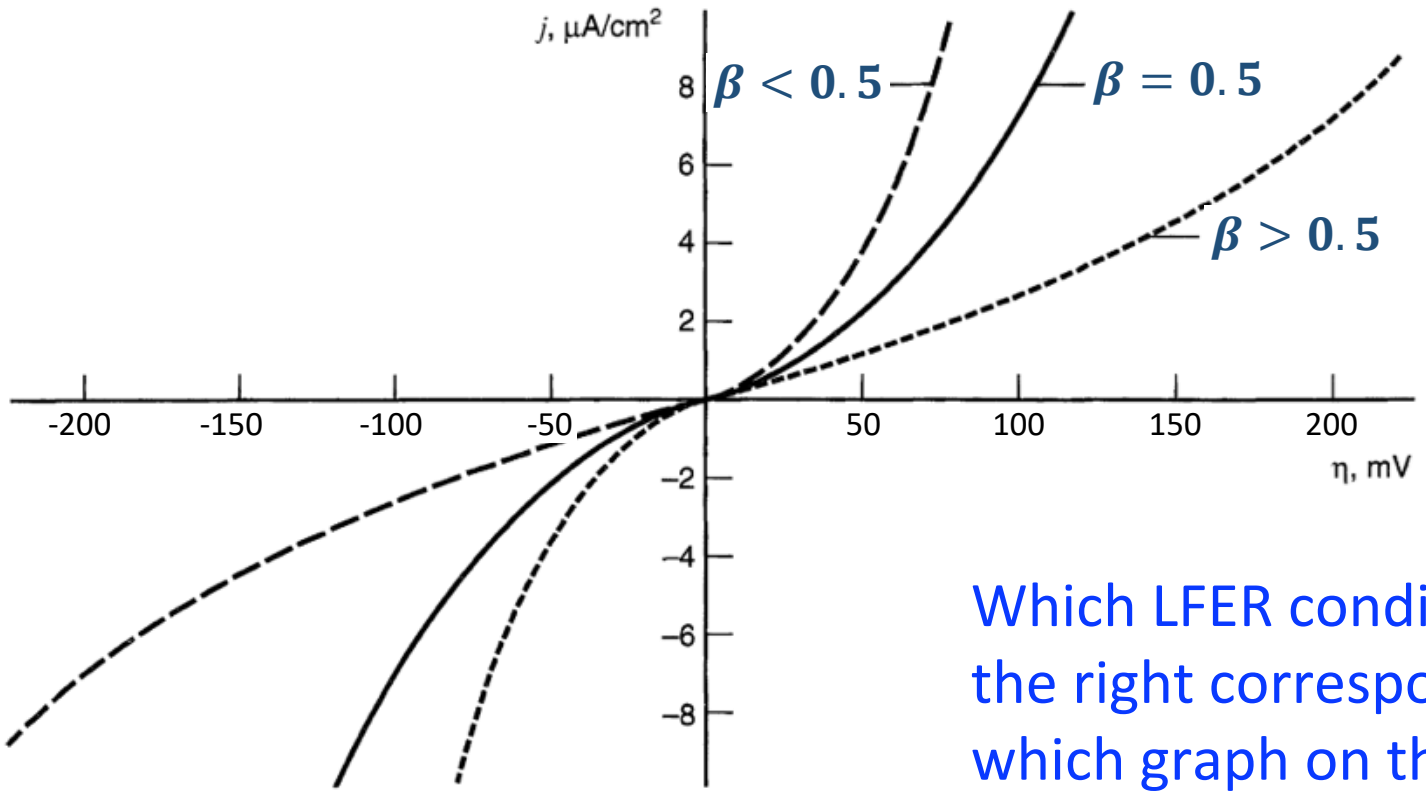
… recall that… $\boldsymbol{\eta} = (\boldsymbol{E} - \boldsymbol{E}_{\mathbf{eq}}) = \boldsymbol{E}_{\mathbf{app}} = \dfrac{\Delta G^{\mathrm{o}}}{-nF}$



Bard & Faulkner, Chapter 3, Figure 3.3.1, Page 93

Butler–Volmer equation

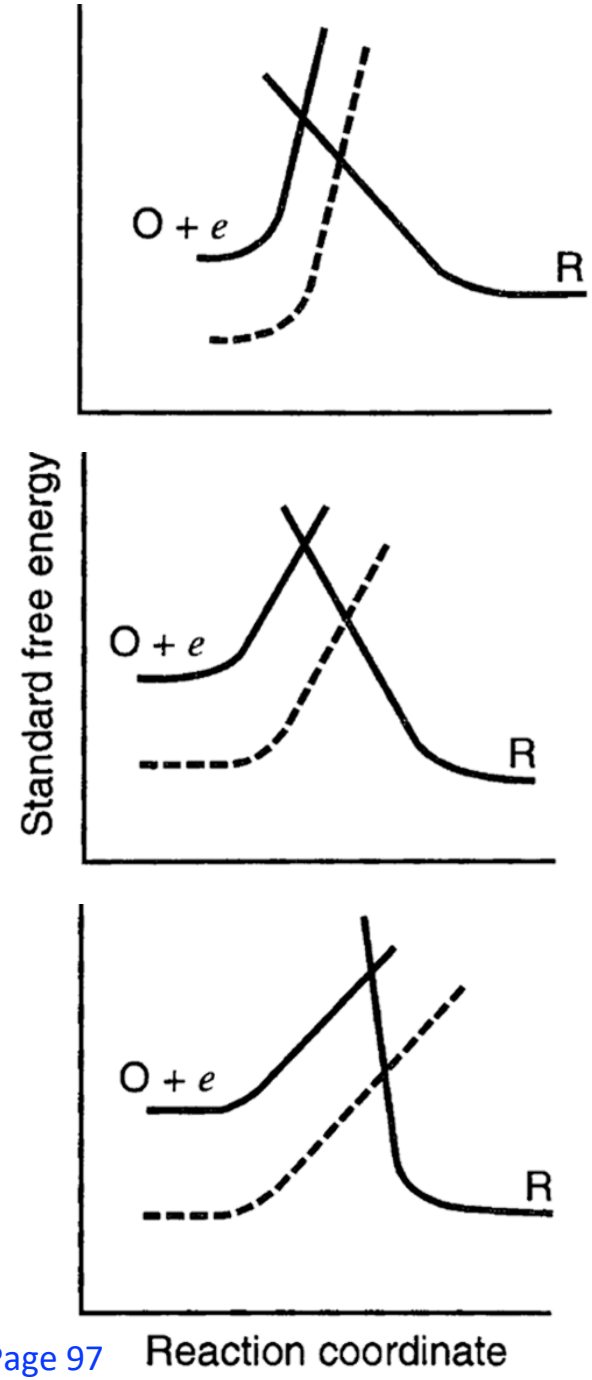
… let's examine effects of $\boldsymbol{\beta}$ (or Tafel slope)…



Bard & Faulkner, Chapter 3, Figure 3.4.3, Page 101

Which LFER condition on the right corresponds to which graph on the left?

… recall that… $\boldsymbol{\eta} = (\boldsymbol{E} - \boldsymbol{E}_{\mathbf{eq}}) = \boldsymbol{E}_{\mathbf{app}} = \frac{\Delta G^{\mathrm{o}}}{-nF}$



Bard & Faulkner, Chapter 3, Figure 3.3.4, Page 97

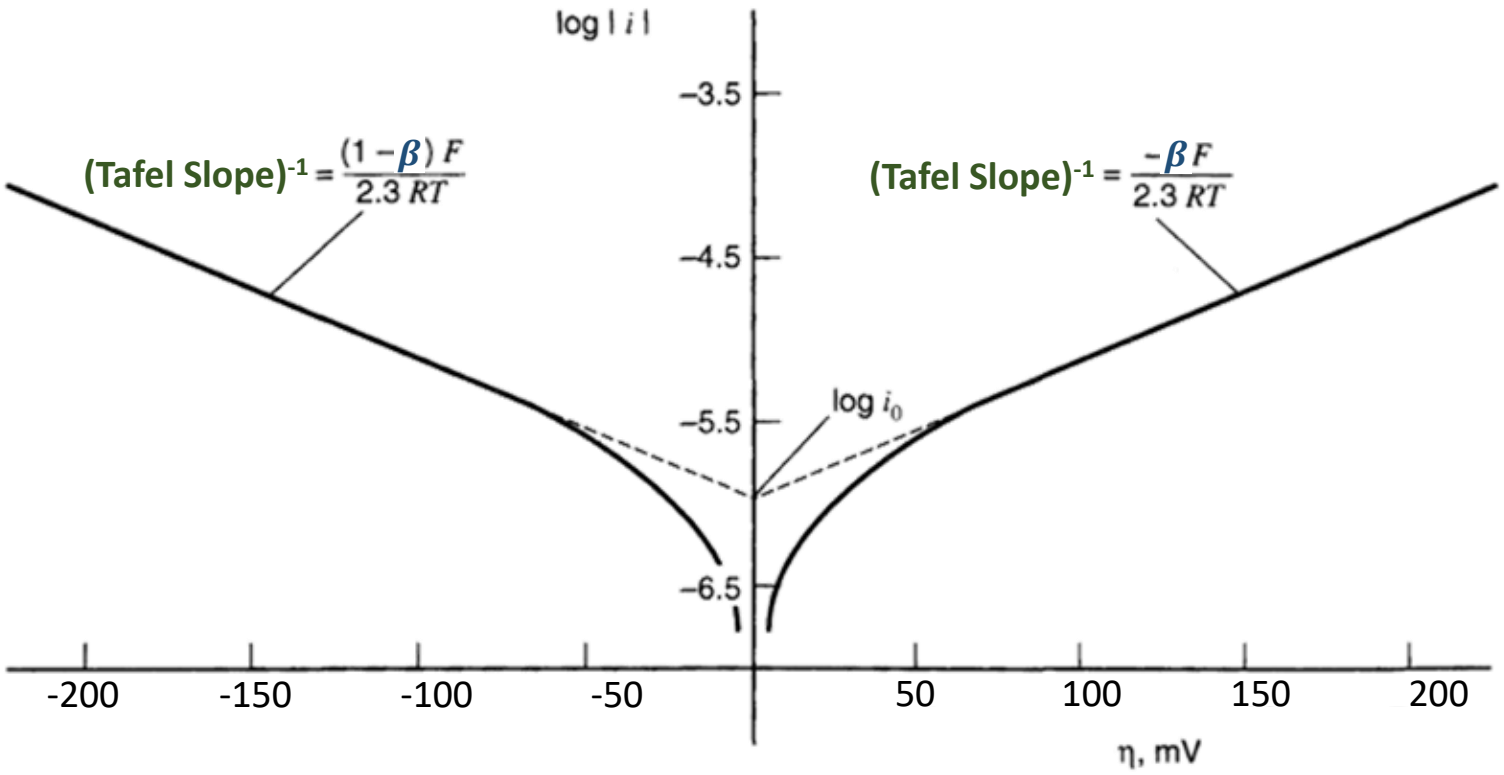
Butler–Volmer equation

… let's examine the tradeoff of j_o and Tafel Slope…

… the latter has units of mV/decade…

… wait, didn't Marcus teach us this should be a parabola?

