



Lecture #6 of 12

{80 min away from being halfway through... tear}

Prof. Shane Ardo

Department of Chemistry

University of California Irvine



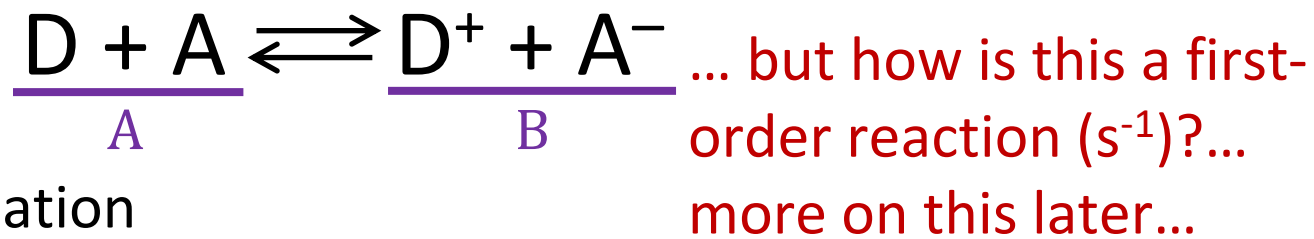
Thermal (Dark) Reactions

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Marcus–Hush Theory



Marcus–Hush (1950s–1960s)

theoretical (semiclassical) rate constant equation

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



Eyring–Polanyi–Evans (1930s)

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

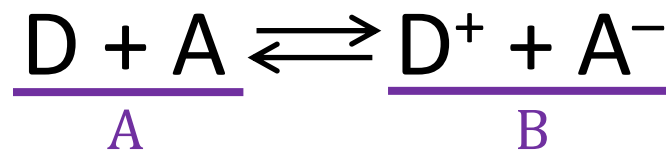
$$k_f = \kappa \nu K^{\ddagger} = \frac{\kappa k_{\text{B}}T}{h} K^{\ddagger} \quad \dots \text{ with transmission coefficient, } \kappa, \text{ and vibrational frequency, } \nu \text{ (s}^{-1}\text{)}$$

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

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

... 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

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

quantum adiabatic
electronic coupling

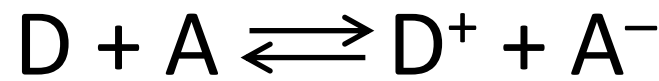
classical nuclear free-
energy dependence

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

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

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

Marcus–Hush Theory



Marcus–Hush (1950s–1960s)

Standard Normal Distribution

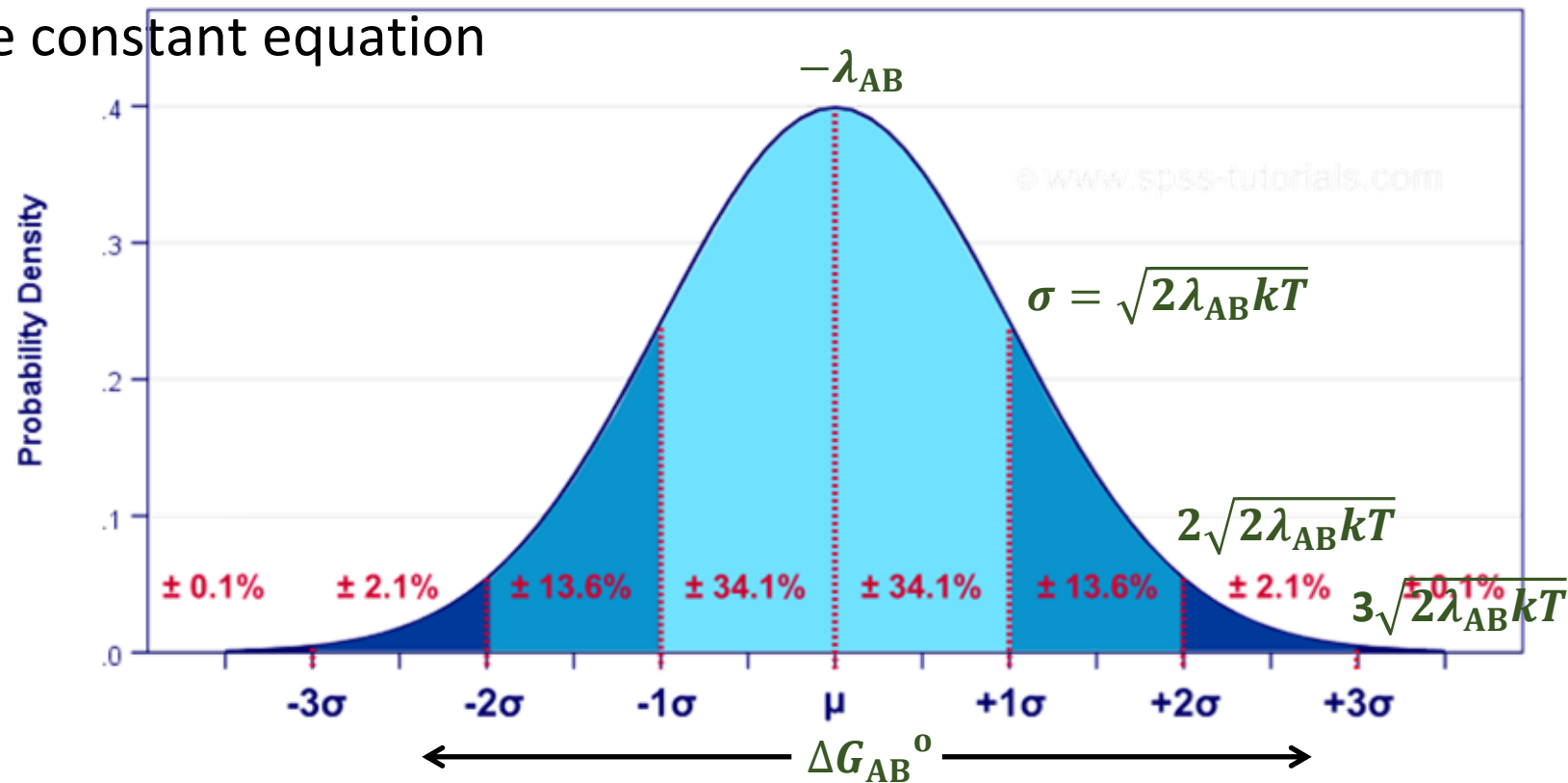
A

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 (ΔG_{AB}^0)?... **Yep!**



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

Inner versus Outer Sphere Reactions

Marcus-Hush (1950s-1960s)

theoretical (semiclassical) rate constant equation

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

Taube (1950s-1970s)

inner sphere electron transfer

Robin-Day MV classification... **label each below!**

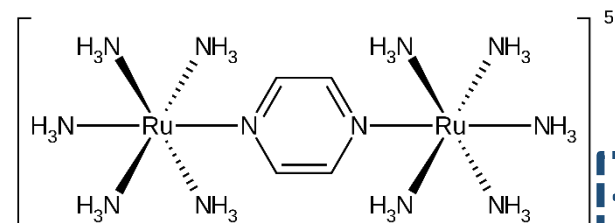
Class I: nonadiabatic ($H_{DA} \approx 0$)

Class II: adiabatic, localized ($0 < 2H_{DA} < \lambda_{AB}$)

Class III: adiabatic, delocalized ($2H_{DA} > \lambda_{AB}$)

... so what is $2H_{DA}$ for Class III [C-T]⁵⁺?

Creutz-Taube ion (1969)



< 1 eV

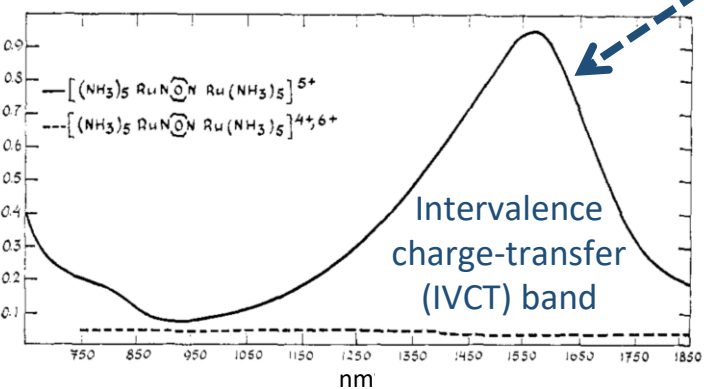
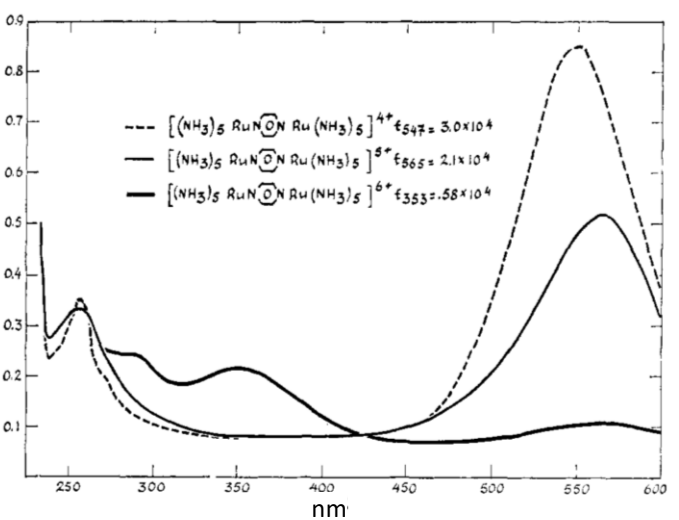
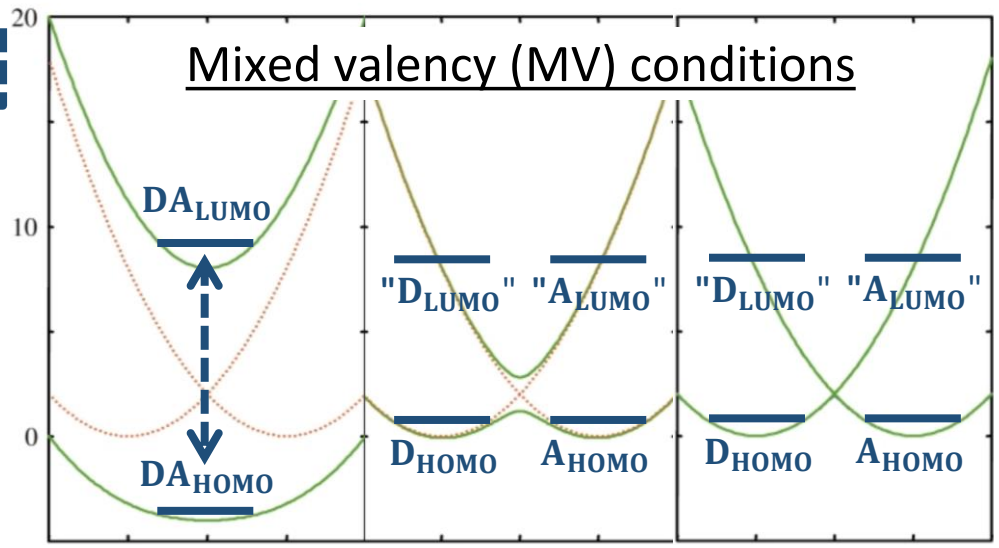


Figure 1. Visible-ultraviolet spectra of [2,2], [2,3], and [3,3] in 0.05 N HClO₄. (Absorbance around 560 nm for [3,3] is probably due to residual [2,3] in the solution; photoreduction of [3,3] takes place readily.) $\epsilon_{[2,2]}$ and $\epsilon_{[2,3]}$ are measured in the range $2-3 \times 10^{-5} M$, path length 1 cm. $\epsilon_{[3,3]}$ is measured at $8 \times 10^{-5} M$, 1-cm path length.

Figure 2. Near-infrared spectrum of [2,3] in D₂O: concentration of [2,3] = $1.5 \times 10^{-4} M$; 1-cm path length. (Dashed line is actually the blank, but accurately indicates the spectra of [2,2] and [3,3] in this range above 750 nm at this concentration level.)



C. Creutz & H. Taube, *J. Am. Chem. Soc.*, **1969**, *91*, 3988-3989

B. S. Brunshwig, C. Creutz & N. Sutin, *Chem. Soc. Rev.*, **2002**, *31*, 168-184

Huang–Rhys Factor

Marcus–Hush (1950s–1960s)

theoretical (semiclassical) rate constant equation

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

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

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

... separable due to the Born–Oppenheimer approximation

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

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

Fermi's Golden Rule

time-dependent perturbation theory

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

$$k_{\text{ET}} = \frac{2\pi}{\hbar} \frac{H_{\text{DA}}^2}{(4\pi\lambda_0 RT)^{1/2}} \sum_v \exp(-S) \frac{S^v}{v!} \exp[-[(\Delta G^\circ + v\hbar\omega + \lambda_0)^2/4\lambda_0 RT]] \quad (25)$$

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

S_j is the electron-vibrational coupling constant, or Huang–Rhys factor:^{99,105}

$$S_j = \frac{1}{2} \left(\frac{M_j \omega_j}{\hbar} \right) (\Delta Q_{e,j})^2 \quad (19)$$

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

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

Thermal (Dark) Reactions

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

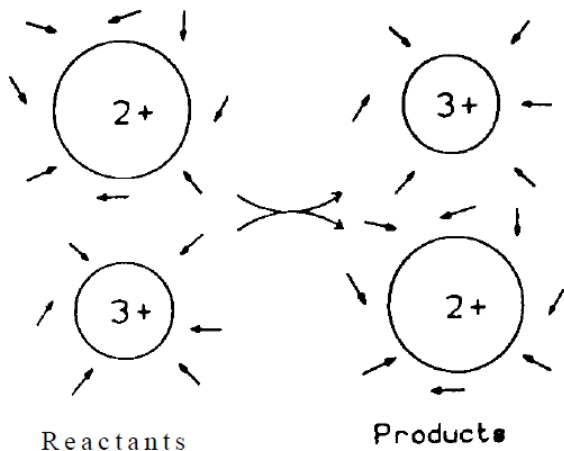
Self-Exchange Reactions

Marcus–Hush (1950s–1960s)

theoretical (semiclassical) rate constant equation

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

What is the fastest way to predict values of parameters?
 ... study self-exchange reactions for each of D and A!



... and then use "half" of every value for D and "half" of every value for A to in order to determine $k_{\text{ET-DA}}$...

... but how are each measured, since the reactants and the products are identical?

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

D. L. Jameson & R. Anand, *J. Chem. Educ.*, **2000**, *77*, 88–89

... use NMR spectroscopy... of course!

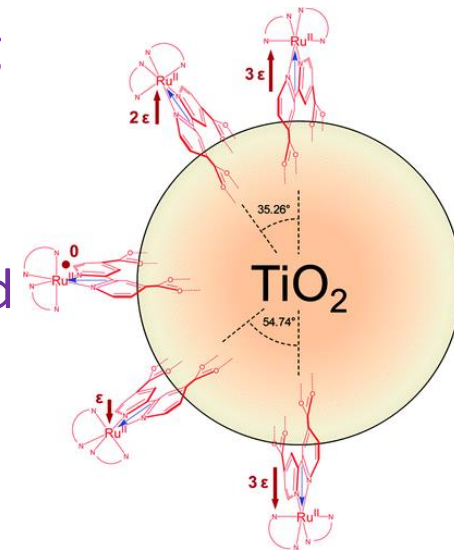
The equation that is used to correlate line-width, chemical shift, and rate is

$$k_{\text{ex}} = 4\pi X_{\text{d}} X_{\text{p}} (\Delta\nu)^2 / (W_{\text{dp}} - X_{\text{p}} W_{\text{p}} - X_{\text{d}} W_{\text{d}}) C_{\text{tot}} \quad (1)$$

where k_{ex} is the rate of electron exchange, X_{d} and X_{p} are the mole fractions of diamagnetic and paramagnetic species, $\Delta\nu$ is the contact shift or chemical shift difference (absolute value) between the pure diamagnetic and paramagnetic species (measured in Hz), W_{dp} is the peak width at half height of the signal of interest for the mixture, W_{d} and W_{p} are the peak widths of the pure diamagnetic and paramagnetic species and C_{tot} is the total concentration of the exchanging species in moles/liter.

... radioisotope labeling of species works too...

... an anisotropic scaffold also works, and then monitor how the polarization of spectra change over time!