… then, why is this "potential relationship" so linear?



Bard & Faulkner, Chapter 3, Figure 3.4.4, Page 103

Quick Quiz: Which catalyst is best?

(A) j_o = 10^{-4} A cm^{-2}, TS = 120 mV decade^{-1}

(B) j_o = 10^{-7} A cm^{-2}, TS = 60 mV decade^{-1}

Well, it depends on the desired j_E…

For 1 mA cm^{-2}, *(A)* is best, but…

For 1 A cm^{-2}, *(B)* is best…

… because catalyst *(A)* requires **η = 480 mV**, while catalyst *(B)* requires **η = 420 mV**!

… and neither may be "best" in practice, if they aren't stable or selective for the reaction of interest!

Take-home point: Each current density has a corresponding overpotential!

Fermi's (Second) Golden Rule

$$j_E = nF\left(-k'_{f,E}c_{O,z_o} + k'_{b,E}c_{R,z_o}\right)$$

k'_j (cm s^{-1})… a velocity!

$$\lambda_{if} = \frac{2\pi}{\hbar}\left|M_{if}\right|^2 \rho_f$$

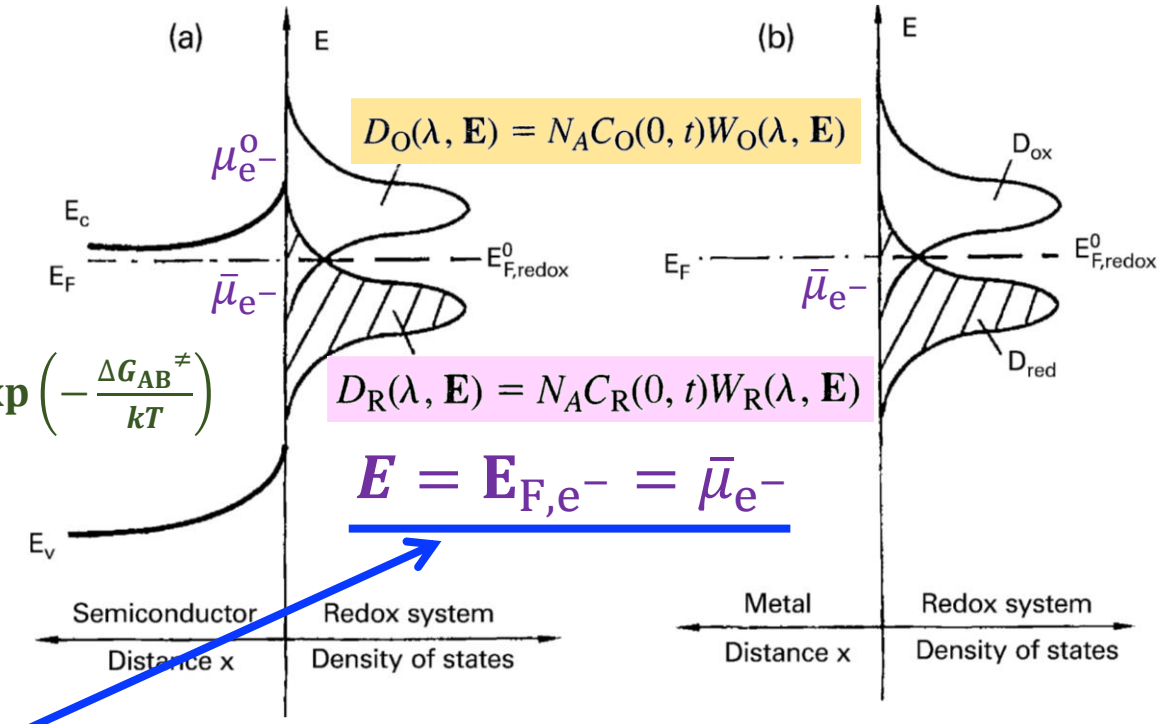
Recall M–H… $k_{ET} = \frac{2\pi}{\hbar}|H_{DA}|^2 \frac{1}{\sqrt{4\pi\lambda_{AB}kT}} \exp\left(-\frac{\Delta G_{AB}^{\neq}}{kT}\right)$

Transition probability

Matrix element for the interaction

Density of final states (DoS)

… divide the DoS by c_{i,z_o}…



$D_O(\lambda, \mathbf{E}) = N_A C_O(0,t) W_O(\lambda, \mathbf{E})$

$D_R(\lambda, \mathbf{E}) = N_A C_R(0,t) W_R(\lambda, \mathbf{E})$

$$E = \mathbf{E}_{F,e^-} = \bar{\mu}_{e^-}$$

applied potential

R. Memming, Chapter 6, Semiconductor Electrochemistry

frequency factor (s^{-1})

$$k_f = \nu \int_{-\infty}^{\infty} \varepsilon_{red}(\mathbf{E}) W_O(\lambda, \mathbf{E}) f(\mathbf{E}) \rho(\mathbf{E}) d\mathbf{E}$$

proportionality function (cm^3 eV)

$$k_b = \nu \int_{-\infty}^{\infty} \varepsilon_{ox}(\mathbf{E}) W_R(\lambda, \mathbf{E}) [1 - f(\mathbf{E})] \rho(\mathbf{E}) d\mathbf{E}$$

$$k'_{f,E,obs} = \int_{-\infty}^{\infty} k'_{f,E}\, d\mathbf{E} \qquad k'_{b,E,obs} = \int_{-\infty}^{\infty} k'_{b,E}\, d\mathbf{E}$$

energy

$$j_{E,obs} = nF\left(-k'_{f,E,obs}c_{O,z_o} + k'_{b,E,obs}c_{R,z_o}\right)$$

Solid-State Physics Terminology

$$\bar{\mu}_i^{\alpha} = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_{j\neq i}}$$

$$\mathrm{Si_{CB}(h^+) + Si_{VB}(e^-) \rightleftharpoons Si_{CB}(e^-) + Si_{VB}(h^+)}$$

At equilibrium,

$$\bar{\mu}^{\mathrm{Si}}_{\mathrm{CB(h^+)}} + \bar{\mu}^{\mathrm{Si}}_{\mathrm{VB(e^-)}} = \bar{\mu}^{\mathrm{Si}}_{\mathrm{CB(e^-)}} + \bar{\mu}^{\mathrm{Si}}_{\mathrm{VB(h^+)}}$$

As reference states, it is useful to define

$$\bar{\mu}^{\mathrm{Si}}_{\mathrm{CB(h^+)}} = \bar{\mu}^{\mathrm{Si}}_{\mathrm{VB(e^-)}} = 0$$

… you can define up to one more $\bar{\mu}_i^{\mathrm{Si}}$, but the last $\bar{\mu}_i^{\mathrm{Si}}$ has to be defined based on calorimetry data

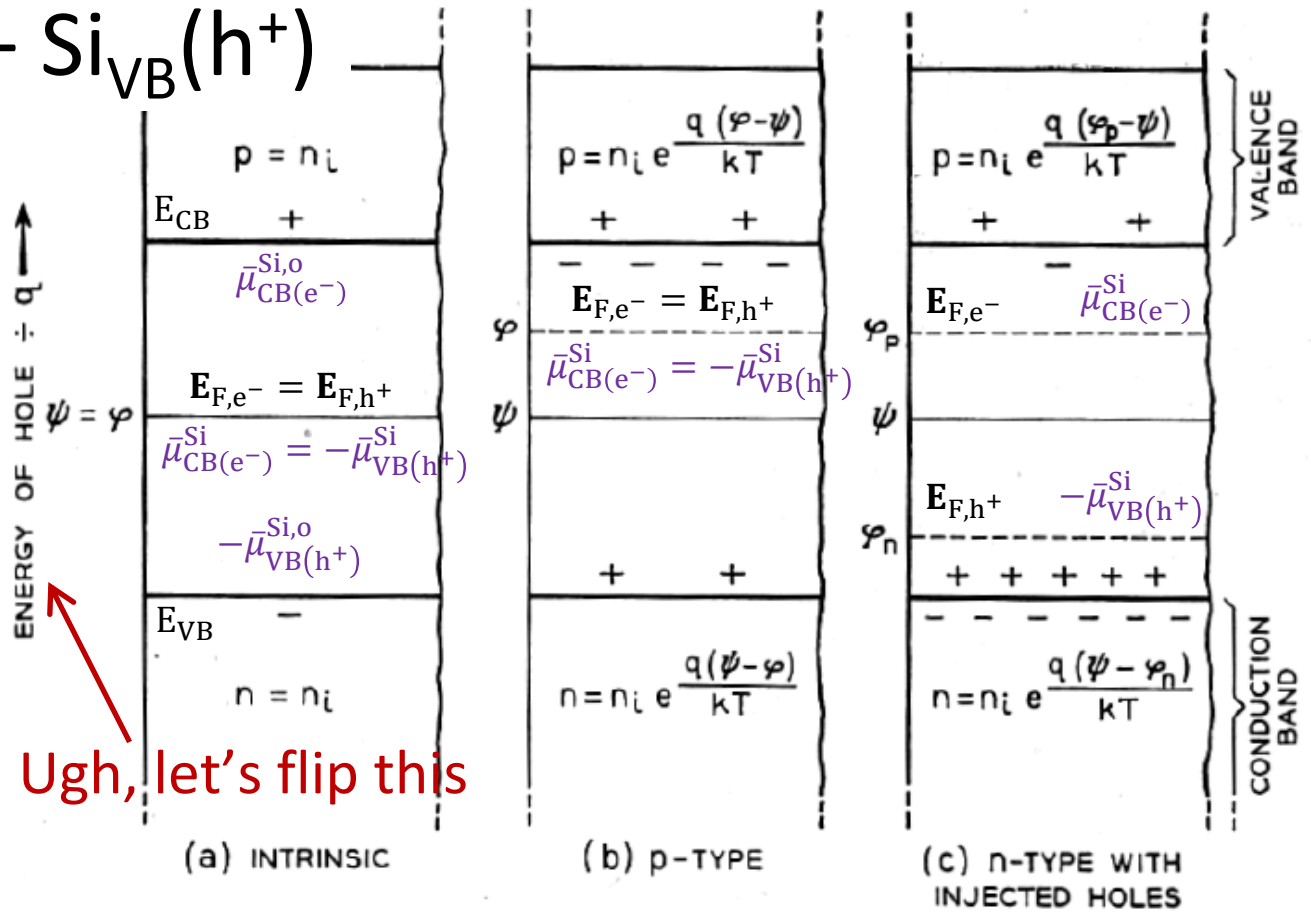
Anyway… therefore,

$$\bar{\mu}^{\mathrm{Si}}_{\mathrm{CB(e^-)}} = -\bar{\mu}^{\mathrm{Si}}_{\mathrm{VB(h^+)}}$$

$$\mathbf{E}_{\mathrm{F,e^-}} = \mathbf{E}_{\mathrm{F,h^+}}$$

$$\mathbf{E}_{\mathrm{F,e^-}} = \bar{\mu}_{\mathrm{e^-}}$$

$$\mathbf{E}_{\mathrm{F,h^+}} = -\bar{\mu}_{\mathrm{h^+}}$$



Ugh, let's flip this

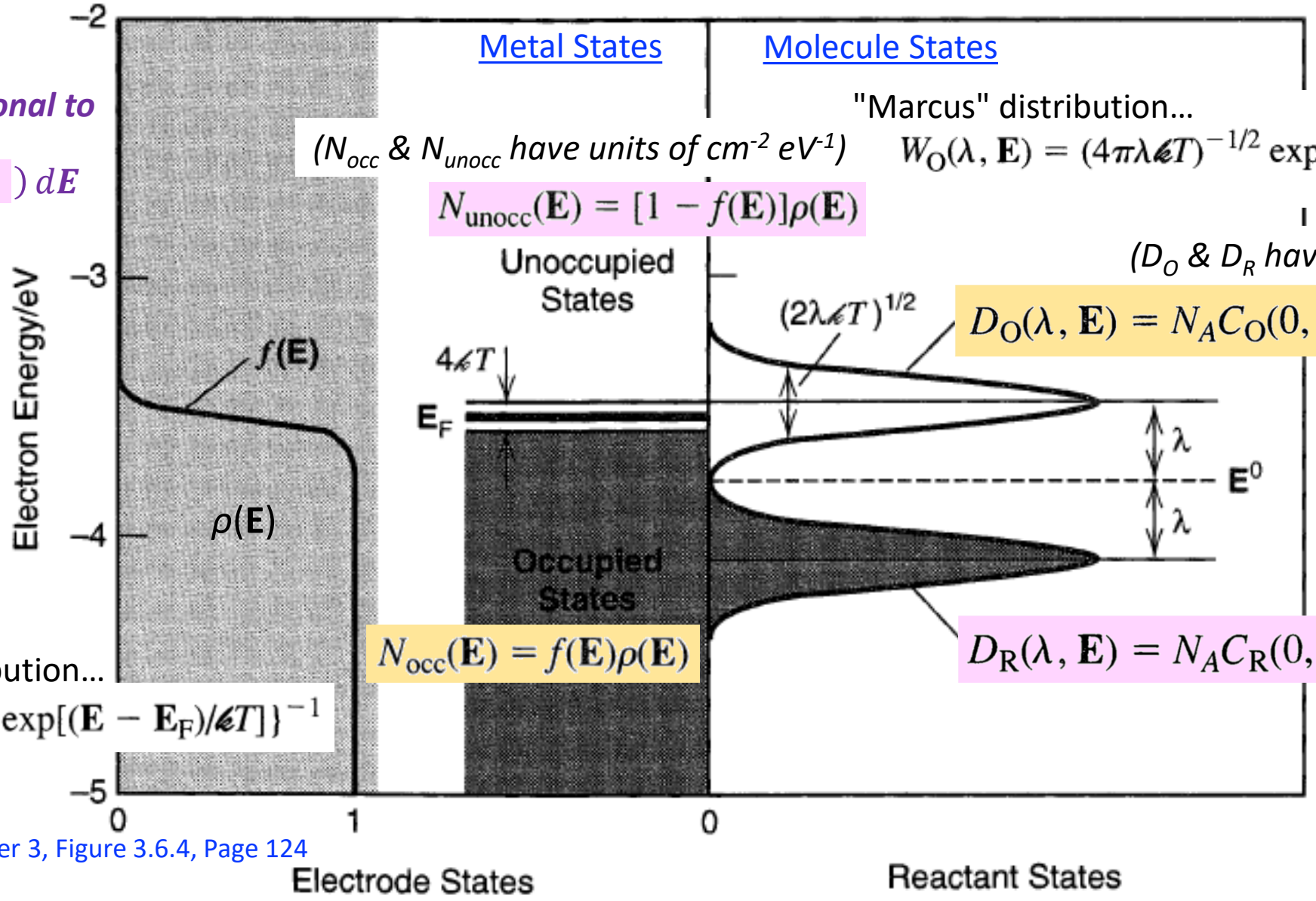
Fig. 2—Electrostatic potential ψ, Fermi level φ and quasi Fermi levels φ_p and φ_n. (In order to show electrostatic potential and energies on the same ordinates, the energies of holes, which are minus the energies of electrons, are plotted upwards in the figures in this paper.)

W. Shockley, *The Bell System Technical Journal*, **1949**, *28*, 435–489

Marcus–Gerischer Theory

ET rate is proportional to

$$\int_{-\infty}^{\infty} (N\ D - N\ D)\, dE$$



(N_{occ} & N_{unocc} have units of $cm^{-2}\ eV^{-1}$)

$$N_{unocc}(\mathbf{E}) = [1 - f(\mathbf{E})]\rho(\mathbf{E})$$

$$N_{occ}(\mathbf{E}) = f(\mathbf{E})\rho(\mathbf{E})$$

Fermi–Dirac distribution…

$$f(\mathbf{E}) = \{1 + \exp[(\mathbf{E} - \mathbf{E}_F)/kT]\}^{-1}$$

"Marcus" distribution…

$$W_O(\lambda, \mathbf{E}) = (4\pi\lambda kT)^{-1/2} \exp\left[-\frac{(\mathbf{E} - \mathbf{E}^0 - \lambda)^2}{4\lambda kT}\right]$$

(D_O & D_R have units of $cm^{-3}\ eV^{-1}$)

$$D_O(\lambda, \mathbf{E}) = N_A C_O(0, t) W_O(\lambda, \mathbf{E})$$

$$D_R(\lambda, \mathbf{E}) = N_A C_R(0, t) W_R(\lambda, \mathbf{E})$$

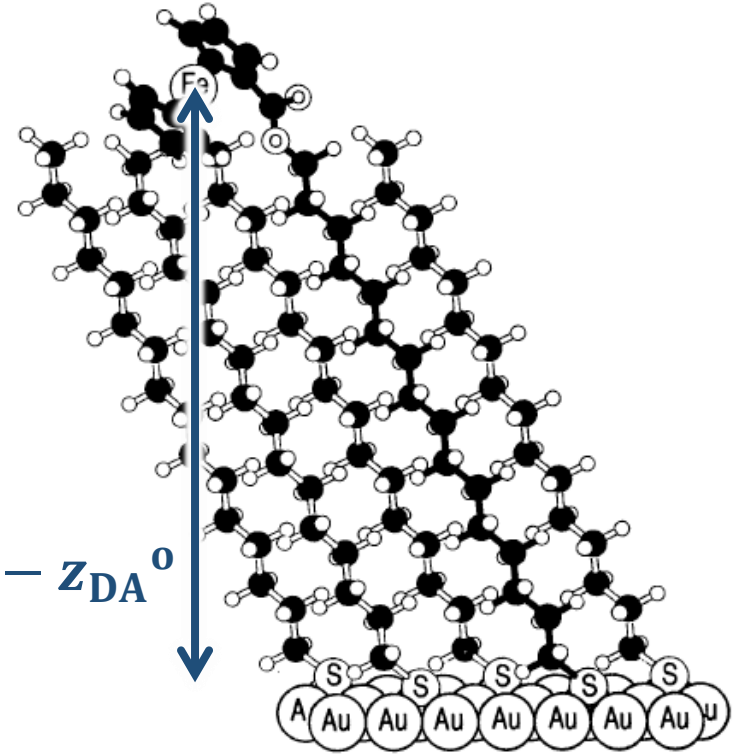
Bard & Faulkner, Chapter 3, Figure 3.6.4, Page 124