S. Ardo & G. J. Meyer, *J. Am. Chem. Soc.*, **2011**, *133*, 15384–15396

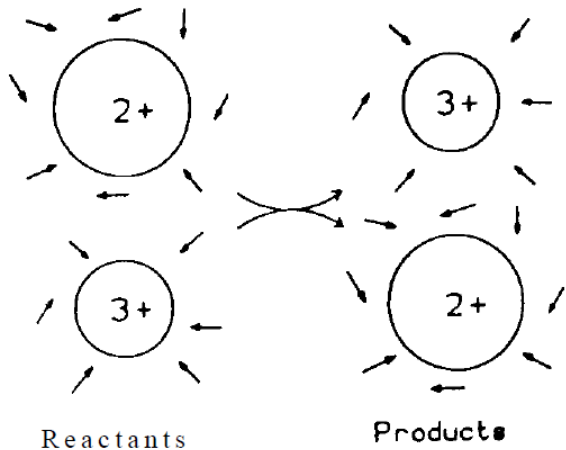
Marcus Cross Relations

Marcus–Hush (1950s–1960s)

theoretical (semiclassical) rate constant equation

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

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



... these are "half" ... $\lambda_{\text{AB}} \approx \frac{\lambda_{\text{AA}} + \lambda_{\text{BB}}}{2}$

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

$$|H_{\text{DA}}| = \sqrt{|H_{\text{DD}}||H_{\text{AA}}|}$$

Marcus Cross Relations

... so, how does one apply knowledge gained from self-exchange reactions? ... meaning what is "half"? ... use this nice equation...

$$k_{\text{AB}} = \sqrt{f_{\text{AB}} k_{\text{AA}} k_{\text{BB}} K_{\text{AB}}} \quad \dots \text{with } f_{\text{AB}} \approx 1$$

$$k_{\text{AB}} \approx \sqrt{k_{\text{AA}} k_{\text{BB}} K_{\text{AB}}}$$

... where $\Delta G_{\text{AB}}^\ddagger$ is similar to Albery's Equation 4...

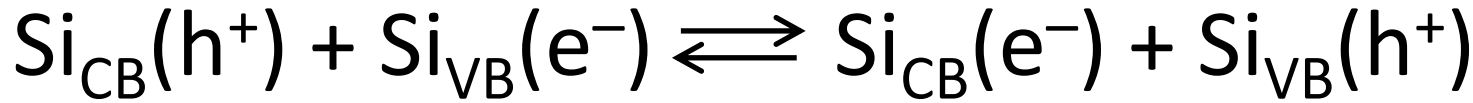
$$\Delta G_{I,II}^\ddagger = \frac{1}{2}\Delta G_{I,I}^\ddagger + \frac{1}{2}\Delta G_{II,II}^\ddagger + \frac{1}{2}\Delta G^\theta + \frac{(\Delta G^\theta)^2}{8(\Delta G_{I,I}^\ddagger + \Delta G_{II,II}^\ddagger)}$$

Today's Critical Guiding Question

Since **Marcus–Hush** theory is sufficient to predict all rate constants (with knowledge of only ΔG_{AB}° , λ_{AB} , and $|H_{DA}|^2$), and mass action makes knowledge of rates facile (and transport is a chemical reaction), can **Marcus–Hush** theory also be used to predict rates of interfacial charge transfer, e.g. current in electrochemistry?

Solid-State Physics Terminology

$$\bar{\mu}_i^\alpha = \left(\frac{\partial G}{\partial n_i} \right)_{T,p,n_{j \neq i}} \quad \text{(REVIEW) 133}$$



At equilibrium,

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

As reference states, it is useful to define

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

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

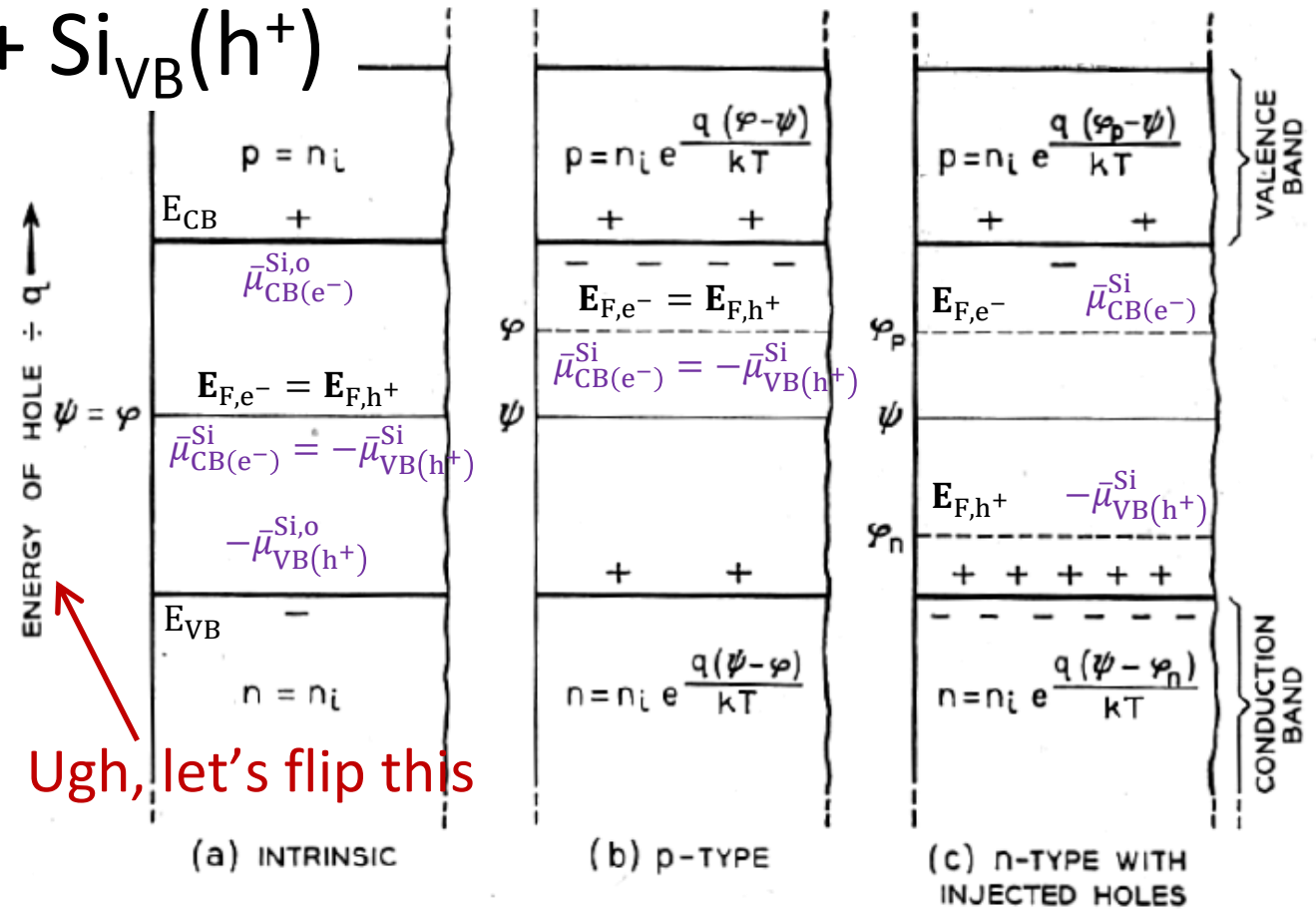
Anyway... therefore,

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

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

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

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



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.)

Charge Transfer across Electrified Interfaces

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



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

$$R_O = \frac{\partial c_{O,z_0}}{\partial t} = -k_f c_O + k_b c_R$$

I did not include primes here, for simplicity

$$j_E = nF(-k'_{f,E} c_{O,z_0} + k'_{b,E} c_{R,z_0})$$

... R_O is a rate... with units of M/s (= mol dm⁻³ s⁻¹)
... k_j (s⁻¹) is an inverse time constant!

... j_E is a current density... with units of A/cm² (= C cm⁻² s⁻¹)
... $k'_{j,E}$ (cm s⁻¹) is a velocity!

... as a specific case choose $E^{o'}$... and thus, $j_{E^{o'}} = nF(-k'_{f,E^{o'}} c_{O,z_0} + k'_{b,E^{o'}} c_{R,z_0})$

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

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

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

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

$$\eta = (E - E_{eq}) = E_{app} = \frac{\Delta G^0}{-nF} \quad \dots \text{where } \eta \text{ (V) is overpotential}$$

... this suggests that we will replace $k'_{j,E}$ velocity rate constants...
... with thermodynamic driving force terms!... But how?... **M–H!**

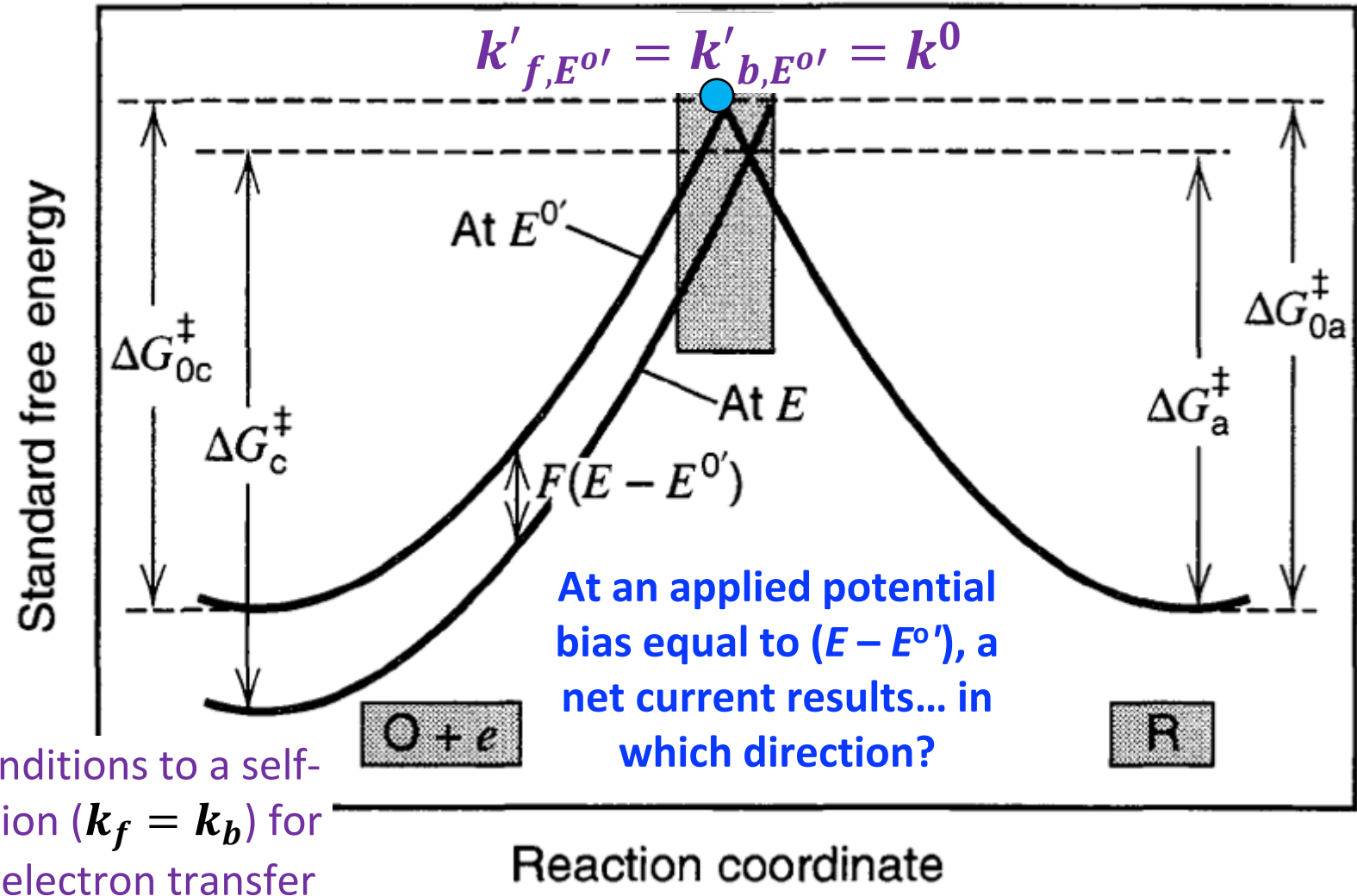
Charge Transfer across Electrified Interfaces

Key Electrochemical Information

- In electrochemistry, application of a potential, E_{app} , varies the electrochemical potential of electrons (e^-) in the (M)etal working electrode, $\bar{\mu}_e^M$
- Based on thermodynamics, when written as a reduction reaction, changing $\bar{\mu}_e^M$ alters the free energy (and also the standard free energy) of the reactants, as $\Delta G_A = \bar{\mu}_e^M + \bar{\mu}_O$ (and $\Delta G_A^0 = \bar{\mu}_e^M + \bar{\mu}_O^0$)
- The derivation here assumes that the electrode is inert, e.g. not like battery electrodes



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



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

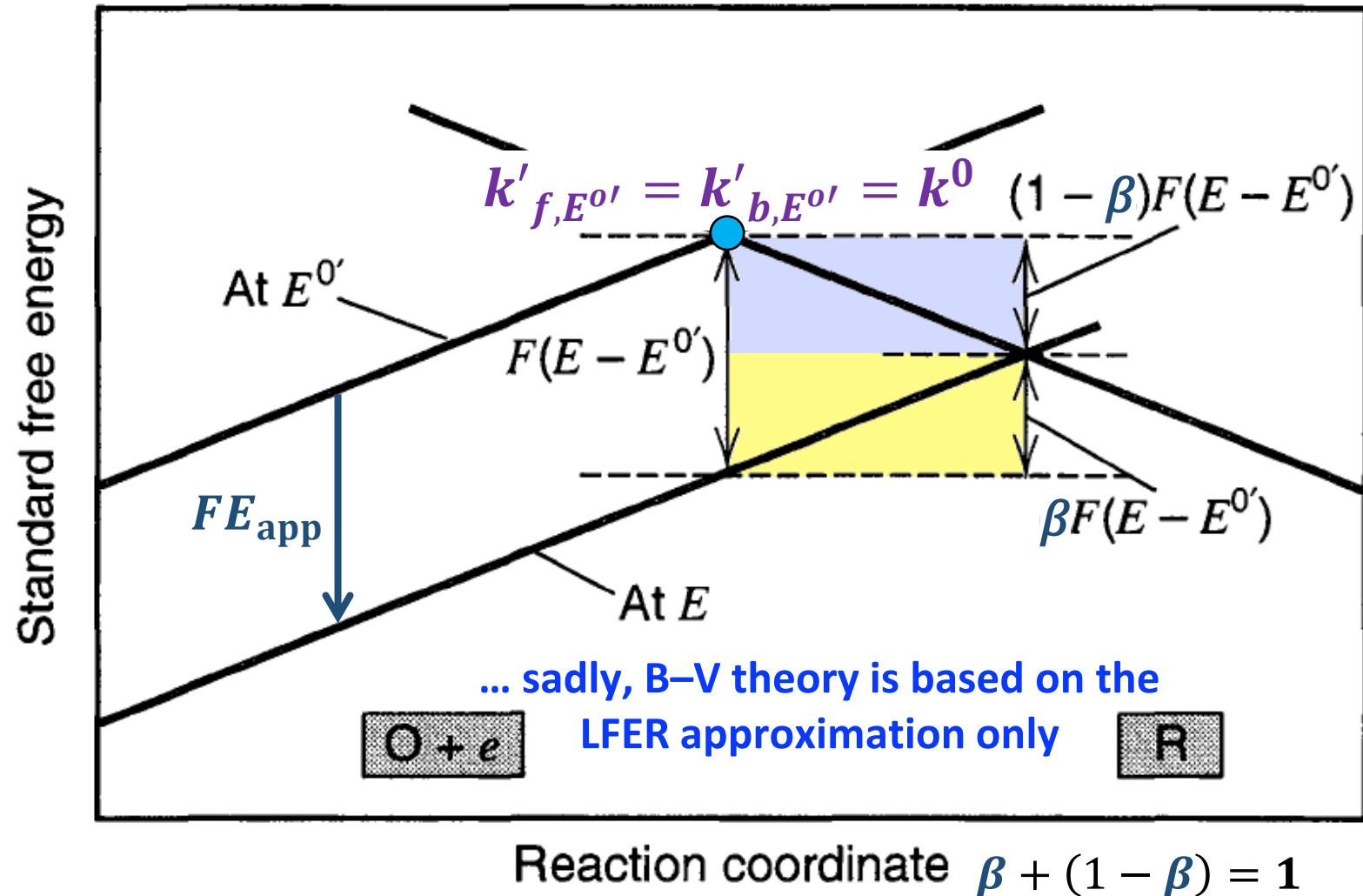
Charge Transfer across Electrified Interfaces

Key Electrochemical Information

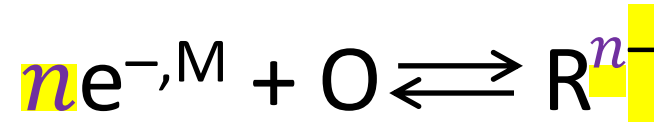
- In electrochemistry, application of a potential, E_{app} , varies the electrochemical potential of electrons (e^-) in the (M)etal working electrode, $\bar{\mu}_e^M$
- Based on thermodynamics, when written as a reduction reaction, changing $\bar{\mu}_e^M$ alters the free energy (and also the standard free energy) of the reactants, as $\Delta G_A = \bar{\mu}_e^M + \bar{\mu}_O$ (and $\Delta G_A^0 = \bar{\mu}_e^M + \bar{\mu}_O^0$)
- Based on approximations, altering ΔG_A changes all ΔG values on the reaction coordinate relative to the initial ΔG_A , and not differently along the parabolic/linear shape of the reactant "surface"... **Should it?**



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



Butler–Volmer equation



$$j_E = nF(k'_{b,E}c_{R,z_0} - k'_{f,E}c_{O,z_0}) \quad \dots \text{for this example, let's assume that } n = 1\dots$$

$$j_E = Fk^0 \left\{ c_{R,z_0} \exp\left(\frac{(1-\beta)F(E-E^{o'})}{RT}\right) - c_{O,z_0} \exp\left(\frac{-\beta F(E-E^{o'})}{RT}\right) \right\} \quad \text{Current–Potential Characteristic}$$

$$j_E = j_o \left\{ \frac{c_{R,z_0}}{c_R^*} \exp\left(\frac{(1-\beta)F\eta}{RT}\right) - \frac{c_{O,z_0}}{c_O^*} \exp\left(\frac{-\beta F\eta}{RT}\right) \right\} \quad \begin{array}{l} \eta = (E - E_{eq}) = E_{app} \\ j_o = Fk^0 c_R^{*\beta} c_O^{*(1-\beta)} \end{array} \quad \text{Current–Overpotential Equation}$$

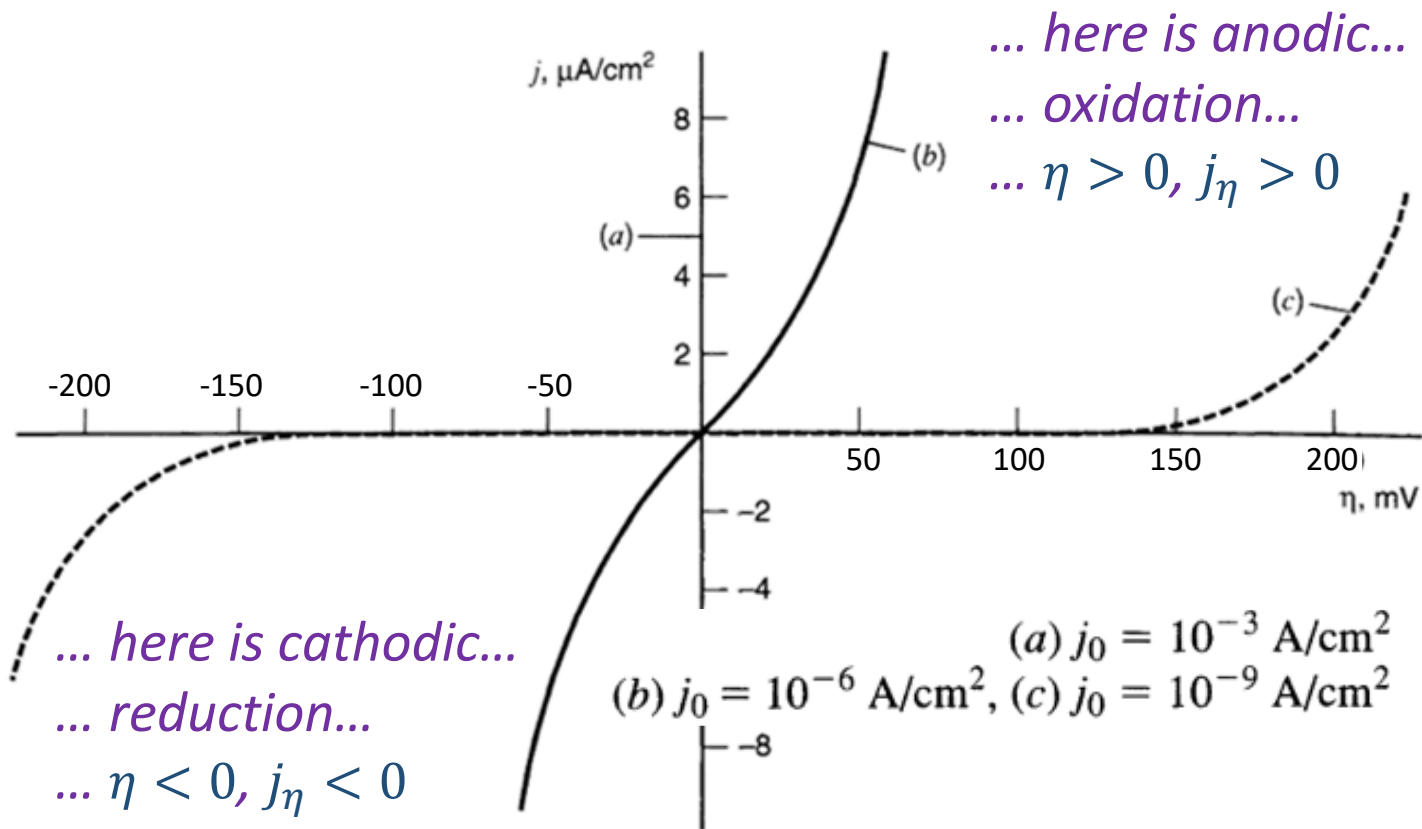
... c^* means bulk concentration... conversion is trivial using $E_{eq} = E^{o'} - \frac{RT}{nF} \ln \frac{c_R^*}{c_O^*}$

$$j_E = j_o \left\{ \exp\left(\frac{(1-\beta)F\eta}{RT}\right) - \exp\left(\frac{-\beta F\eta}{RT}\right) \right\} \quad \text{Butler–Volmer Equation} \quad \text{Tafel Slopes} \quad \begin{array}{l} TS_{cath}^{-1} = \left(\frac{d(\log |j_E|)}{d|\eta|}\right)_{cath} = \frac{-\beta F}{2.303RT} \\ TS_{an}^{-1} = \left(\frac{d(\log j_E)}{d\eta}\right)_{an} = \frac{(1-\beta)F}{2.303RT} \end{array}$$

... assuming a rapidly stirred solution

Butler–Volmer equation

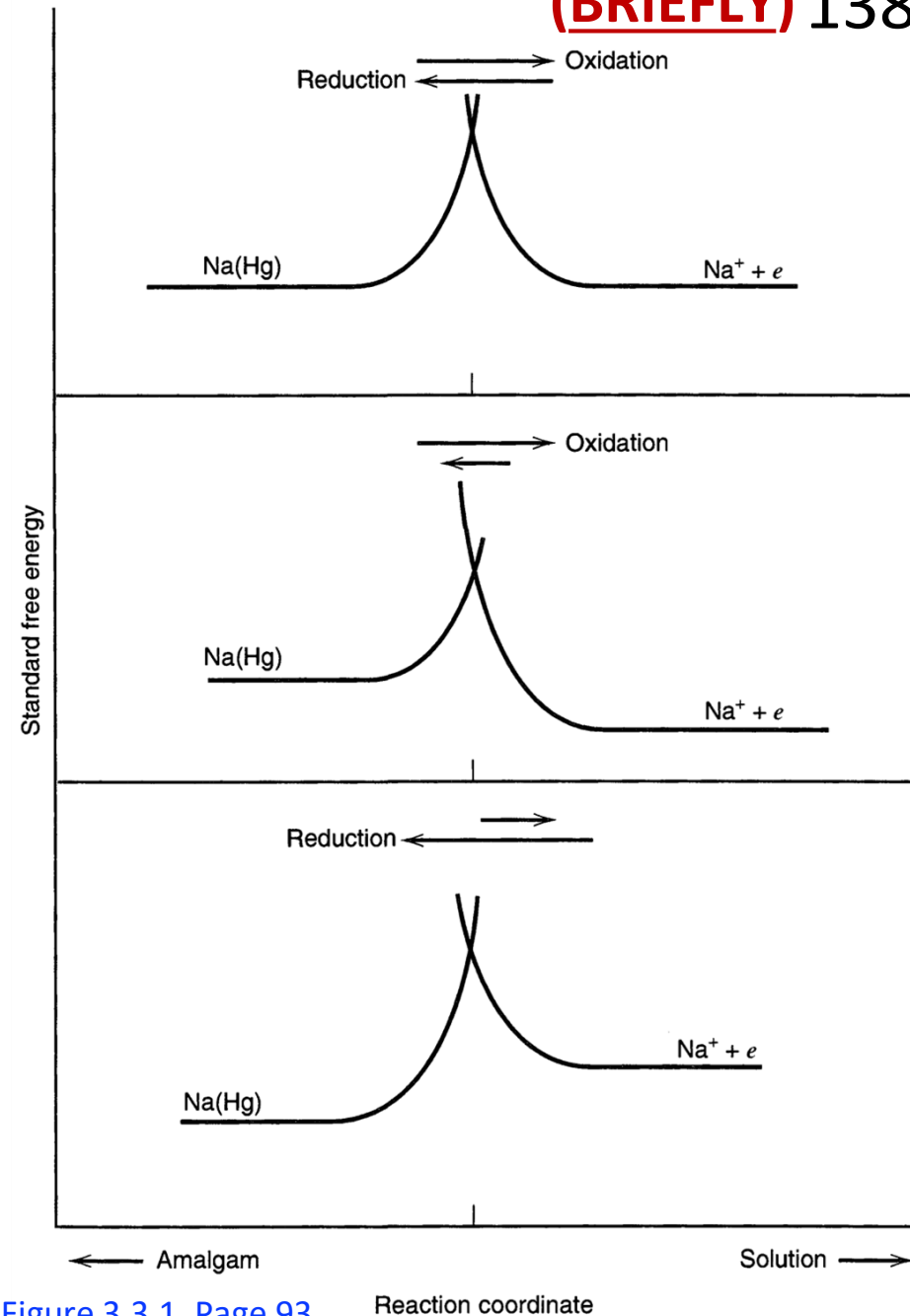
... let's examine effects of j_0 (or k^0)...



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

... recall that... $\eta = (E - E_{\text{eq}}) = E_{\text{app}} = \frac{\Delta G^0}{-nF}$

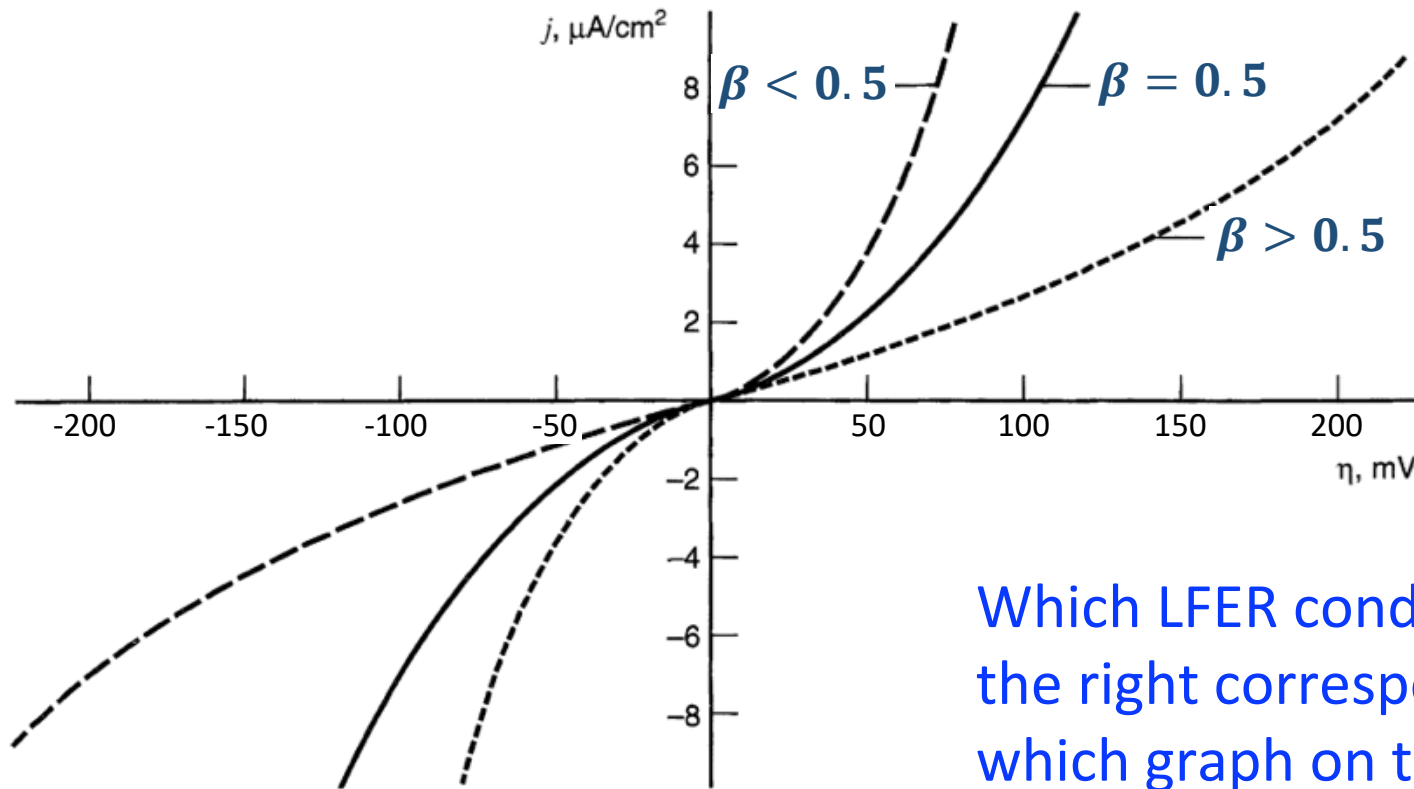
Bard & Faulkner, Chapter 3, Figure 3.3.1, Page 93



Reaction coordinate

Butler–Volmer equation

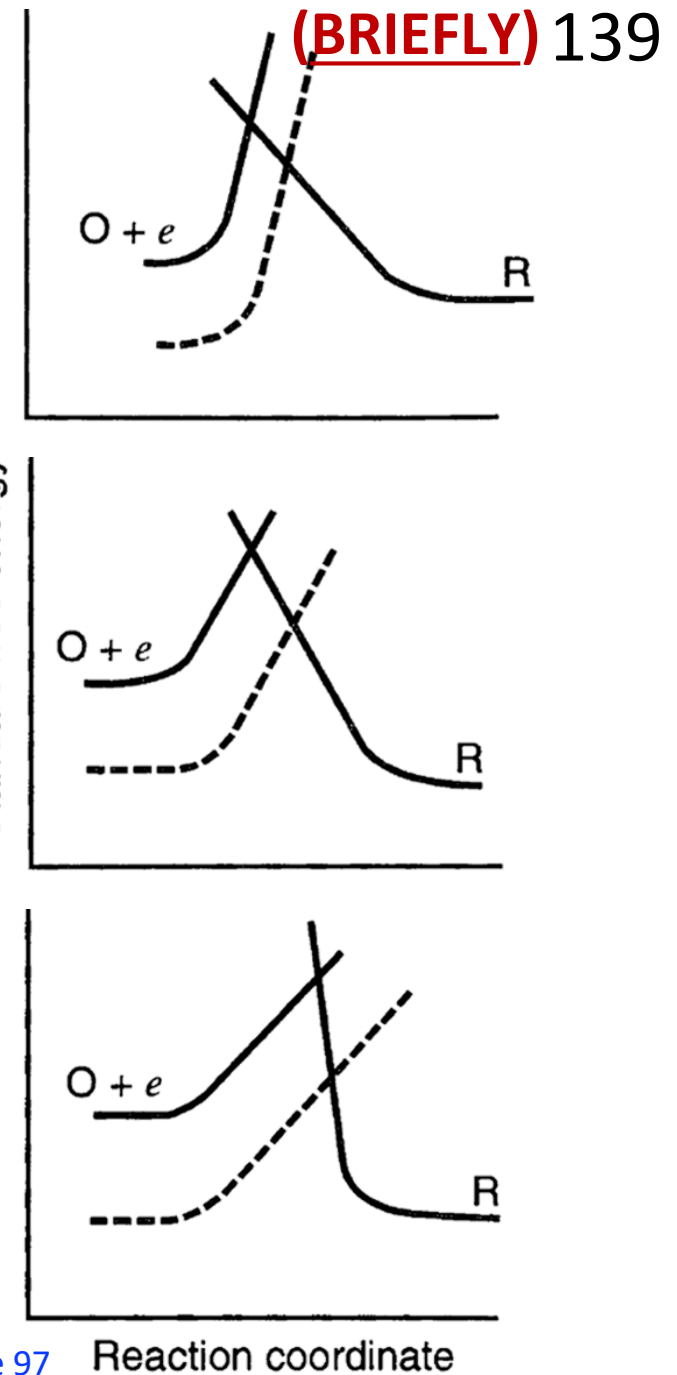
... let's examine effects of β (or Tafel slope)...