Marcus–Gerischer Theory

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

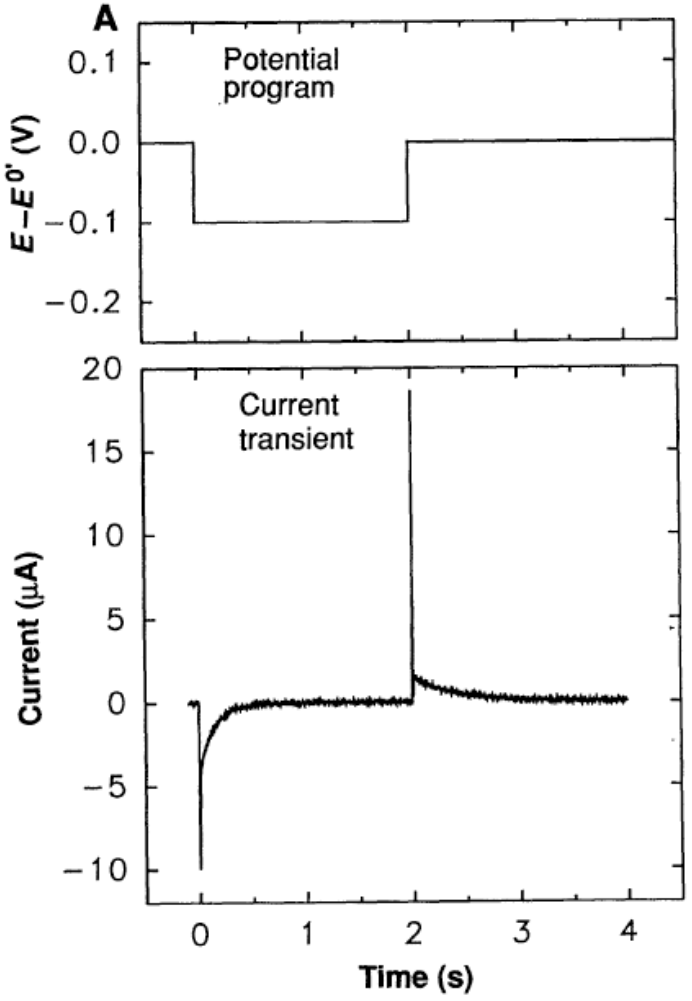
quantum adiabatic electronic coupling

classical nuclear free-energy dependence



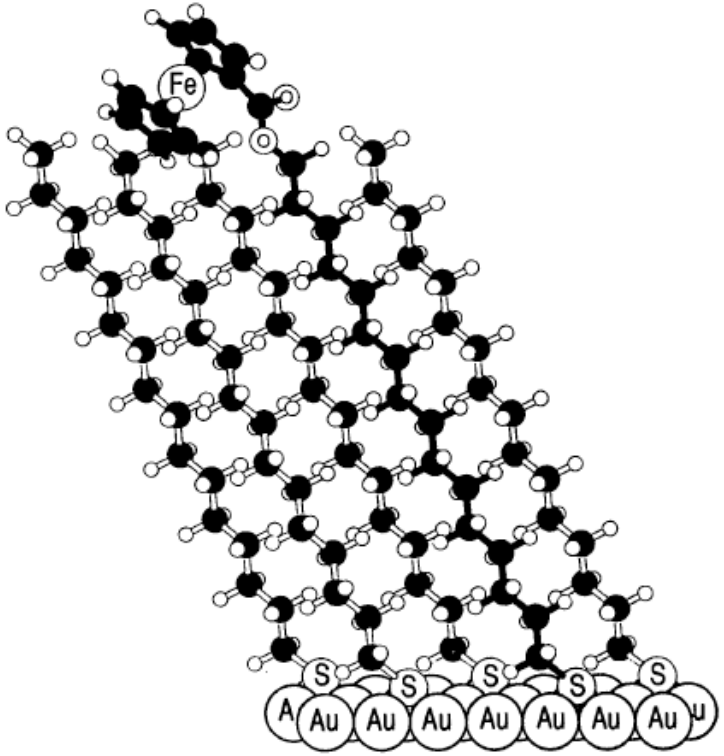
… as an aside… why is the data biphasic for the Current?

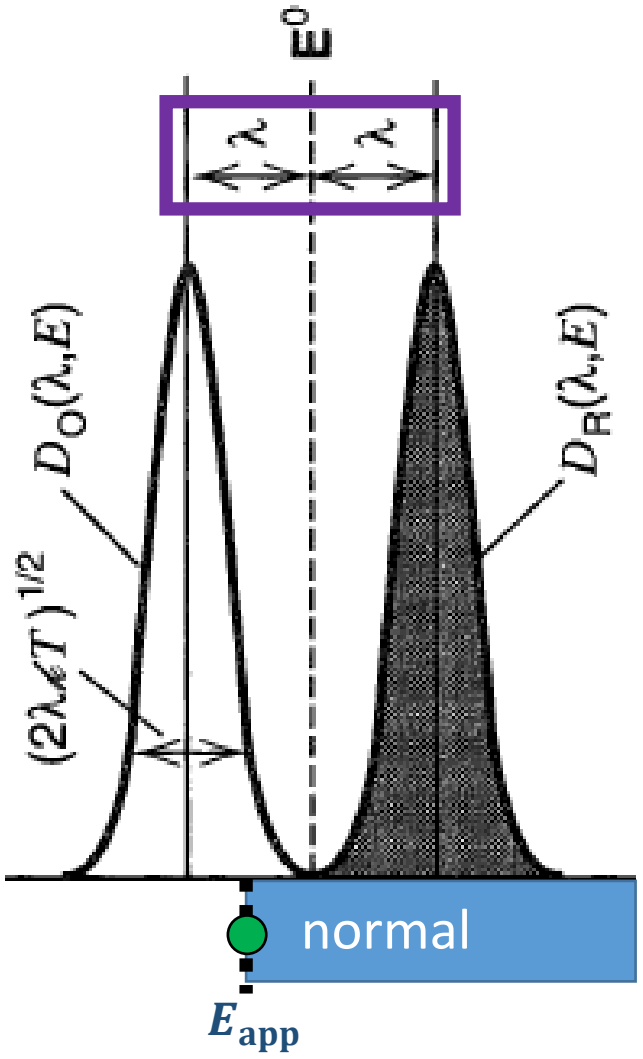
… RC-circuit double layer charging… followed by 1st-order ET kinetics

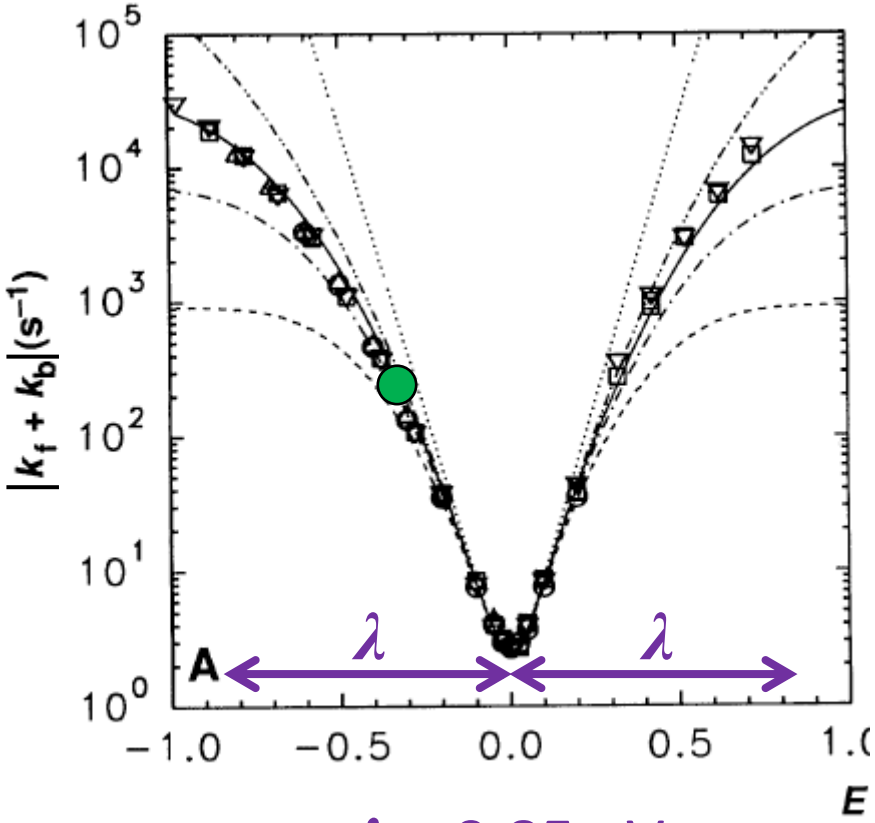


C. E. D. Chidsey, *Science*, **1991**, *251*, 919–922
H. D. Sikes, J. F. Smalley, S. P. Dudek, A. R. Cook, M. D. Newton, C. E. D. Chidsey & S. W. Feldberg, *Science*, **2001**, *291*, 1519–1523