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

... recall that... $\eta = (E - E_{\text{eq}}) = E_{\text{app}} = \frac{\Delta G^0}{-nF}$

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

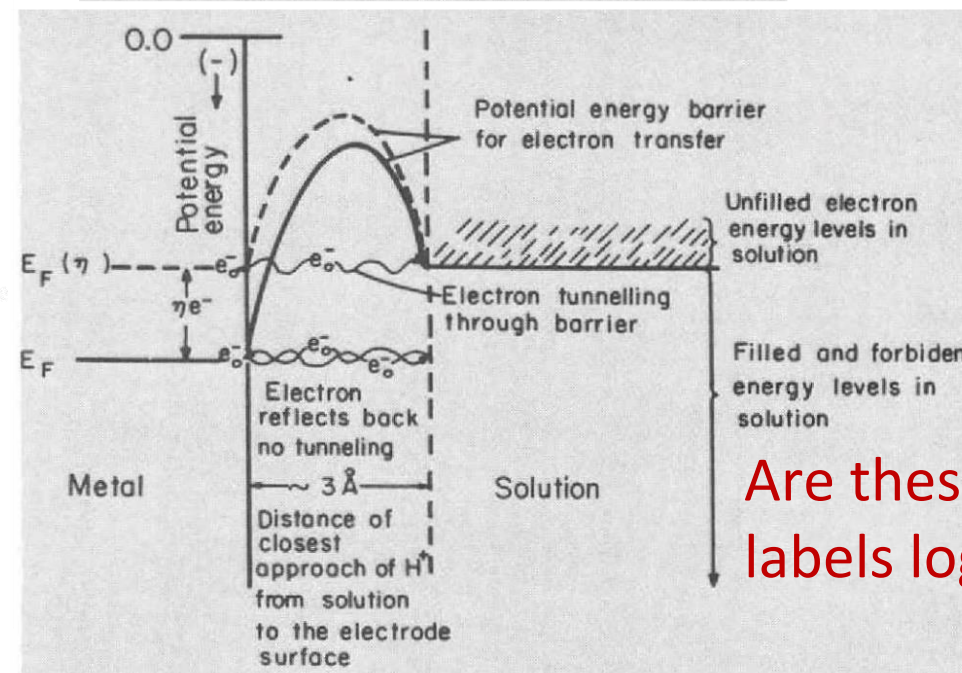
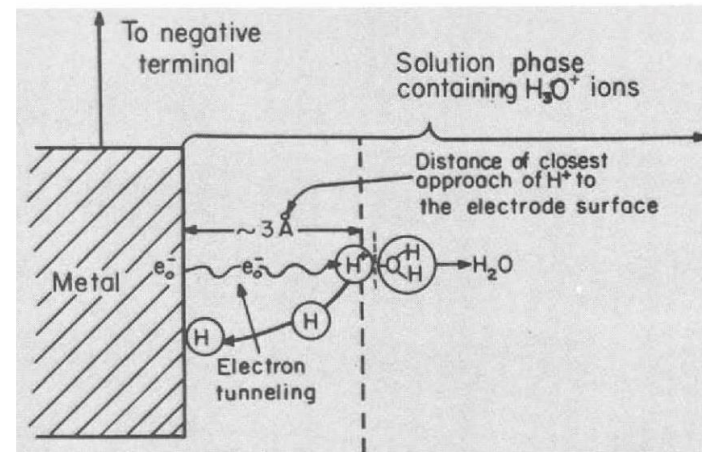
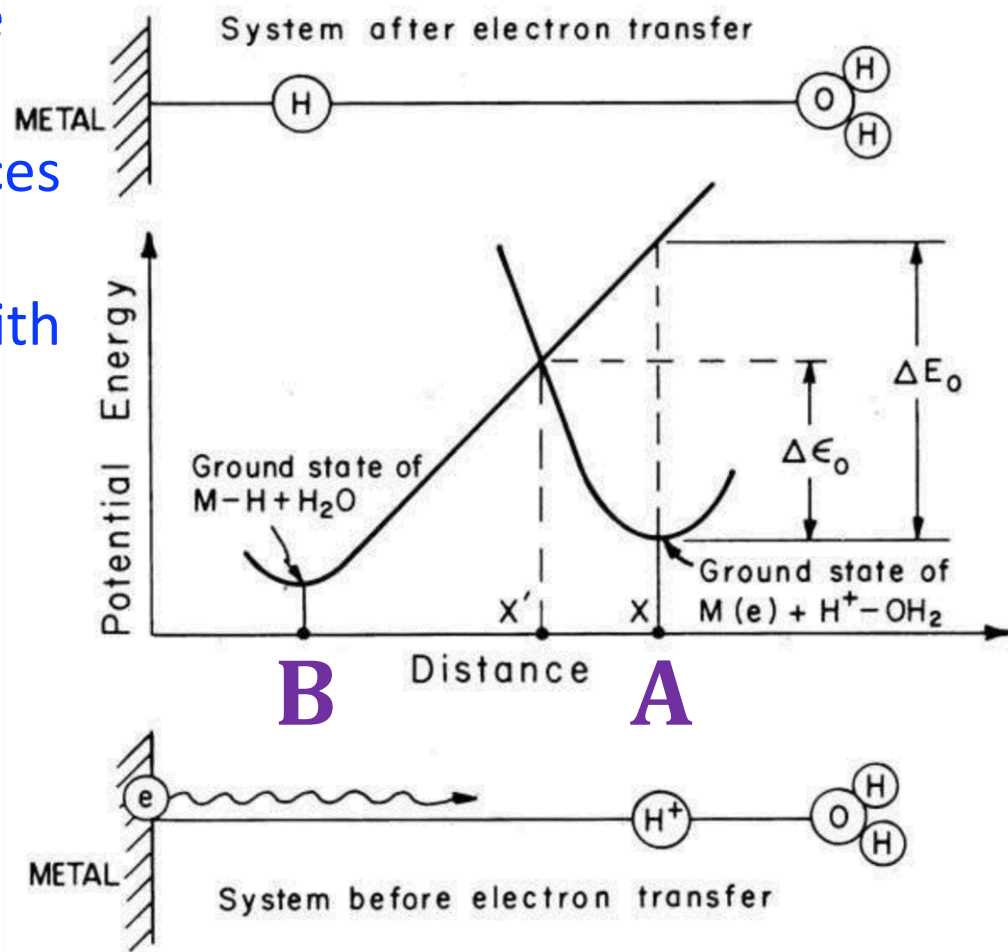


Charge Transfer across Electrified Interfaces

Why are these "Potential Energy" surfaces so linear and asymmetric with "Distance"?

$$E_{app} \ll \frac{\lambda_{AB}}{2}$$

... with a transition state that is more reactant-like, i.e. A



Are these labels logical?

Fermi's (Second) Golden Rule

$$j_E = nF(-k'_{f,E}c_{O,z_0} + k'_{b,E}c_{R,z_0})$$

k'_j (cm s⁻¹)... a velocity!

Transition probability

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

Matrix element for the interaction

Density of final states (DoS)

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

... divide the DoS term by c_{i,z_0} ...

frequency factor (s⁻¹)

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

proportionality function (cm³ eV)

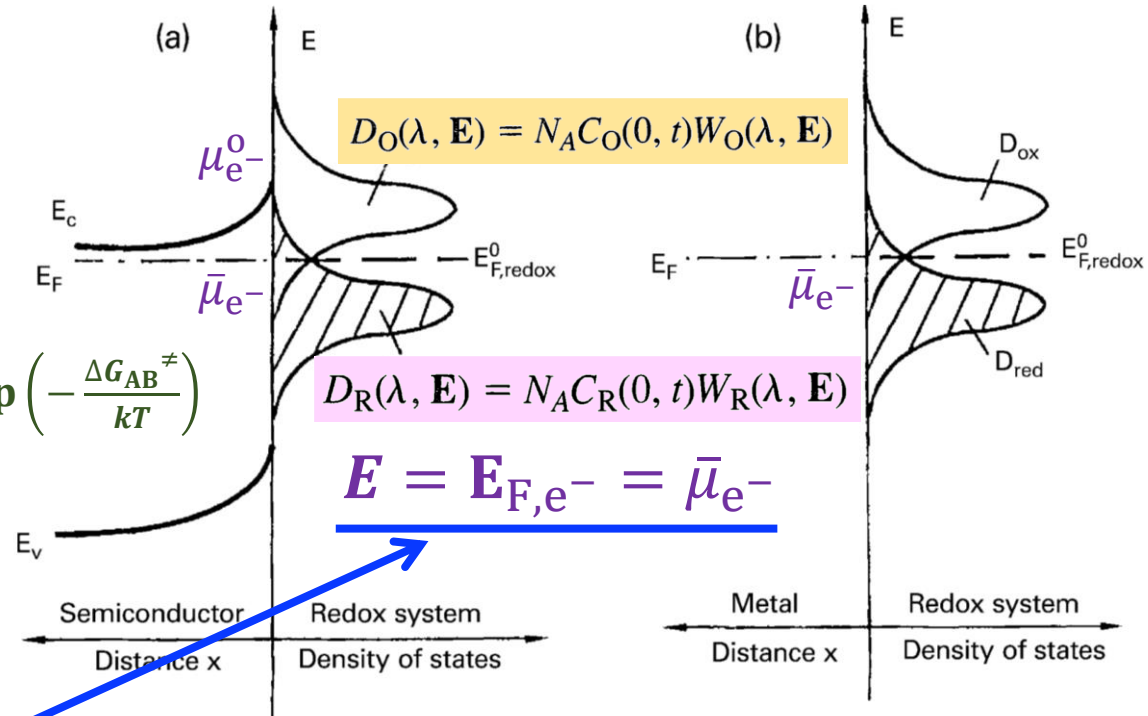
$$k_b = \nu \int_{-\infty}^{\infty} \epsilon_{ox}(\mathbf{E}) W_R(\lambda, \mathbf{E}) [1 - f(\mathbf{E})] \rho(\mathbf{E}) d\mathbf{E}$$

applied potential

$$k'_{f,E,obs} = \int_{-\infty}^{\infty} k'_{f,E} dE \quad k'_{b,E,obs} = \int_{-\infty}^{\infty} k'_{b,E} dE$$

energy

$$j_{E,obs} = nF(-k'_{f,E,obs}c_{O,z_0} + k'_{b,E,obs}c_{R,z_0})$$

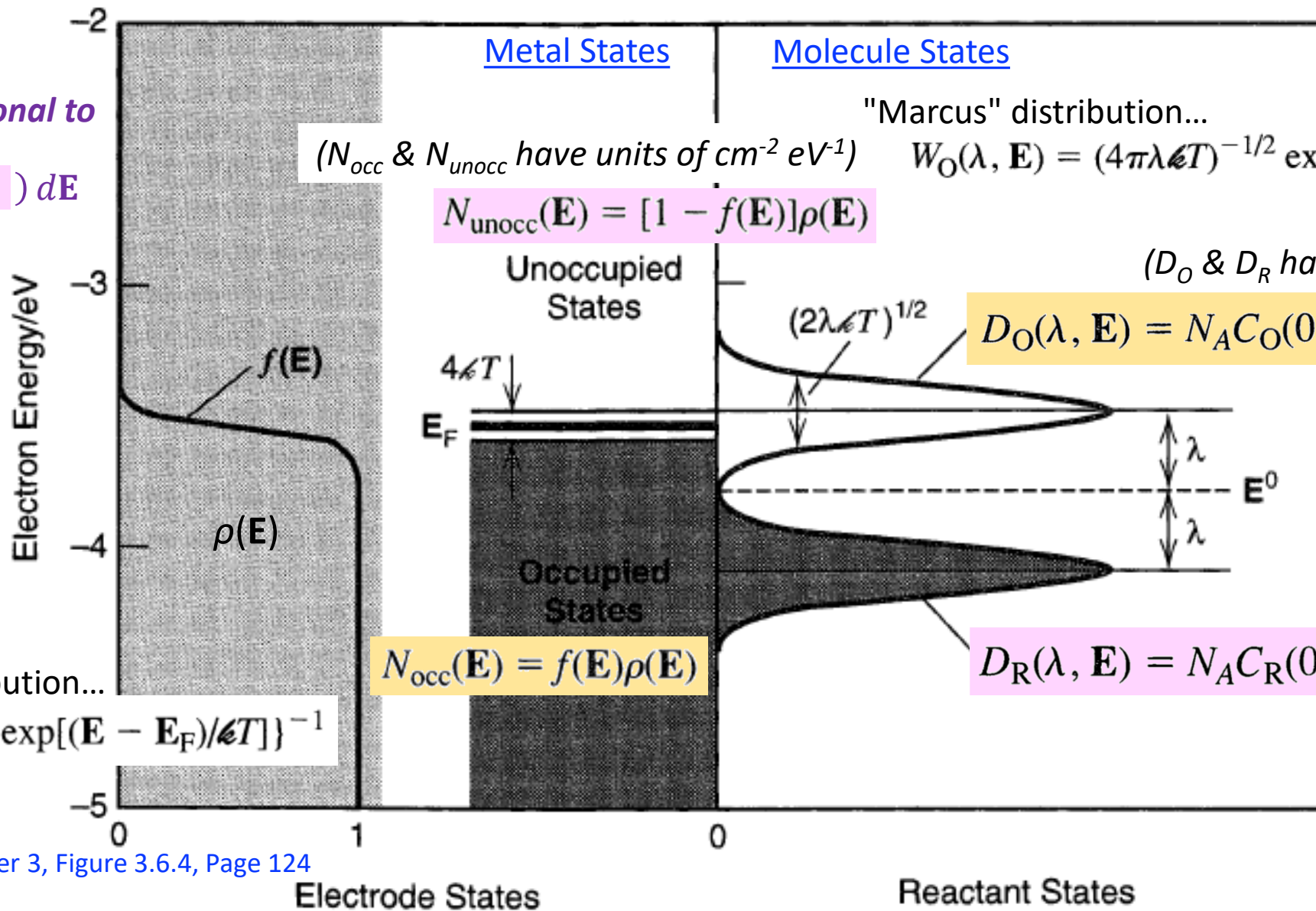


R. Memming, Chapter 6, Semiconductor Electrochemistry

Marcus–Gerischer Theory

ET rate is proportional to

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



Metal States

Molecule States

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

"Marcus" distribution...

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

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

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

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

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

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

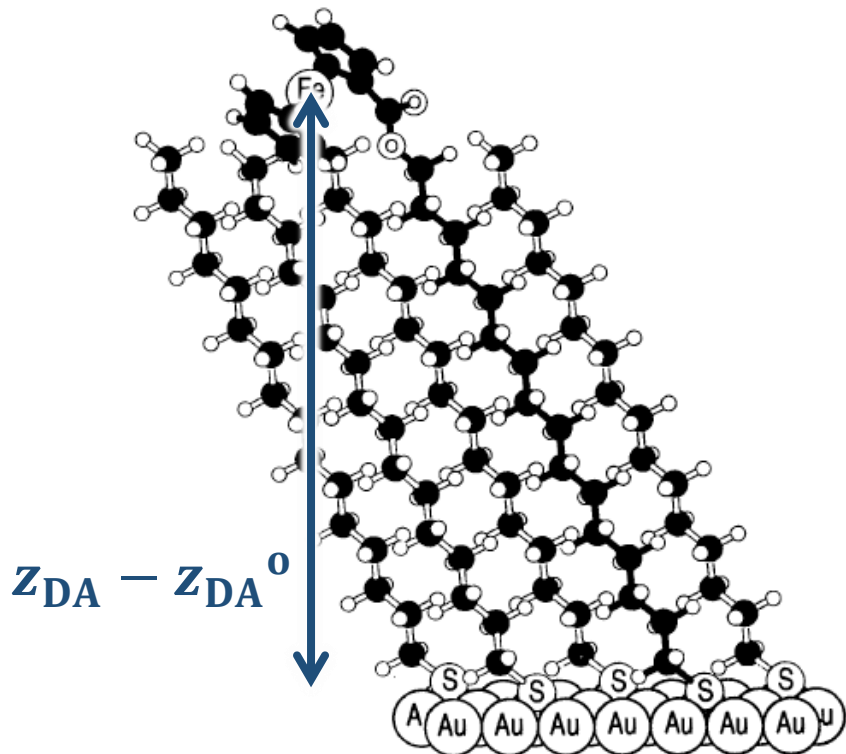
Fermi-Dirac distribution...