Marcus–Gerischer Theory



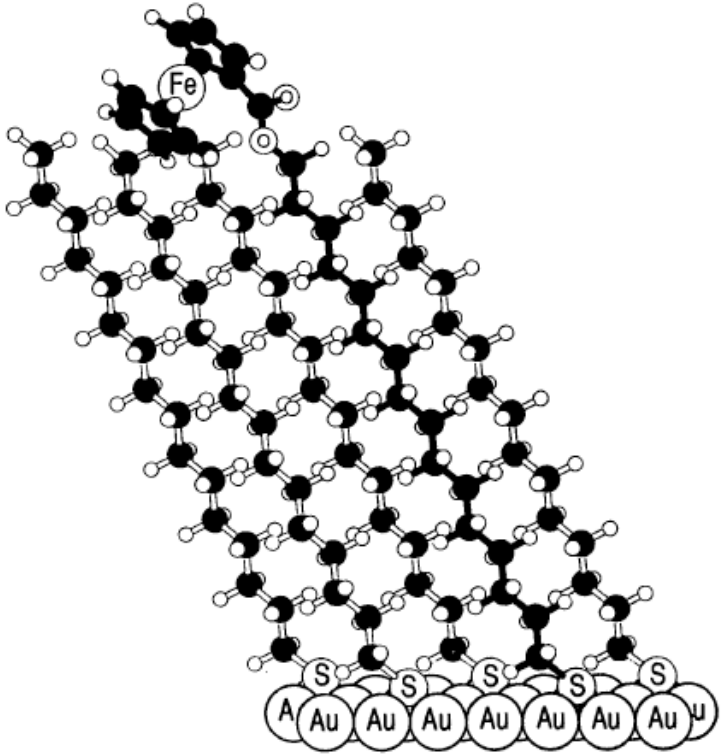


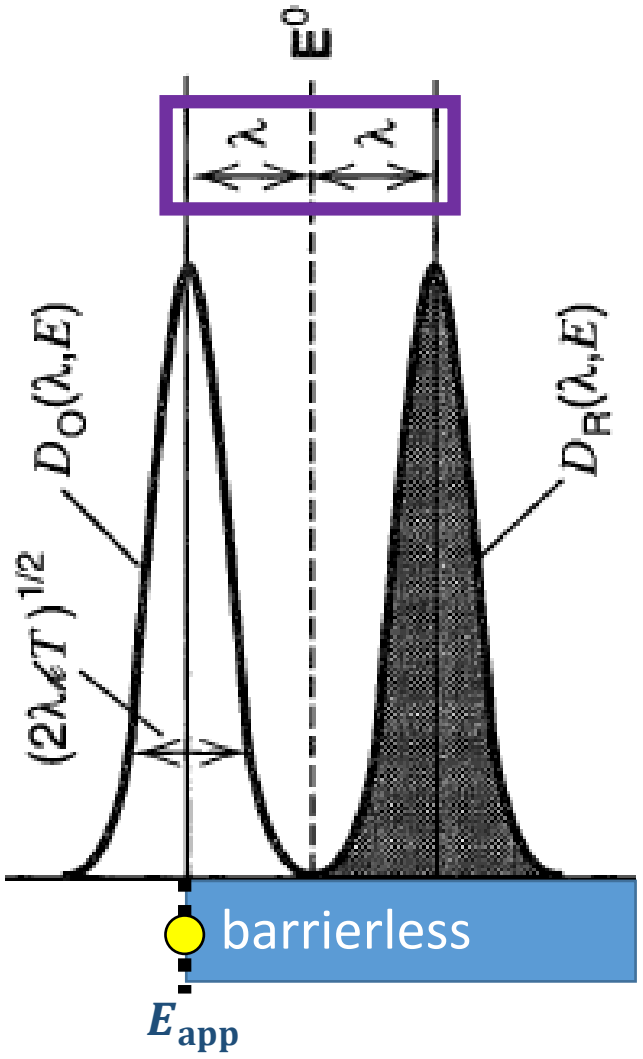


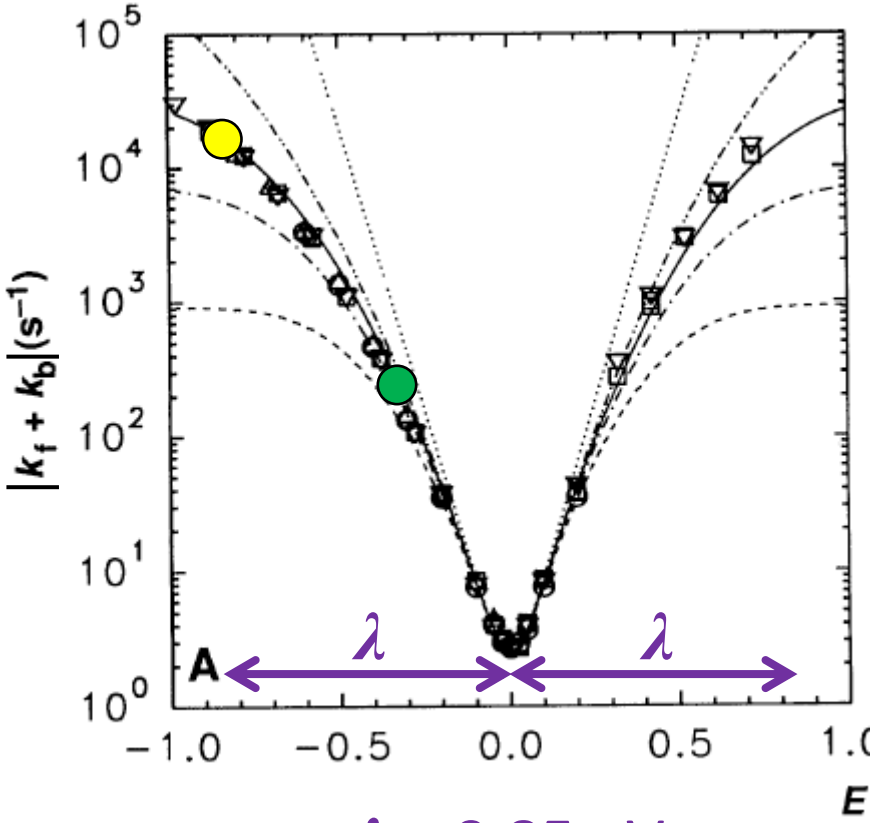
λ = 0.85 eV

C. E. D. Chidsey, *Science*, **1991**, *251*, 919–922

Marcus–Gerischer Theory







λ = 0.85 eV

C. E. D. Chidsey, *Science*, **1991**, *251*, 919–922

Marcus–Gerischer Theory

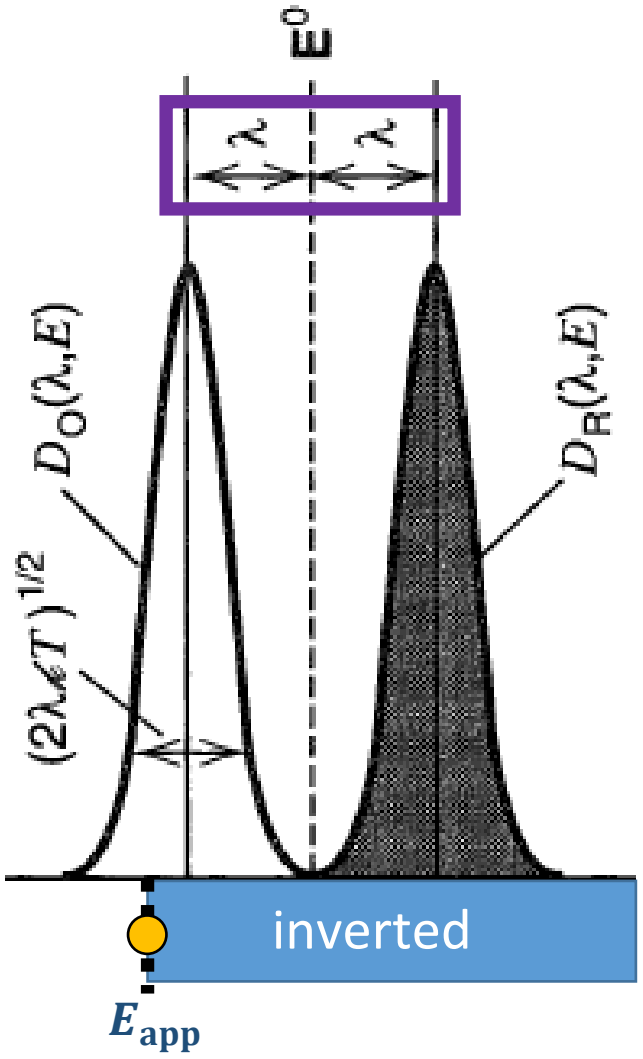
- It is easy to sweep/vary the driving force, ΔG_{AB}, by simply changing the electrochemical potential of electrons (e^-) in the (M)etal working electrode, $\bar{\mu}_e^{\mathrm{M}}$, through variations in E_{app}

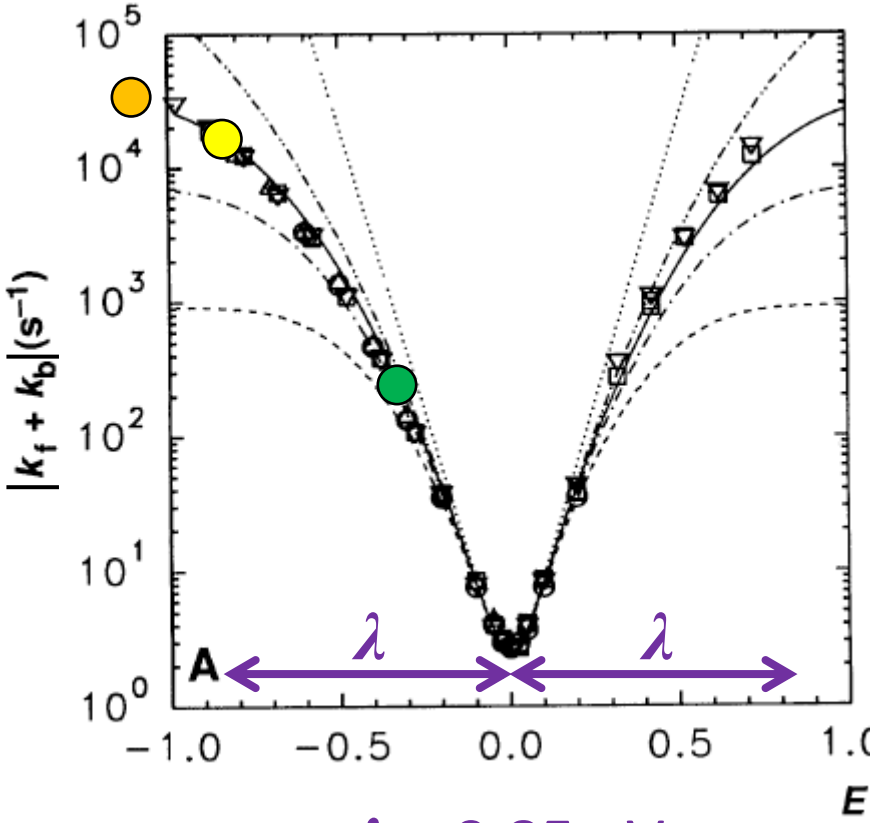
- **But evidence of the inverted region is a little challenging to clearly observe**

… what if Chidsey had plotted the derivative of his data on the right?

… what do you expect that would have looked like?… a nice Marcus parabola!

… I wish he had done that!