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

Marcus–Gerischer Theory

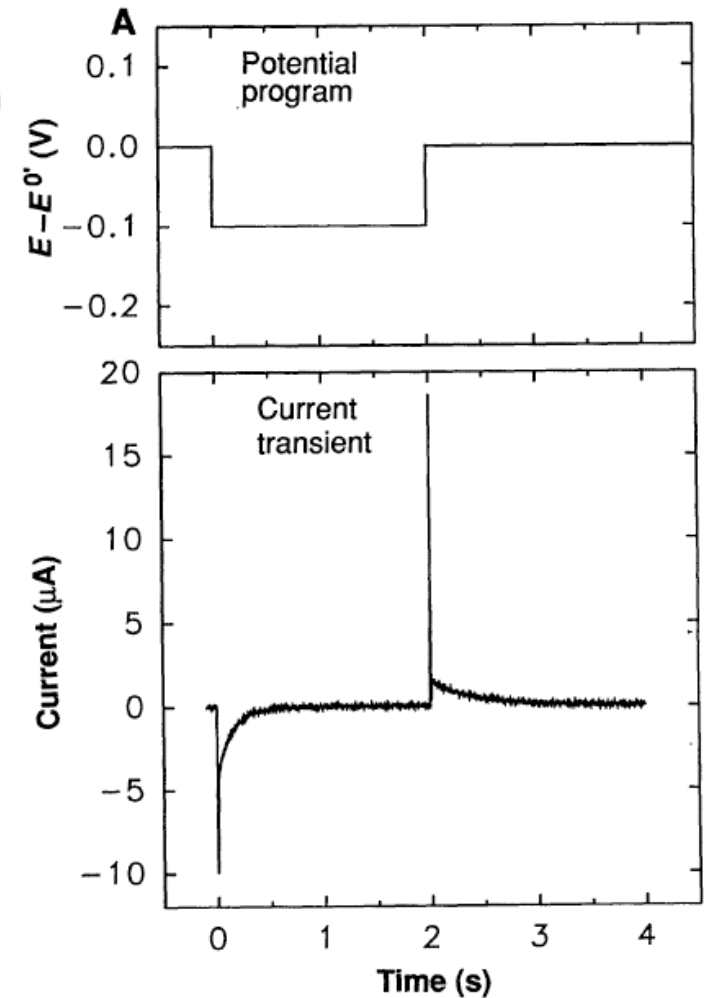
$$k_{ET} = \frac{2\pi}{\hbar} |H_{DA}^0|^2 e^{-2\beta(z_{DA} - z_{DA}^0)} \frac{1}{\sqrt{4\pi\lambda_{AB}kT}} \exp\left(-\frac{(\lambda_{AB} + \Delta G_{AB}^0)^2}{4\lambda_{AB}kT}\right)$$

quantum adiabatic electronic coupling classical nuclear free-energy dependence

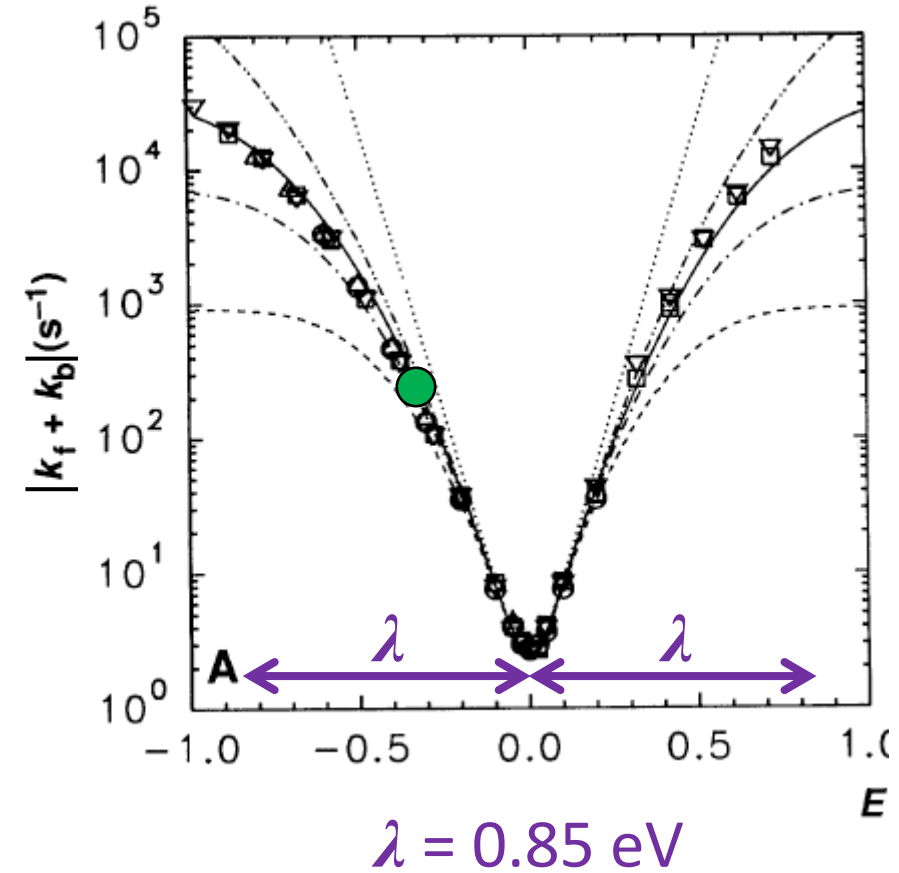
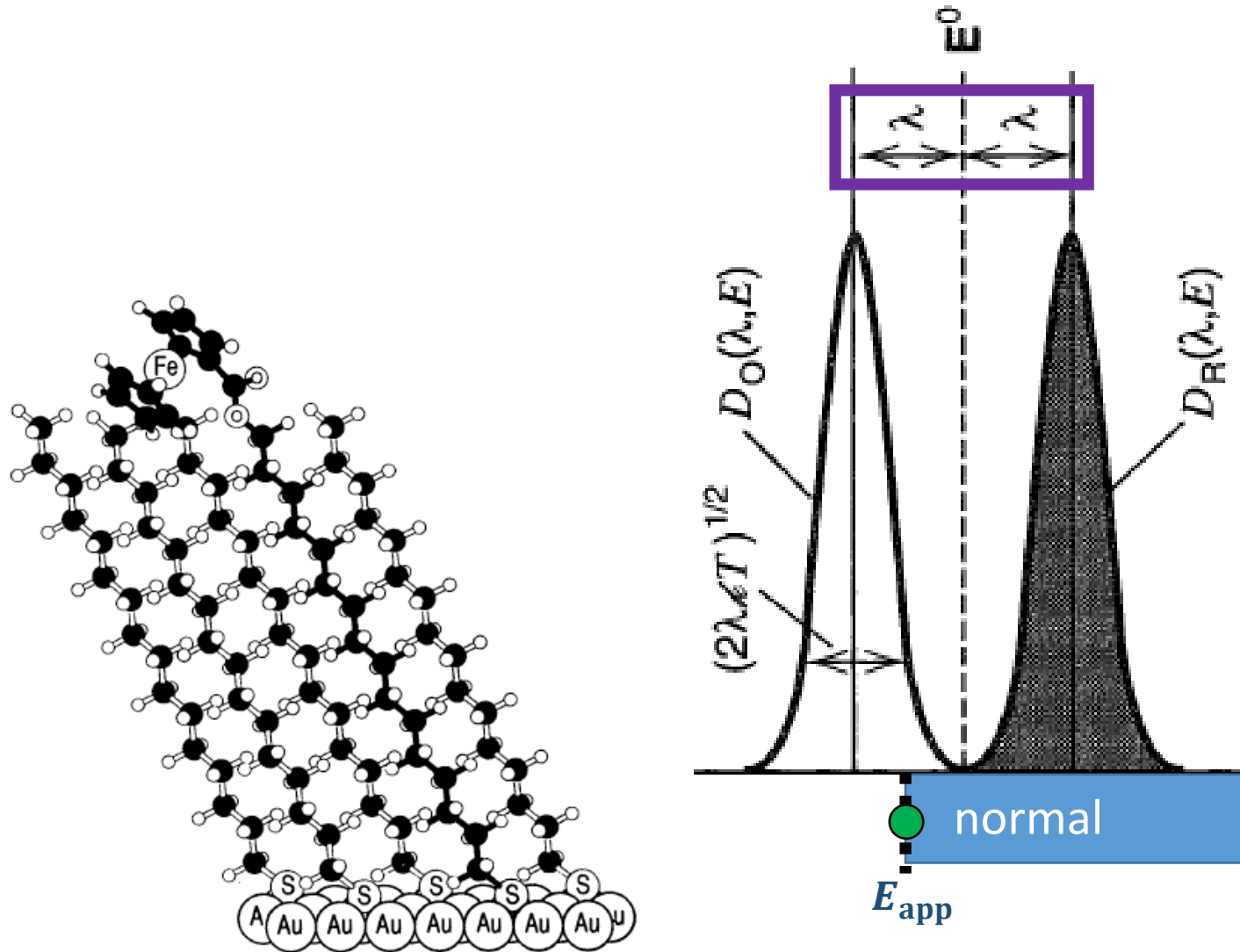


... as an aside... why is the data biphasic for the Current?

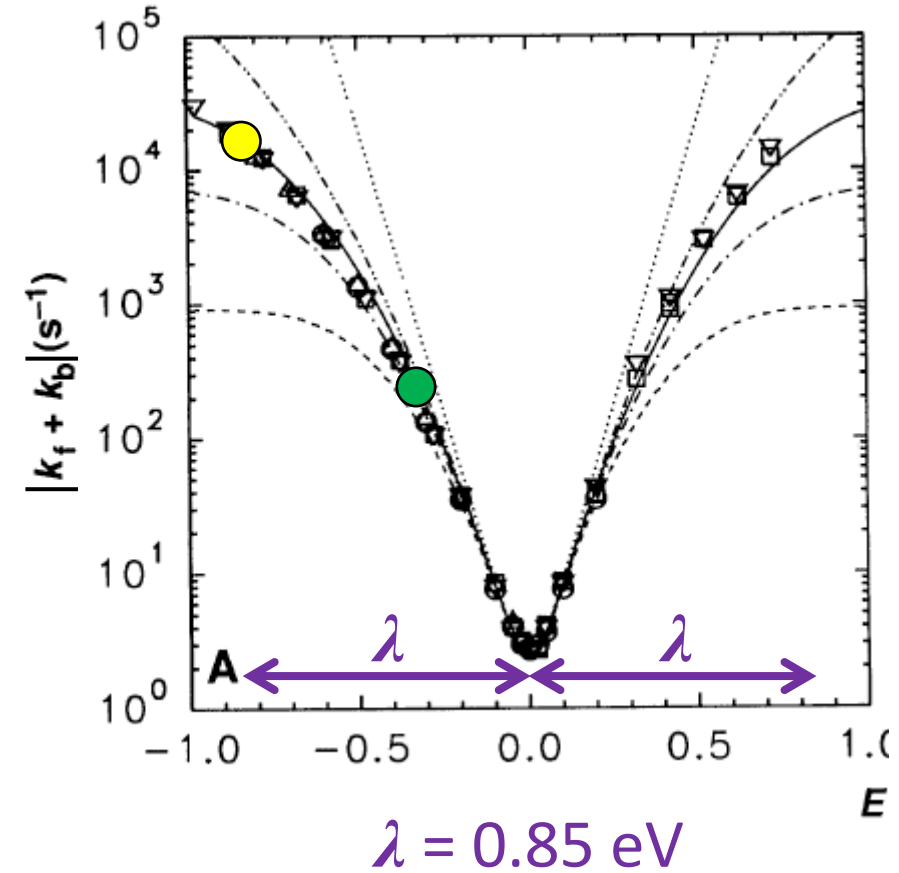
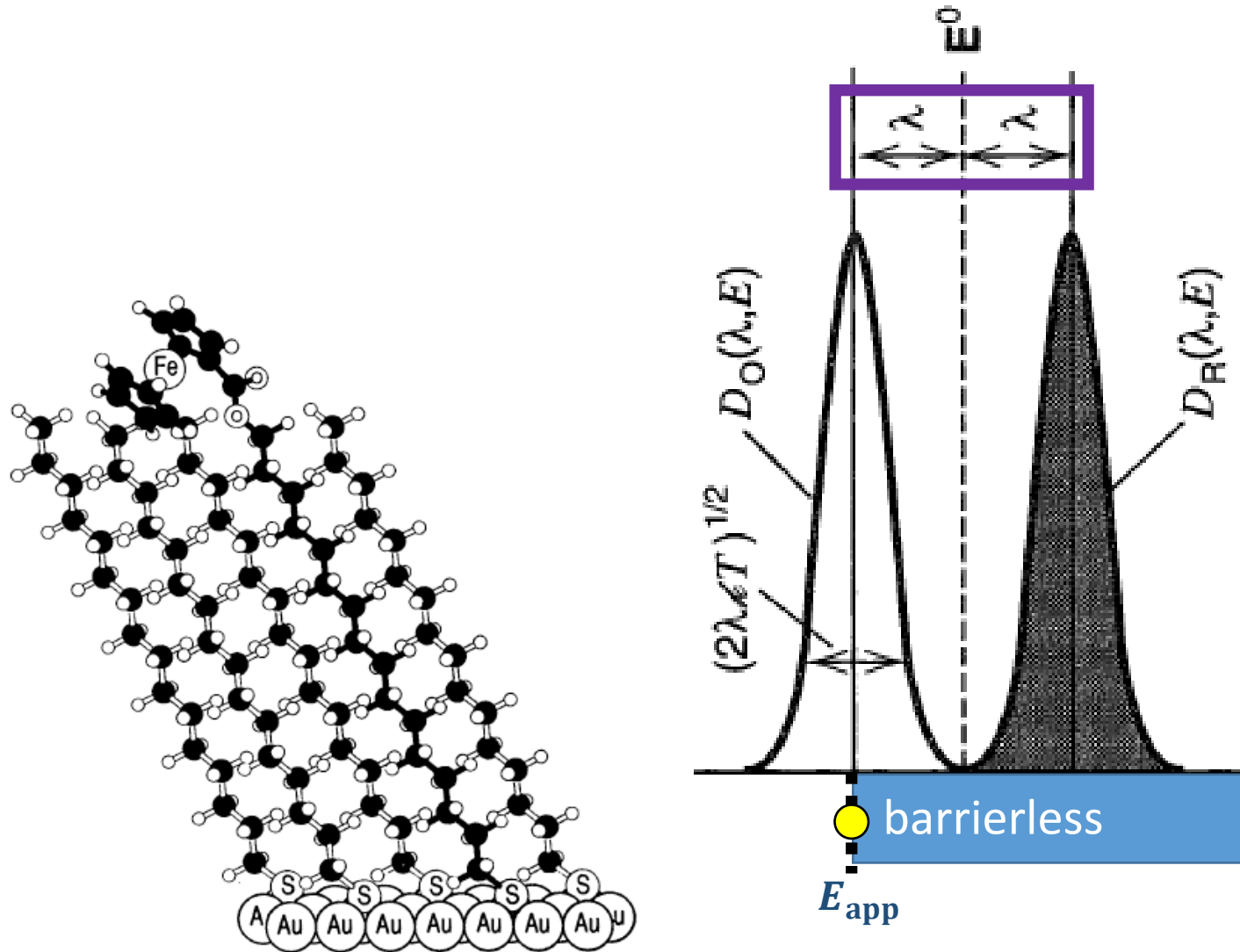
... RC-circuit double layer charging... followed by 1st-order ET kinetics



Marcus–Gerischer Theory



Marcus–Gerischer Theory



Marcus–Gerischer Theory

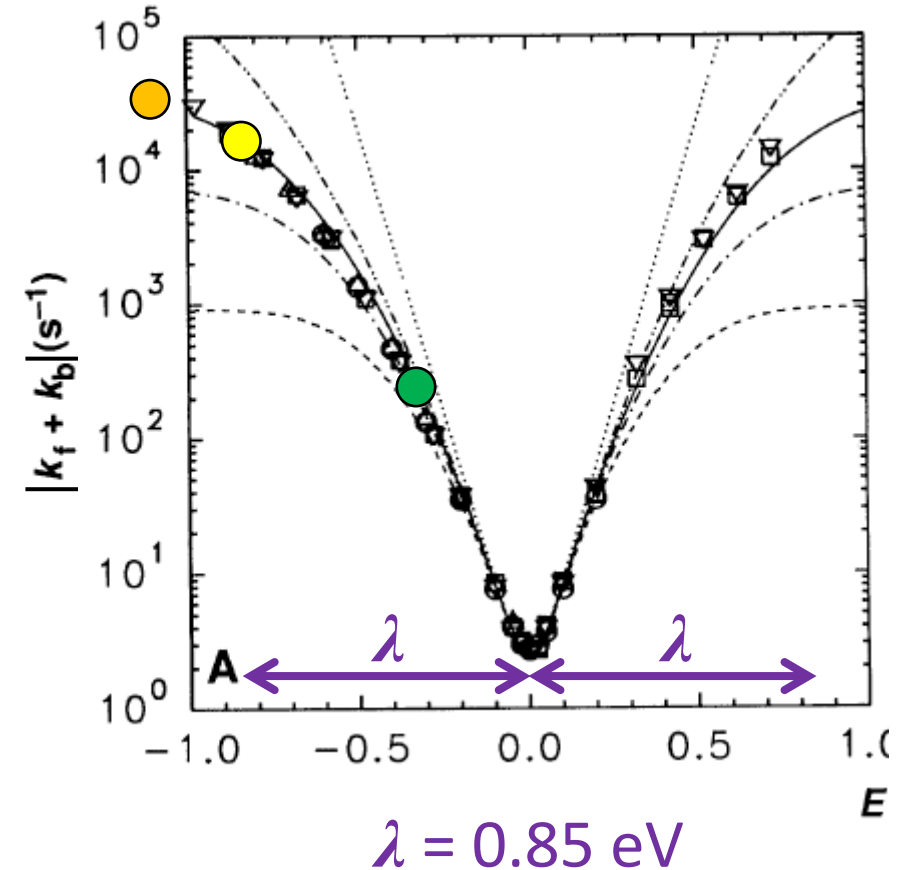
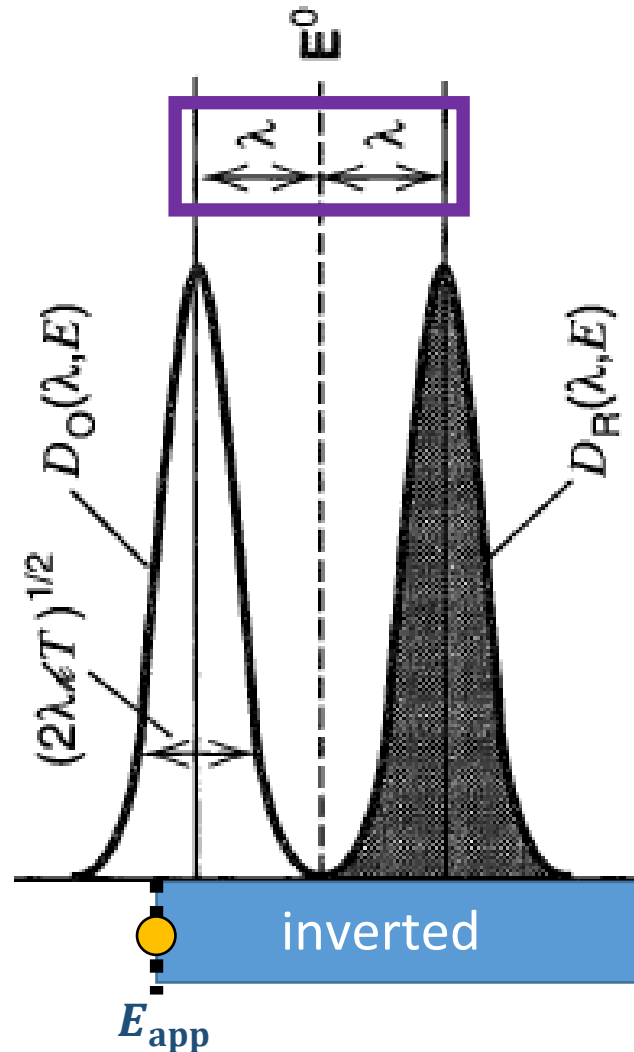
- It is easy to sweep/vary the driving force, ΔG_{AB} , by simply changing the electrochemical potential of electrons (e^-) in the (M)etal working electrode, $\bar{\mu}_e^M$, through variations in E_{app}

- 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!



Today's Critical Guiding Question

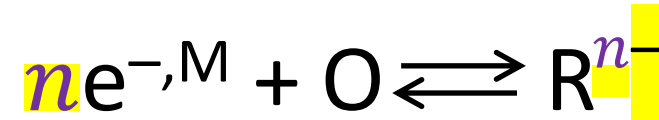
*Since **Marcus–Hush** theory is sufficient to predict all rate constants (with knowledge of only ΔG_{AB}° , λ_{AB} , and $|H_{DA}|^2$), and mass action makes knowledge of rates facile (and transport is a chemical reaction), can **Marcus–Hush** theory also be used to predict rates of interfacial charge transfer, e.g. current in electrochemistry?*

Thermal (Dark) Reactions

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

DISCUSSION SESSION TOPICS

Butler–Volmer equation



$$j_E = nF(k'_{b,E}c_{R,z_0} - k'_{f,E}c_{O,z_0}) \quad \dots \text{for this example, let's assume that } n = 1\dots$$

$$j_E = Fk^0 \left\{ c_{R,z_0} \exp\left(\frac{(1-\beta)F(E-E^{o'})}{RT}\right) - c_{O,z_0} \exp\left(\frac{-\beta F(E-E^{o'})}{RT}\right) \right\} \quad \text{Current–Potential Characteristic}$$

$$j_E = j_o \left\{ \frac{c_{R,z_0}}{c_R^*} \exp\left(\frac{(1-\beta)F\eta}{RT}\right) - \frac{c_{O,z_0}}{c_O^*} \exp\left(\frac{-\beta F\eta}{RT}\right) \right\} \quad \begin{array}{l} \eta = (E - E_{eq}) = E_{app} \\ j_o = Fk^0 c_R^{*\beta} c_O^{*(1-\beta)} \end{array} \quad \text{Current–Overpotential Equation}$$

... c^* means bulk concentration... conversion is trivial using $E_{eq} = E^{o'} - \frac{RT}{nF} \ln \frac{c_R^*}{c_O^*}$

$$j_E = j_o \left\{ \exp\left(\frac{(1-\beta)F\eta}{RT}\right) - \exp\left(\frac{-\beta F\eta}{RT}\right) \right\} \quad \text{Butler–Volmer Equation}$$

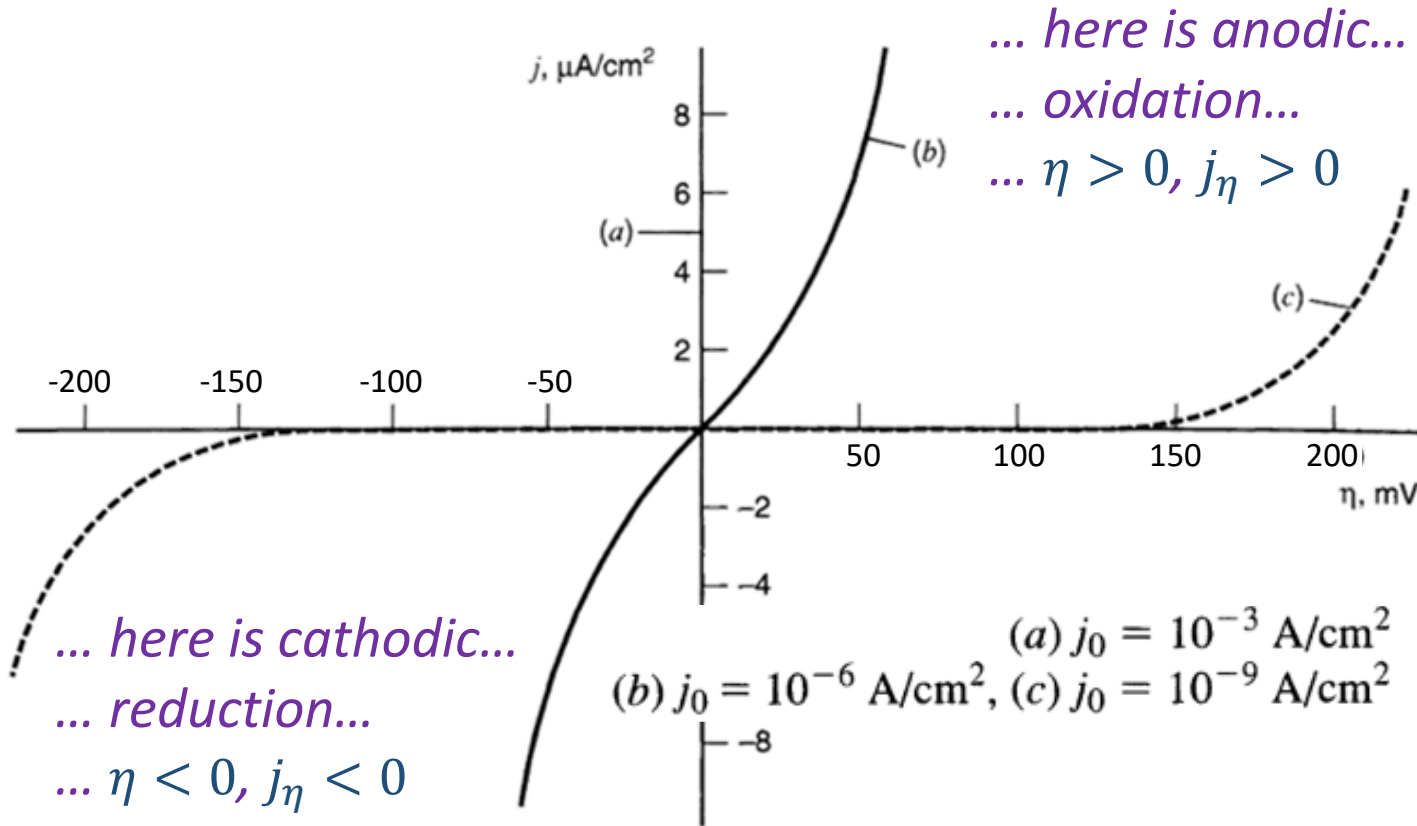
... assuming a rapidly stirred solution

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

$$\text{Tafel Slopes } \text{TS}_{\text{an}}^{-1} = \left(\frac{d(\log j_E)}{d\eta} \right)_{\text{an}} = \frac{(1-\beta)F}{2.303RT}$$

Butler–Volmer equation

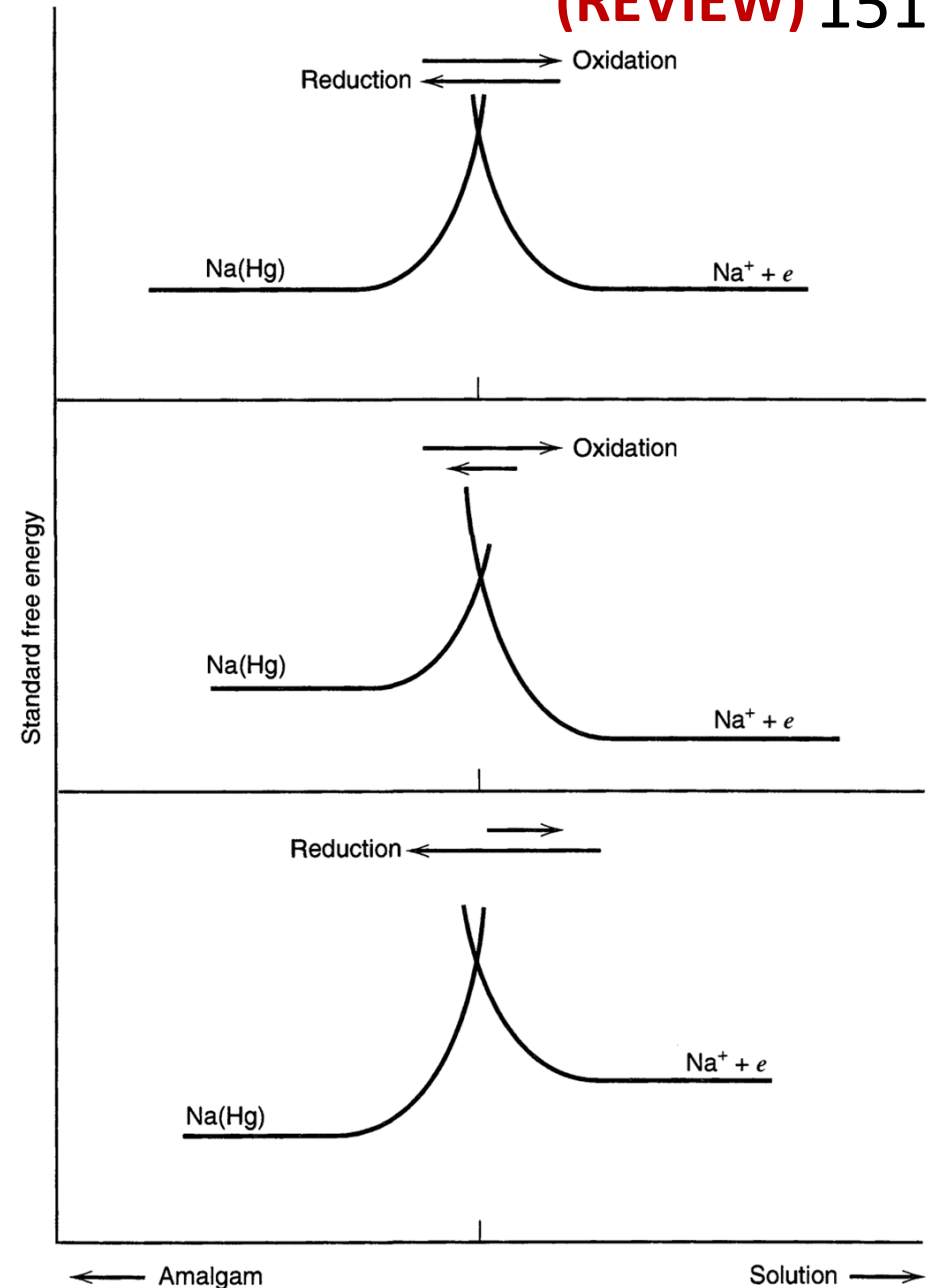
... let's examine effects of j_0 (or k^0)...