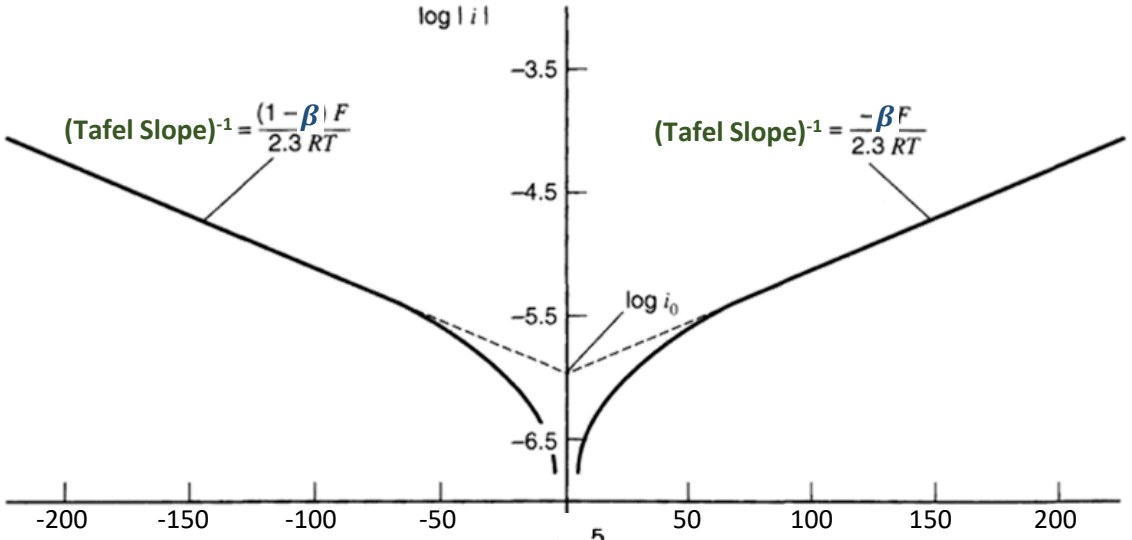


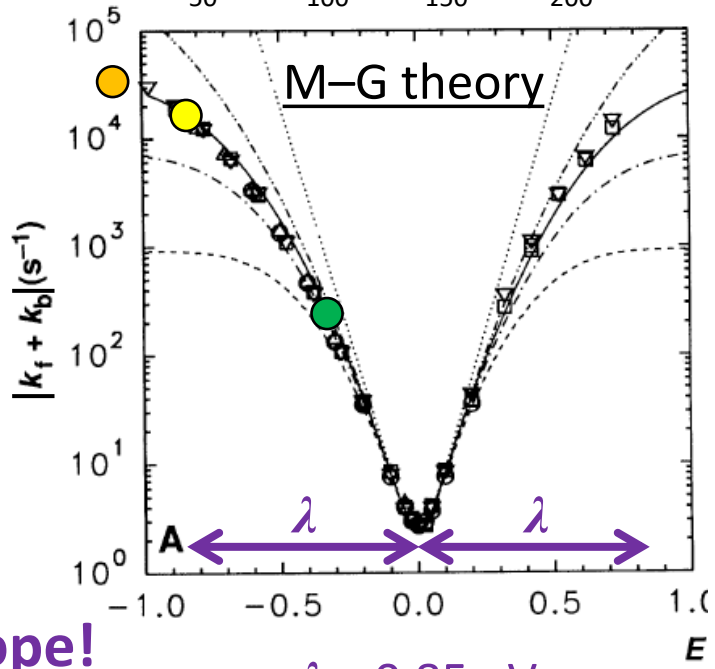


λ = 0.85 eV

C. E. D. Chidsey, *Science*, **1991**, *251*, 919–922

Limiting Processes

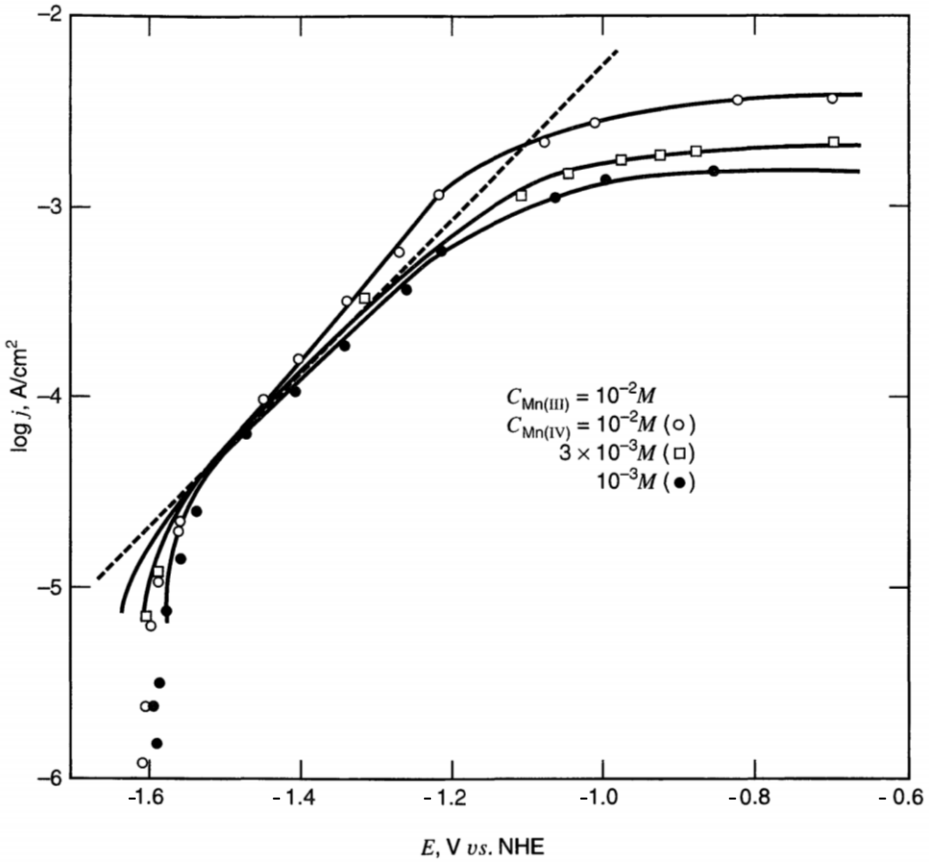




λ = 0.85 eV

Since Butler–Volmer theory is based on the LFER approximation only, can it report on aspects of the inverted region? **… Nope!**

B–V theory
(Current–Overpotential Equation)



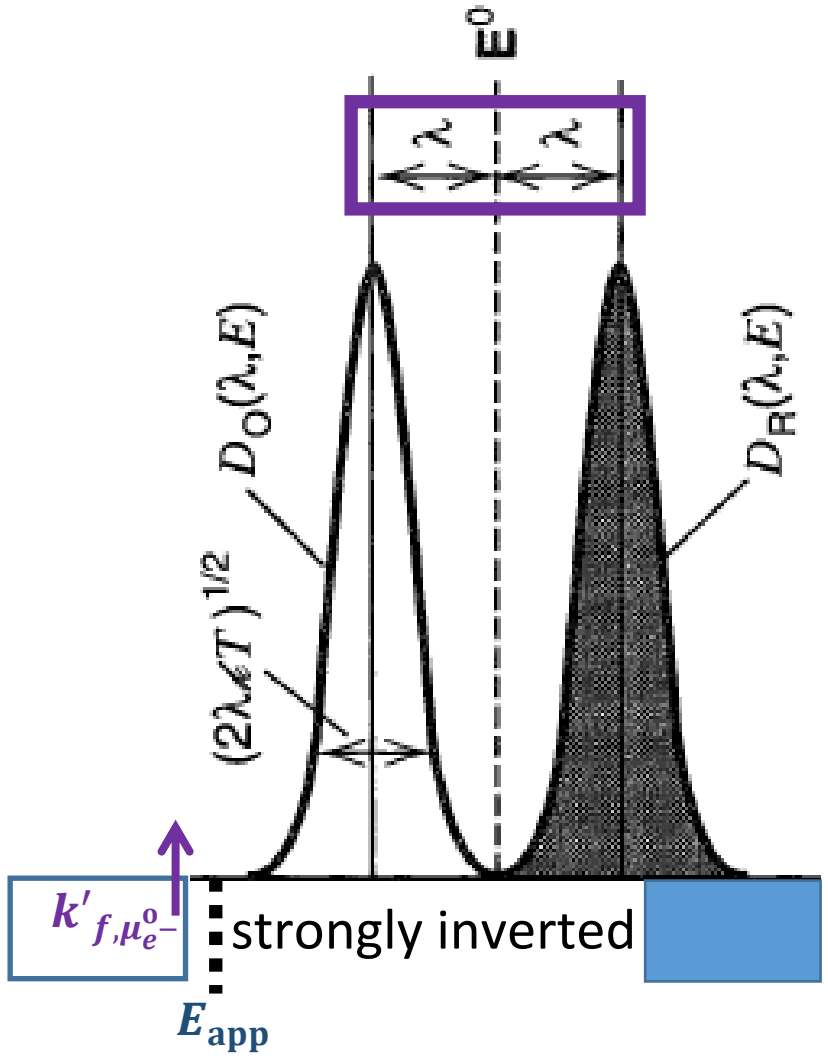
Bard & Faulkner, Chapter 3, Figure 3.4.5, Page 104

… but why do these current densities, j_E, and rate constants, $k'_{j,E,\mathrm{obs}}$, plateau at large overpotential, η? **… Not for the same reasons!**

Marcus–Gerischer Theory

- Use of a semiconductor limits the electronic states to those with (approximately) a single $\mu_{e^-}^{o}$, which makes analysis of data simpler, i.e. one does not need to consider a distribution of states in the electrode

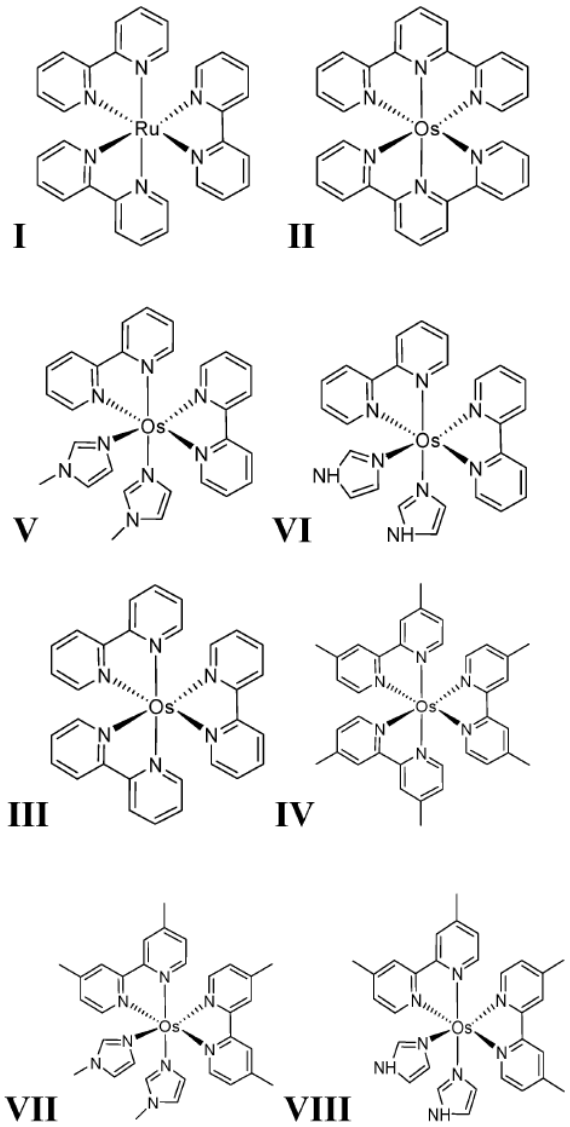
- **But one cannot alter the driving force, ΔG_{AB}^{o}, by simply changing the electrochemical potential of electrons (e^-) in the <u>(S)emi(C)onductor</u> working electrode, $\overline{\mu}_e^{SC}$, through variations in E_{app}, because instead that changes the concentration of e^-**

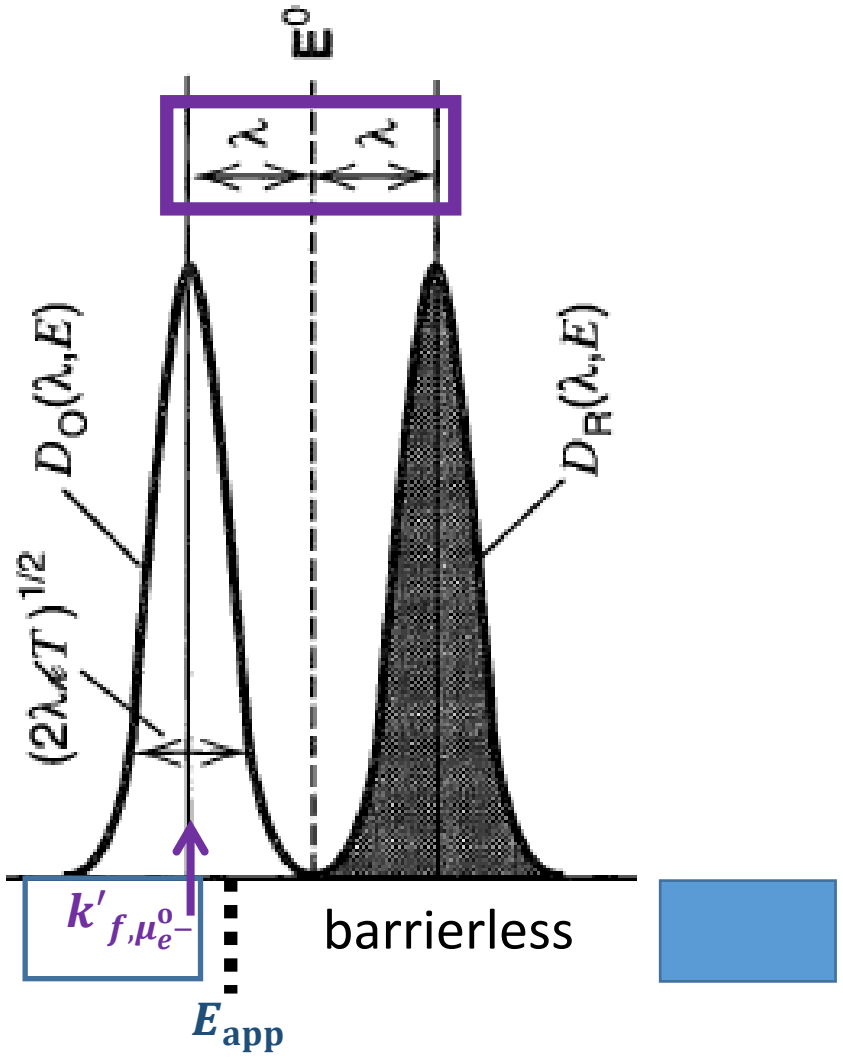


How can one use a semiconductor to study the inverted region?

Think solution studies… vary the molecule!

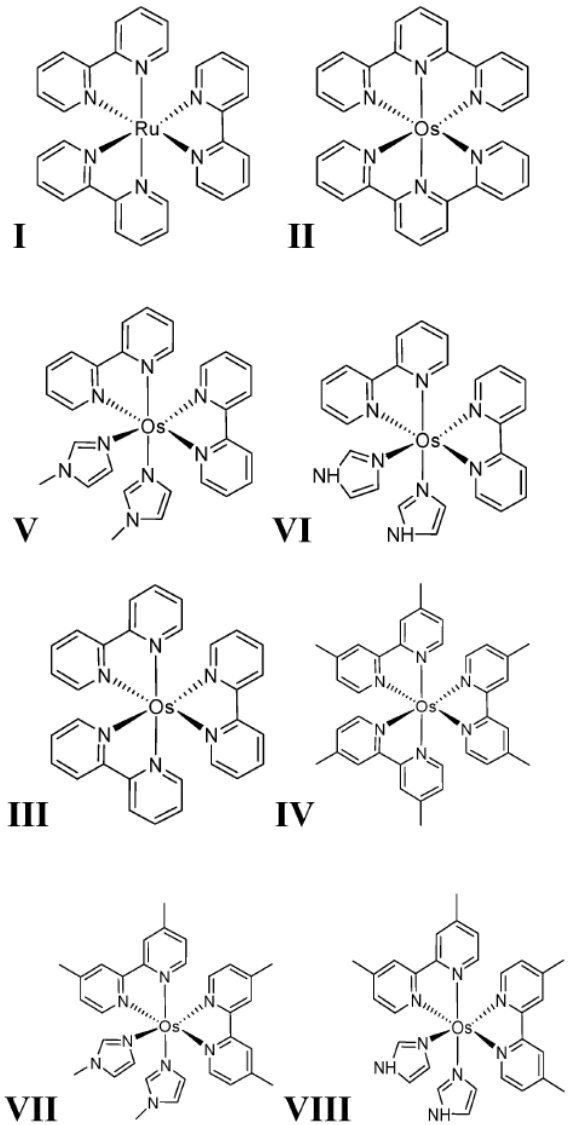
Marcus–Gerischer Theory

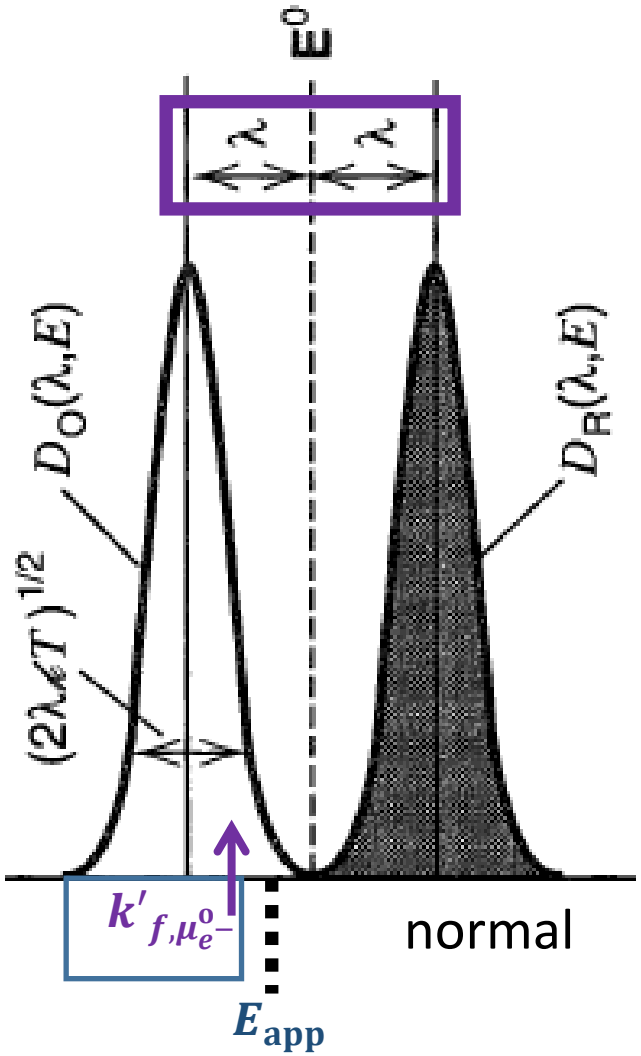


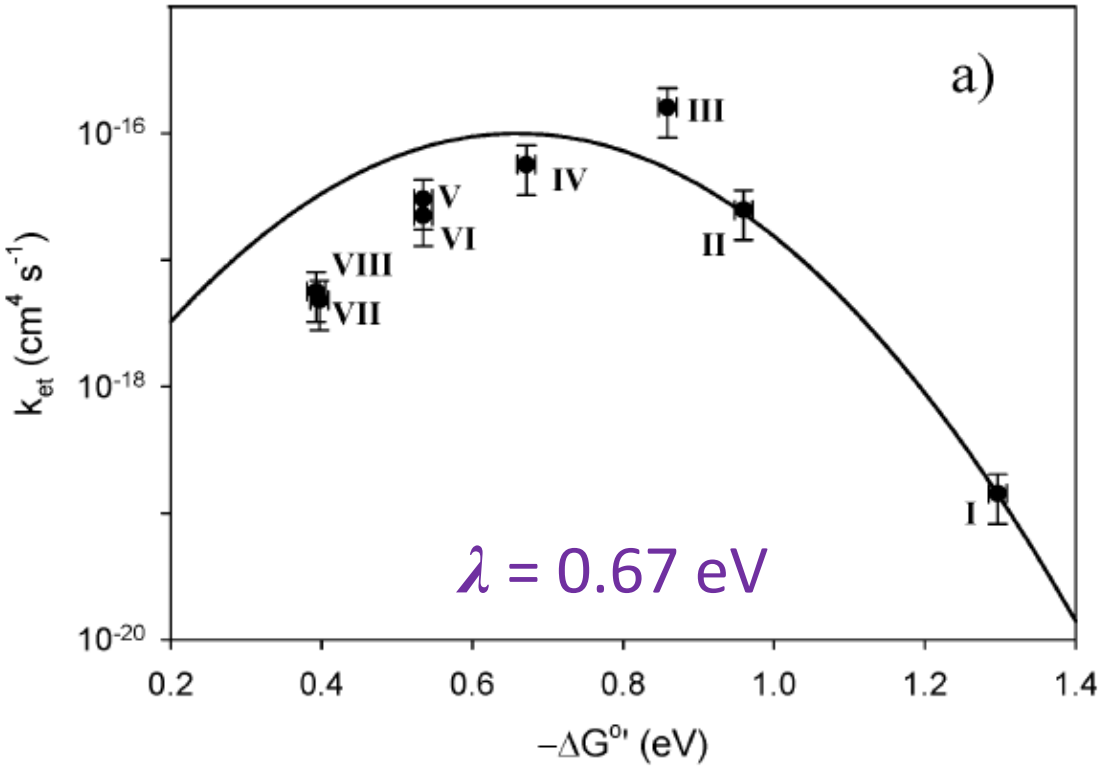


T. W. Hamann, F. Gstrein, B. S. Brunschwig & N. S. Lewis, *J. Am. Chem. Soc.*, **2005**, *127*, 7815–7824
T. W. Hamann, F. Gstrein, B. S. Brunschwig & N. S. Lewis, *J. Am. Chem. Soc.*, **2005**, *127*, 13949–13954

Marcus–Gerischer Theory







k_{IET} (cm^4 s^{-1})… a second-order rate constant!