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

... recall that... $\eta = (E - E_{\text{eq}}) = E_{\text{app}} = \frac{\Delta G^0}{-nF}$

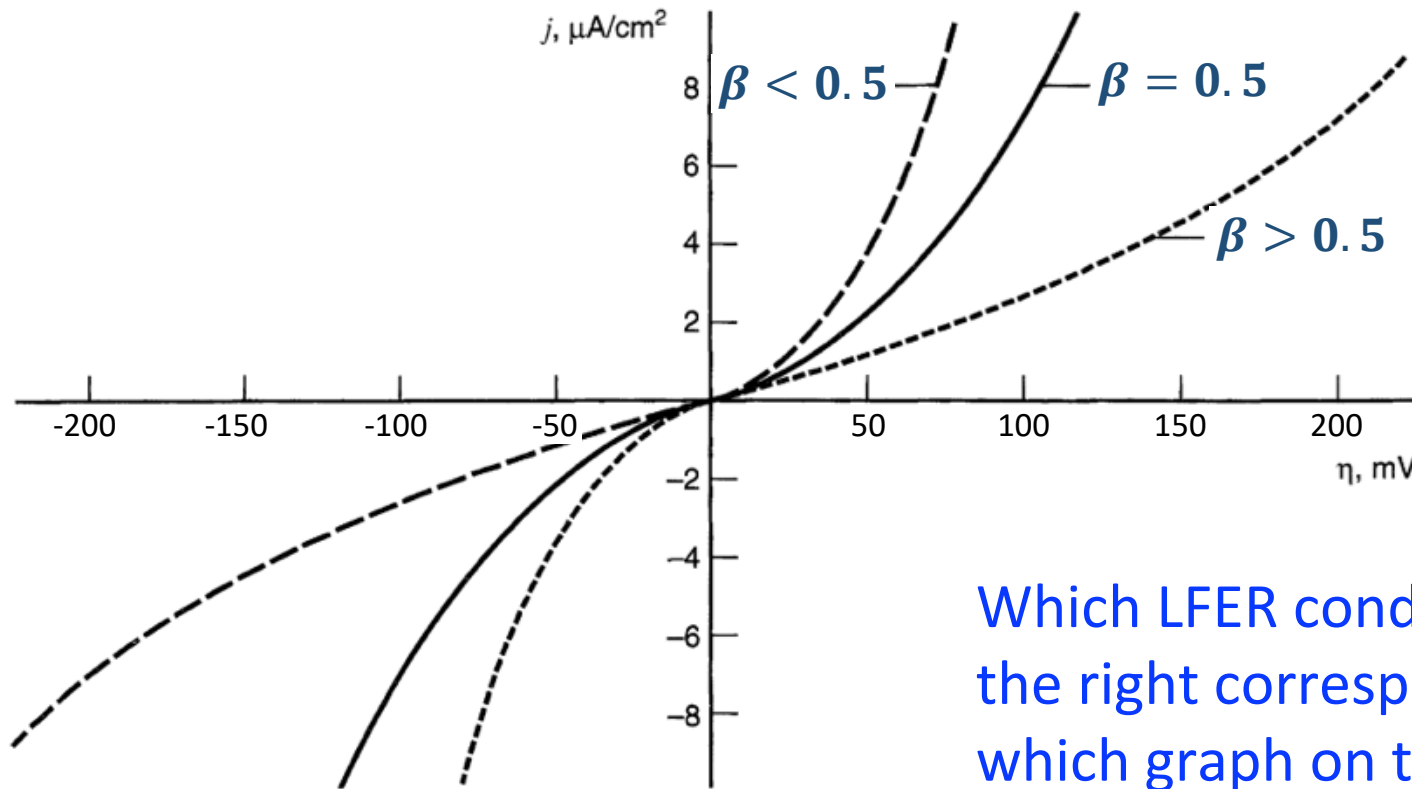
Bard & Faulkner, Chapter 3, Figure 3.3.1, Page 93



Reaction coordinate

Butler–Volmer equation

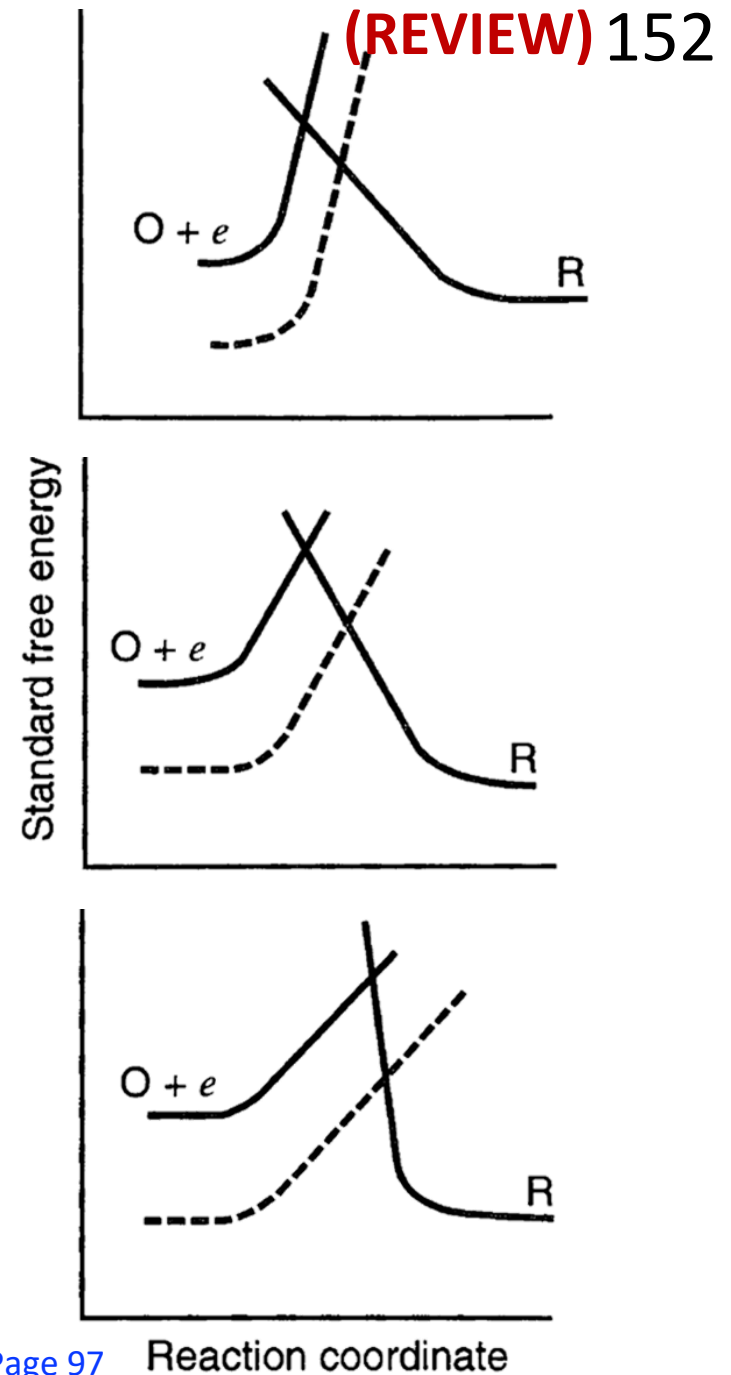
... let's examine effects of β (or Tafel slope)...



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

... recall that... $\eta = (E - E_{\text{eq}}) = E_{\text{app}} = \frac{\Delta G^0}{-nF}$

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

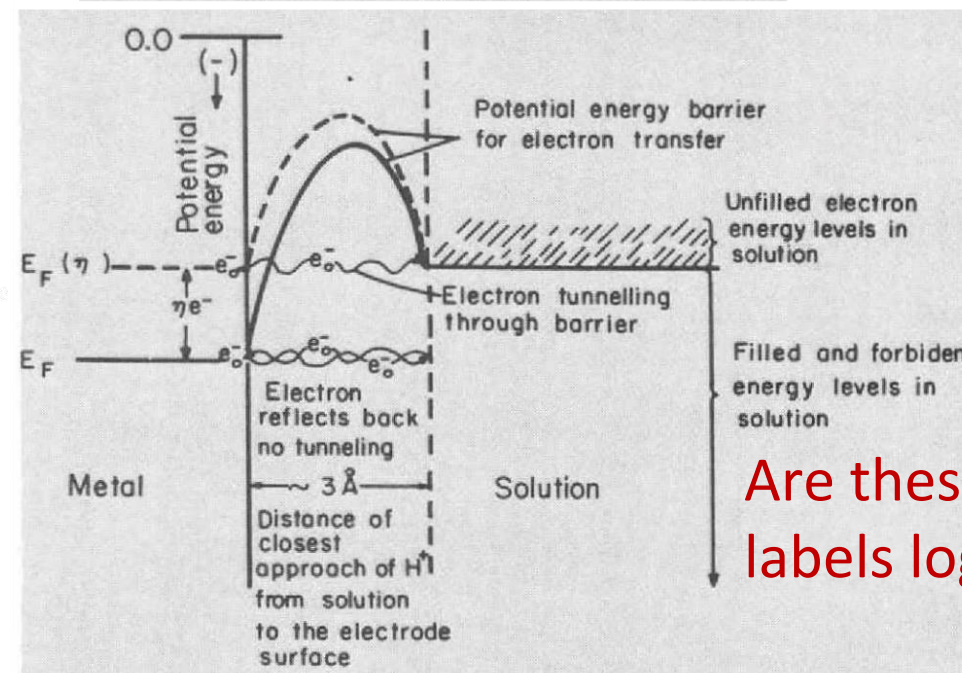
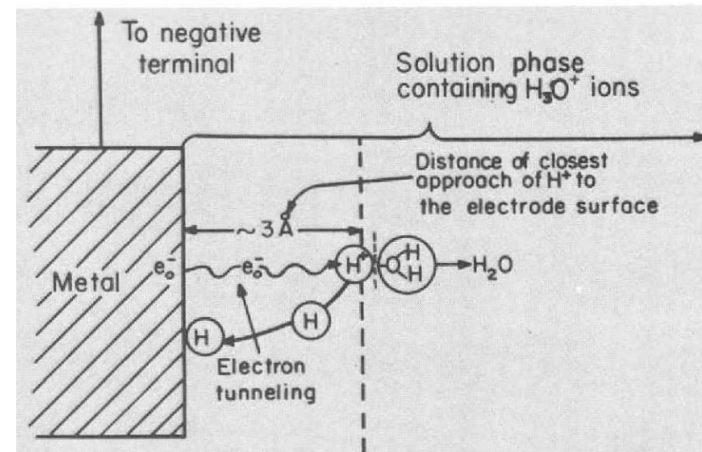
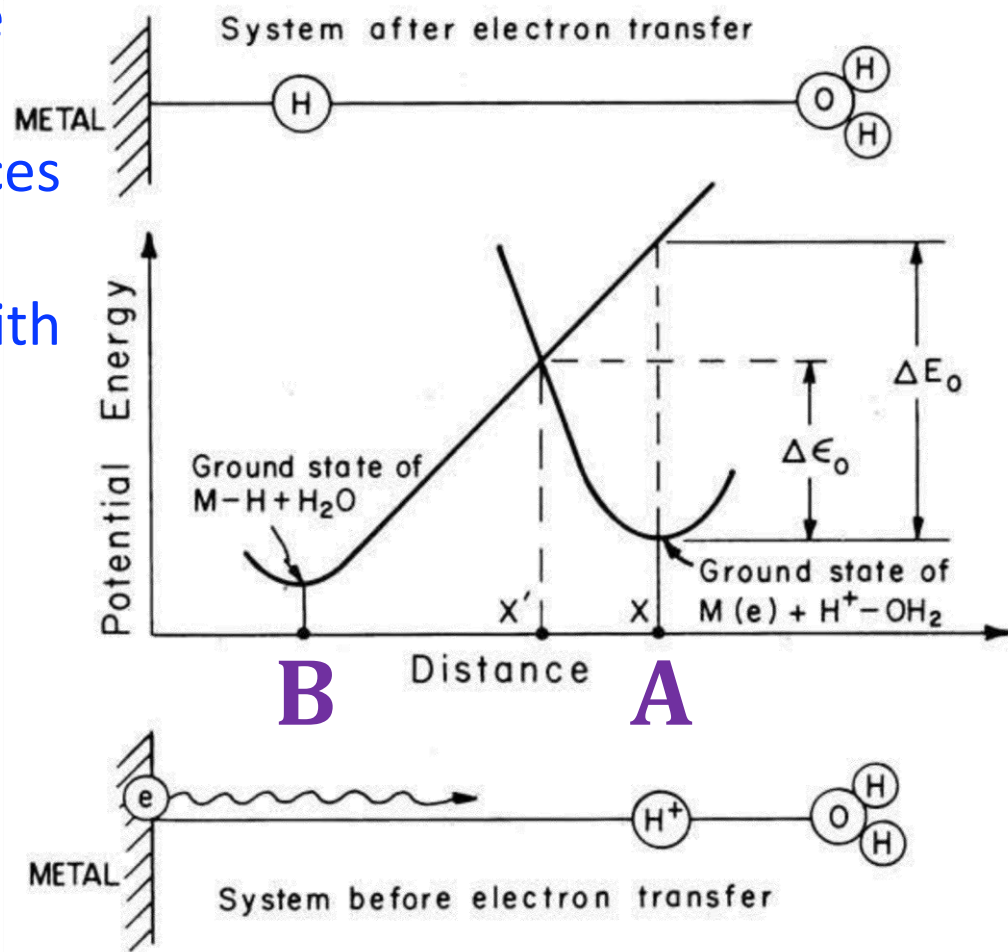


Charge Transfer across Electrified Interfaces

Why are these "Potential Energy" surfaces so linear and asymmetric with "Distance"?

$$E_{app} \ll \frac{\lambda_{AB}}{2}$$

... with a transition state that is more reactant-like, i.e. A



Are these labels logical?

Fermi's (Second) Golden Rule

$$j_E = nF(-k'_{f,E}c_{O,z_0} + k'_{b,E}c_{R,z_0})$$

k'_j (cm s⁻¹)... a velocity!

Transition probability $\lambda_{if} = \frac{2\pi}{\hbar} |M_{if}|^2 \rho_f$

Matrix element for the interaction M_{if}

Density of final states (DoS) ρ_f

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

... divide the DoS term by c_{i,z_0} ...

frequency factor (s⁻¹)

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

proportionality function (cm³ eV)