T. W. Hamann, F. Gstrein, B. S. Brunschwig & N. S. Lewis, *J. Am. Chem. Soc.*, **2005**, *127*, 7815–7824
T. W. Hamann, F. Gstrein, B. S. Brunschwig & N. S. Lewis, *J. Am. Chem. Soc.*, **2005**, *127*, 13949–13954

Charge Transfer across Electrified Interfaces

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β α

Symmetry Factor and Transfer Coefficient

A source of confusion in electrode kinetics

Symmetry factor (β): change in the activation free energy of the cathodic elementary reaction step, expressed as a fraction of E_{app}

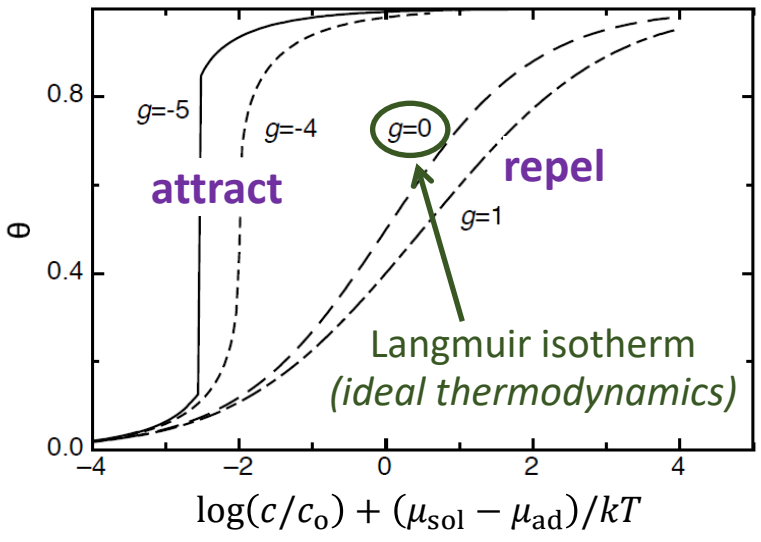
Transfer coefficient (α_j): change in the total observed (cath)odic/(an)odic reaction rate expressed as a change in observed activation free energies as a fraction of E_{app}

$$\mathrm{TS_{cath}}^{-1} = \left(\frac{d(\log|j_E|)}{d|\eta|}\right)_{\mathrm{cath}} = \frac{-\alpha_{\mathrm{cath}}F}{2.303RT}$$

$$\mathrm{TS_{an}}^{-1} = \left(\frac{d(\log j_E)}{d\eta}\right)_{\mathrm{an}} = \frac{\alpha_{\mathrm{an}}F}{2.303RT}$$

Do the two transfer coefficients always have to sum to one?

Frumkin isotherms



* g is a lateral interaction term

Schmickler & Santos, Chapter 6, Figure 6.1, Page 53

J. O'M. Bockris & Z. Nagy, *J. Chem. Educ.*, **1973**, *50*, 839–843

Rate-Determining Step (RDS)

$$D + A \rightleftarrows D^+ + A^-$$

Poisson's Equation (from Gauss's law)

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

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

But wait… is this the elementary reaction step for electron transfer between a (D)onor and an (A)cceptor in solution?

Nope!

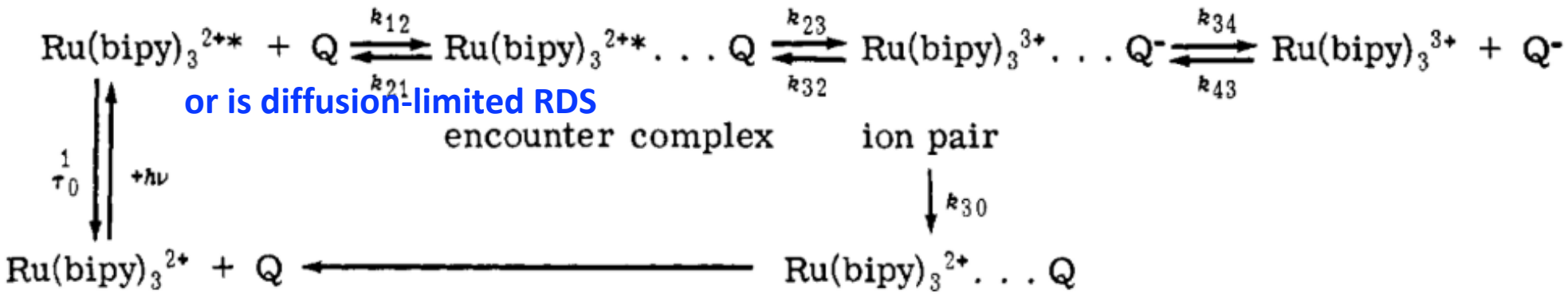
Ground-state electron transfer

$$D + A \Leftrightarrow \underbrace{(D, A)}_{R_0} \Leftrightarrow \underbrace{(D, A)^{\#}}_{R^{\#}} \Leftrightarrow \underbrace{(D^+, A^-)}_{P^{\#}} \Leftrightarrow \underbrace{(D^+, A^-)}_{P_0} \Leftrightarrow D^+ + A^-$$

ΔG_R^o due to entropy/sterics

ΔG_p^o due to entropy/sterics

Excited-state electron transfer



RDS: Pre-Equilibrium Approximation

… seemingly totally unrelated… how does one determine the **observed** resistance of 3 resistors in parallel, or 3 capacitors in series? … it's approximately equal to the smaller one… okay…
but mathematically, add their reciprocals… and reciprocate

$$\mathrm{D} + \mathrm{A} \overset{1}{\rightleftharpoons} (\mathrm{D}, \mathrm{A}) \overset{2}{\rightleftharpoons} (\mathrm{D}^+, \mathrm{A}^-) \overset{3}{\rightleftharpoons} \mathrm{D}^+ + \mathrm{A}^-$$

… so how does one determine the **observed** rate constant for 3 reactions **in series**?

… it's the same general idea… $\frac{1}{\boldsymbol{k}_{f,\mathbf{obs}}} = \frac{1}{k_{1f}} + \frac{1}{k'_{2f}} + \frac{1}{k'_{3f}}$… where $\frac{\partial[\mathrm{D}]}{\partial t} = \frac{\partial[\mathrm{A}]}{\partial t} = -\boldsymbol{k}_{f,\mathbf{obs}}[\mathrm{D}][\mathrm{A}]$

… except that <u>Step 2</u> is preceded by Step 1… and <u>Step 3</u> is preceded by Steps 1 and 2

… and only one of those <u>Steps</u> will dictate the observed rate when it is the slowest step

… so the (pre)ceding steps must be much faster… thus assume they are in equilibrium…

$$\frac{1}{\boldsymbol{k}_{f,\mathbf{obs}}} = \frac{1}{k_{1f}} + \frac{1}{K_1 k_{2f}} + \frac{1}{K_1 K_2 k_{3f}} = \frac{1}{k_{1f}} + \frac{k_{1b}}{k_{1f} k_{2f}} + \frac{k_{1b} k_{2b}}{k_{1f} k_{2f} k_{3f}}$$

… and for completion, what if 3 (same-order) reactions are **in parallel**?

… it's as easy as it seems… $\boldsymbol{k}_{f,\mathbf{obs}} = k_{1f} + k_{2f} + k_{3f} = \frac{1}{\tau_{1f}} + \frac{1}{\tau_{2f}} + \frac{1}{\tau_{3f}} = \frac{\mathbf{1}}{\boldsymbol{\tau}_{f,\mathbf{obs}}}$

RDS: Steady-State Approximation

… but what if we want to determine $\frac{\partial[\mathrm{D}^+]}{\partial t} = \frac{\partial[\mathrm{A}^-]}{\partial t}$… and some preceding steps are fast?

… when all are fast, except Step 1, won't $\boldsymbol{k_{f,\mathrm{obs}}} = k_{1f}$ then?… not always…

$$\mathrm{D} + \mathrm{A} \overset{1}{\rightleftharpoons} (\mathrm{D}, \mathrm{A}) \overset{2}{\rightleftharpoons} (\mathrm{D}^+, \mathrm{A}^-) \overset{3}{\rightleftharpoons} \mathrm{D}^+ + \mathrm{A}^-$$

Assume that the middle steps come and go quickly… so each has a small steady-state conc…

$\frac{\partial[(\mathrm{D},\mathrm{A})]}{\partial t} = \mathbf{0} = -k_{2f}[(\mathrm{D},\mathrm{A})] + k_{1f}[\mathrm{D}][\mathrm{A}]$… and thus $[(\mathrm{D},\mathrm{A})] = \frac{k_{1f}[\mathrm{D}][\mathrm{A}]}{k_{2f}}$

$\frac{\partial[(\mathrm{D}^+,\mathrm{A}^-)]}{\partial t} = \mathbf{0} = -k_{3f}[(\mathrm{D}^+,\mathrm{A}^-)] + k_{2f}[(\mathrm{D},\mathrm{A})]$ … and thus $[(\mathrm{D}^+,\mathrm{A}^-)] = \frac{k_{2f}[(\mathrm{D},\mathrm{A})]}{k_{3f}}$

… which means that $[(\mathrm{D}^+,\mathrm{A}^-)] = \frac{k_{1f}k_{2f}[\mathrm{D}][\mathrm{A}]}{k_{2f}k_{3f}} = \frac{k_{1f}[\mathrm{D}][\mathrm{A}]}{k_{3f}}$

… since $\frac{\partial[\mathrm{D}^+]}{\partial t} = \frac{\partial[\mathrm{A}^-]}{\partial t} = k_{3f}[(\mathrm{D}^+,\mathrm{A}^-)]$… this is just equal to $k_{1f}[\mathrm{D}][\mathrm{A}]$… and $\boldsymbol{k_{f,\mathrm{obs}}} = k_{1f}$

… which is what the pre-equilibrium approximation would have predicted too, so… unexciting!

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**

Paper Time!