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

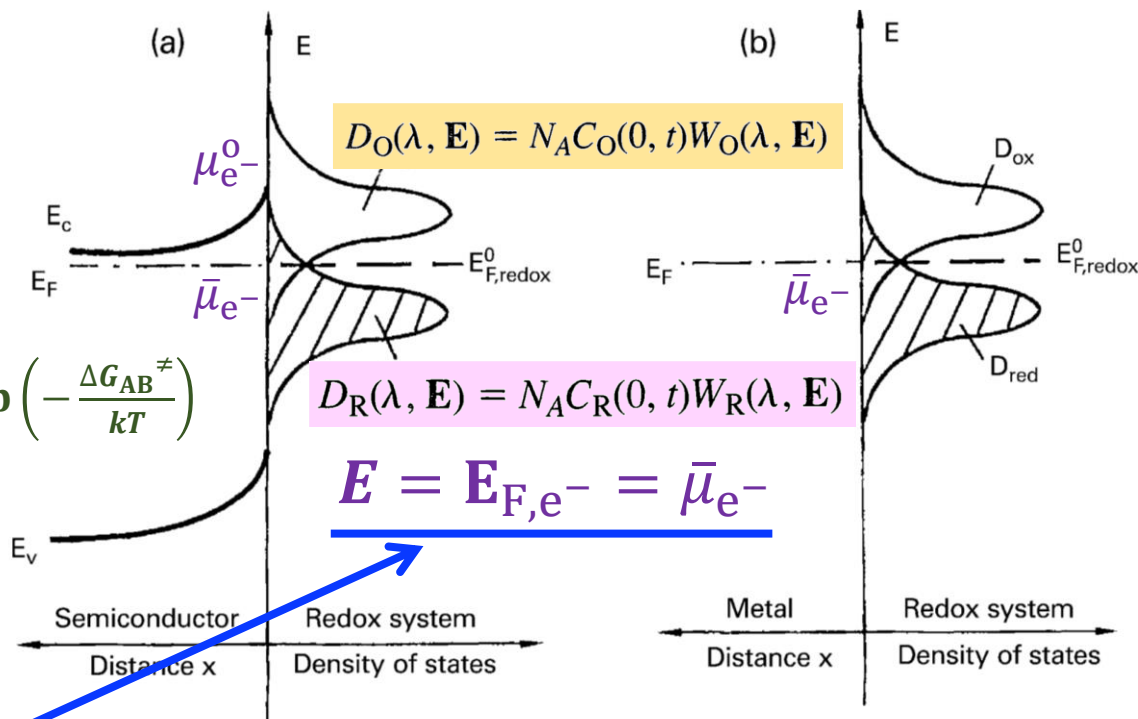
applied potential

$$k'_{f,E,obs} = \int_{-\infty}^{\infty} k'_{f,E} dE$$

$$k'_{b,E,obs} = \int_{-\infty}^{\infty} k'_{b,E} dE$$

energy

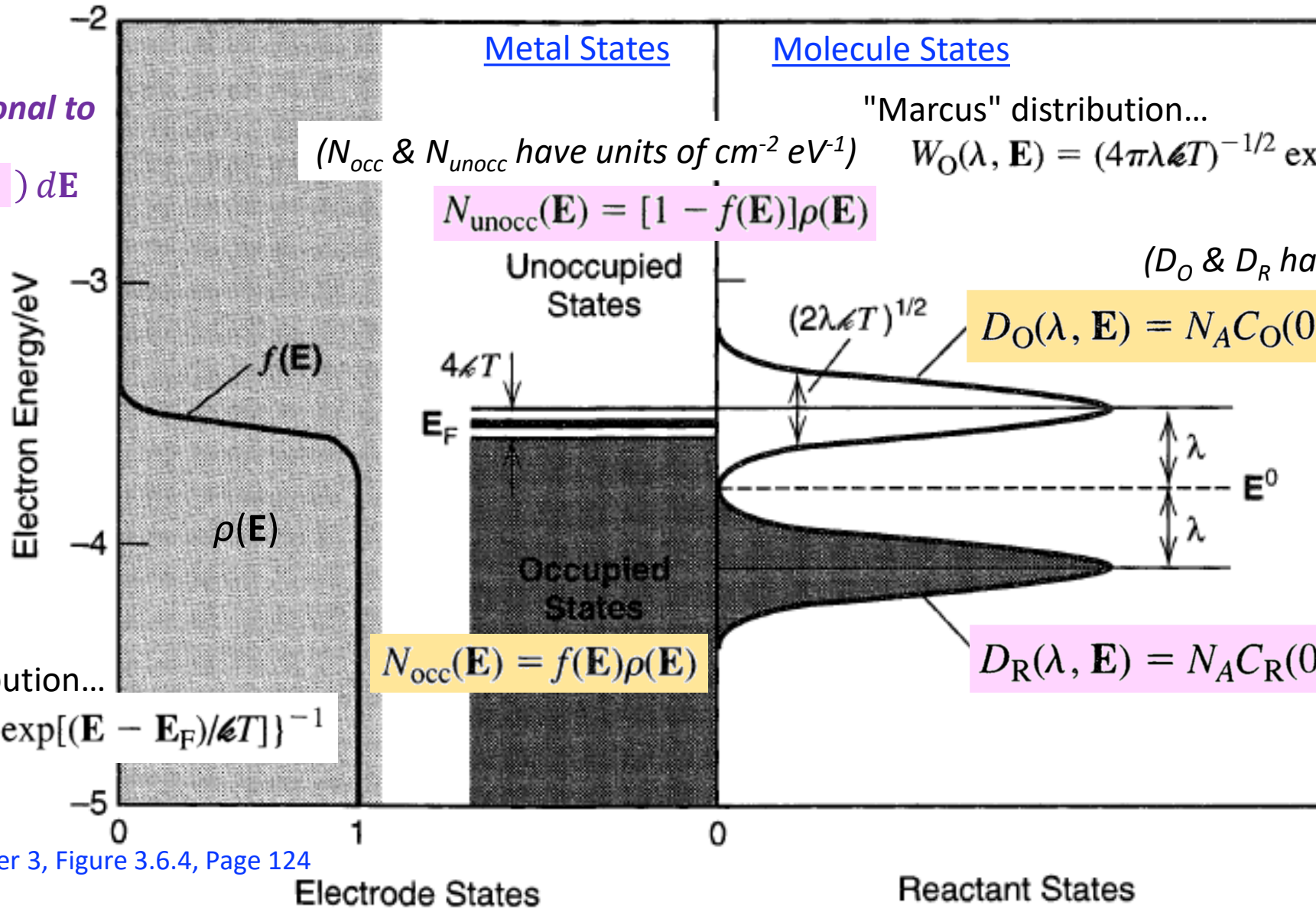
$$j_{E,obs} = nF(-k'_{f,E,obs}c_{O,z_0} + k'_{b,E,obs}c_{R,z_0})$$



Marcus–Gerischer Theory

ET rate is proportional to

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



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

"Marcus" distribution...

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

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

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

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

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

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

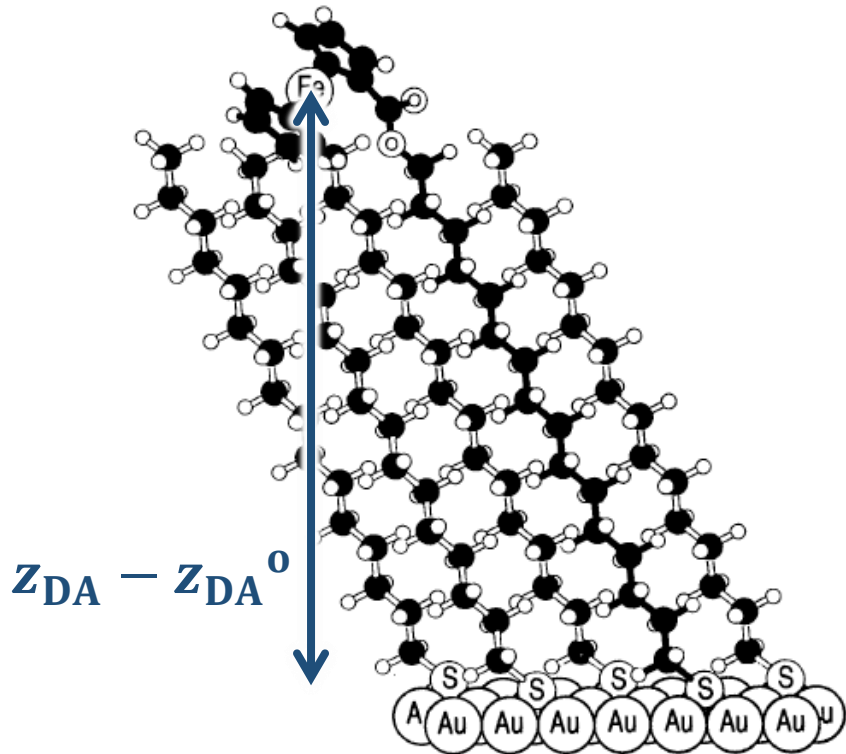
Fermi-Dirac distribution...

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

Marcus–Gerischer Theory

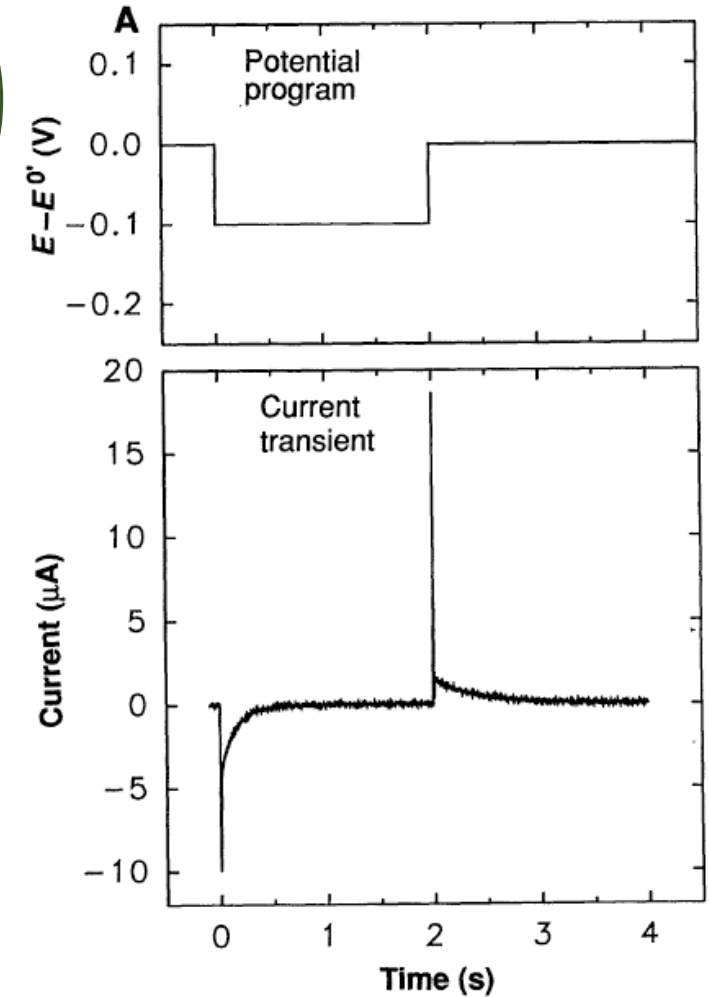
$$k_{\text{ET}} = \frac{2\pi}{\hbar} |H_{\text{DA}}^0|^2 e^{-2\beta(z_{\text{DA}} - z_{\text{DA}}^0)} \frac{1}{\sqrt{4\pi\lambda_{\text{AB}}kT}} \exp\left(-\frac{(\lambda_{\text{AB}} + \Delta G_{\text{AB}}^0)^2}{4\lambda_{\text{AB}}kT}\right)$$

quantum adiabatic electronic coupling classical nuclear free-energy dependence



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

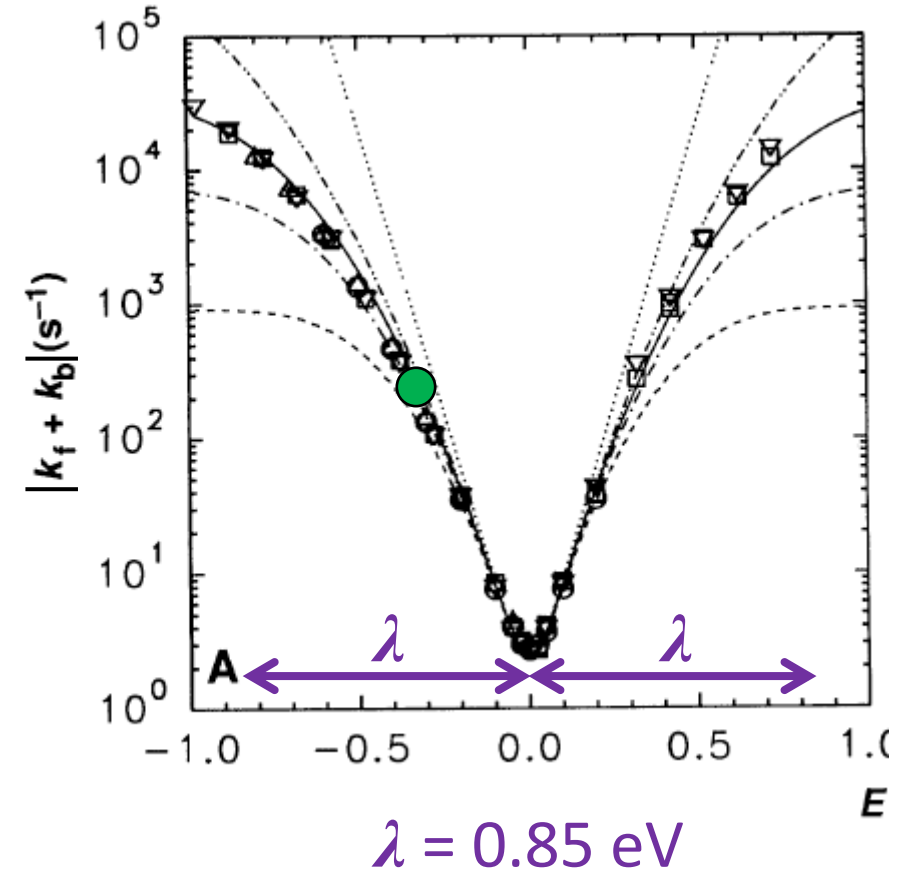
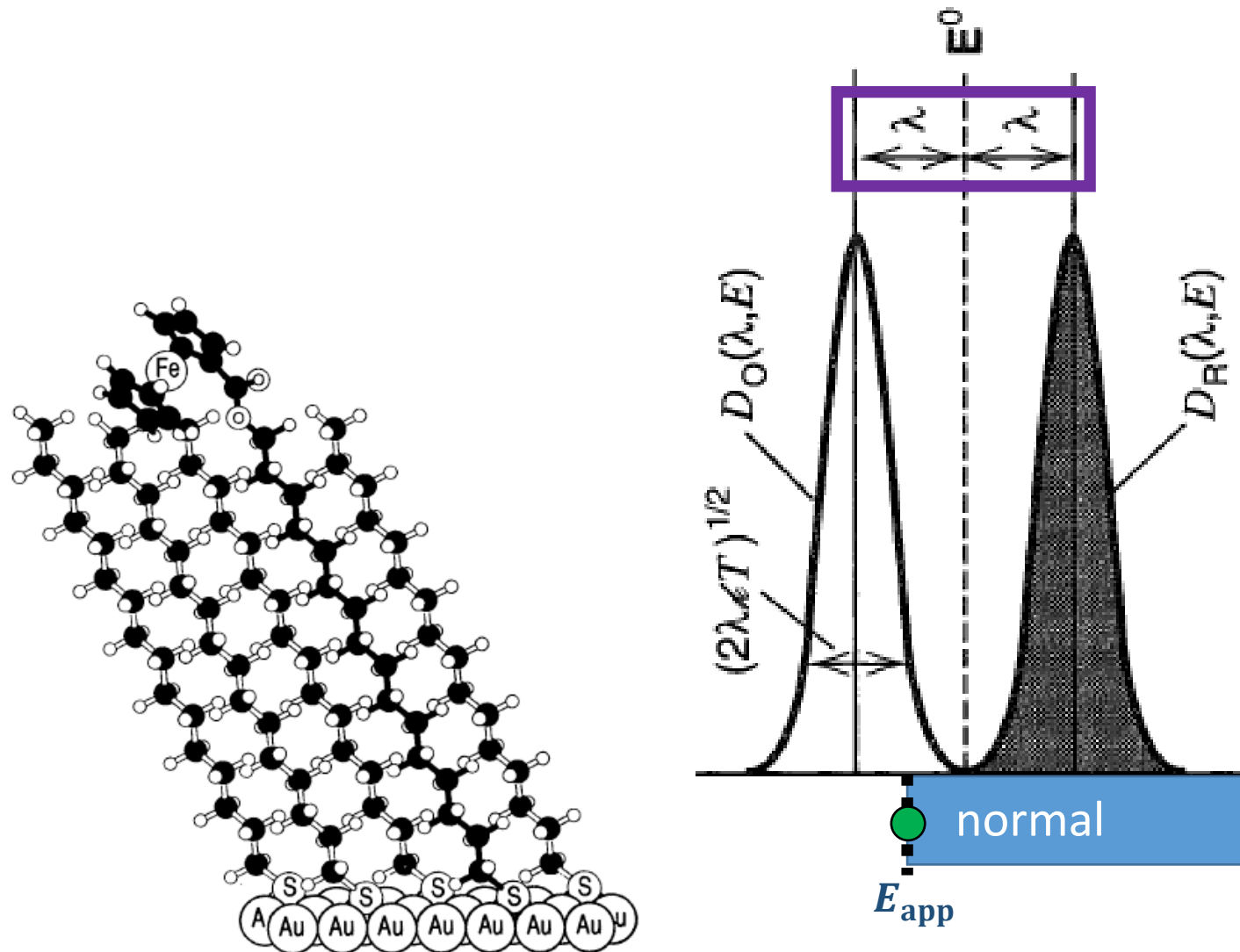
... RC-circuit double layer charging... followed by 1st-order ET kinetics



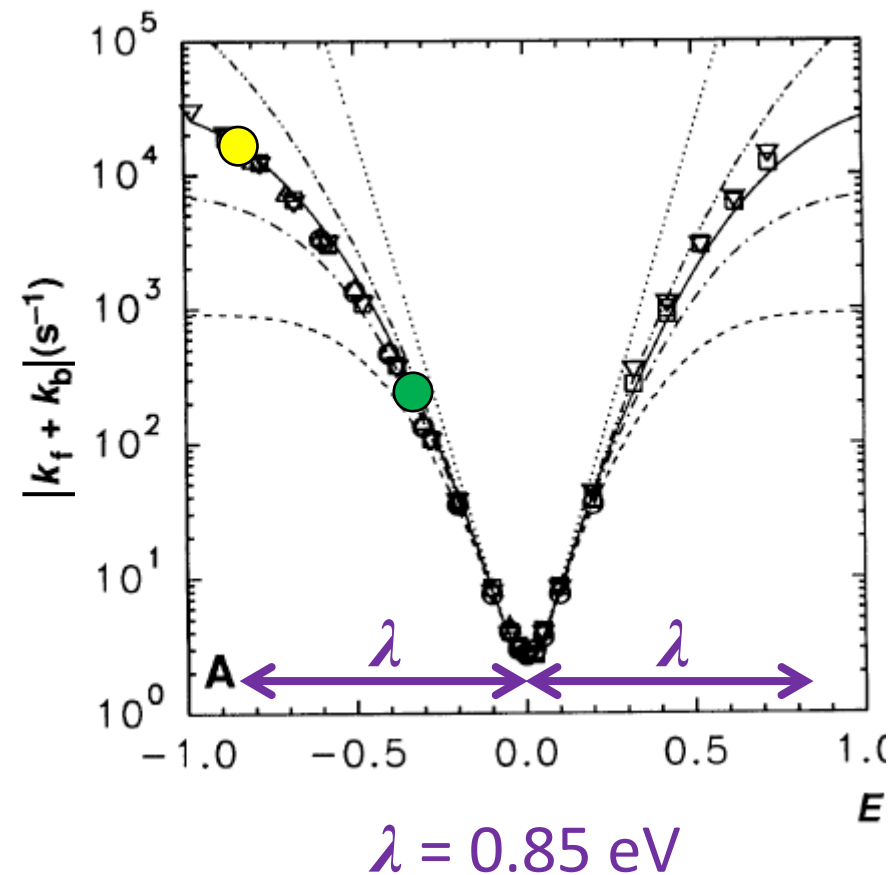
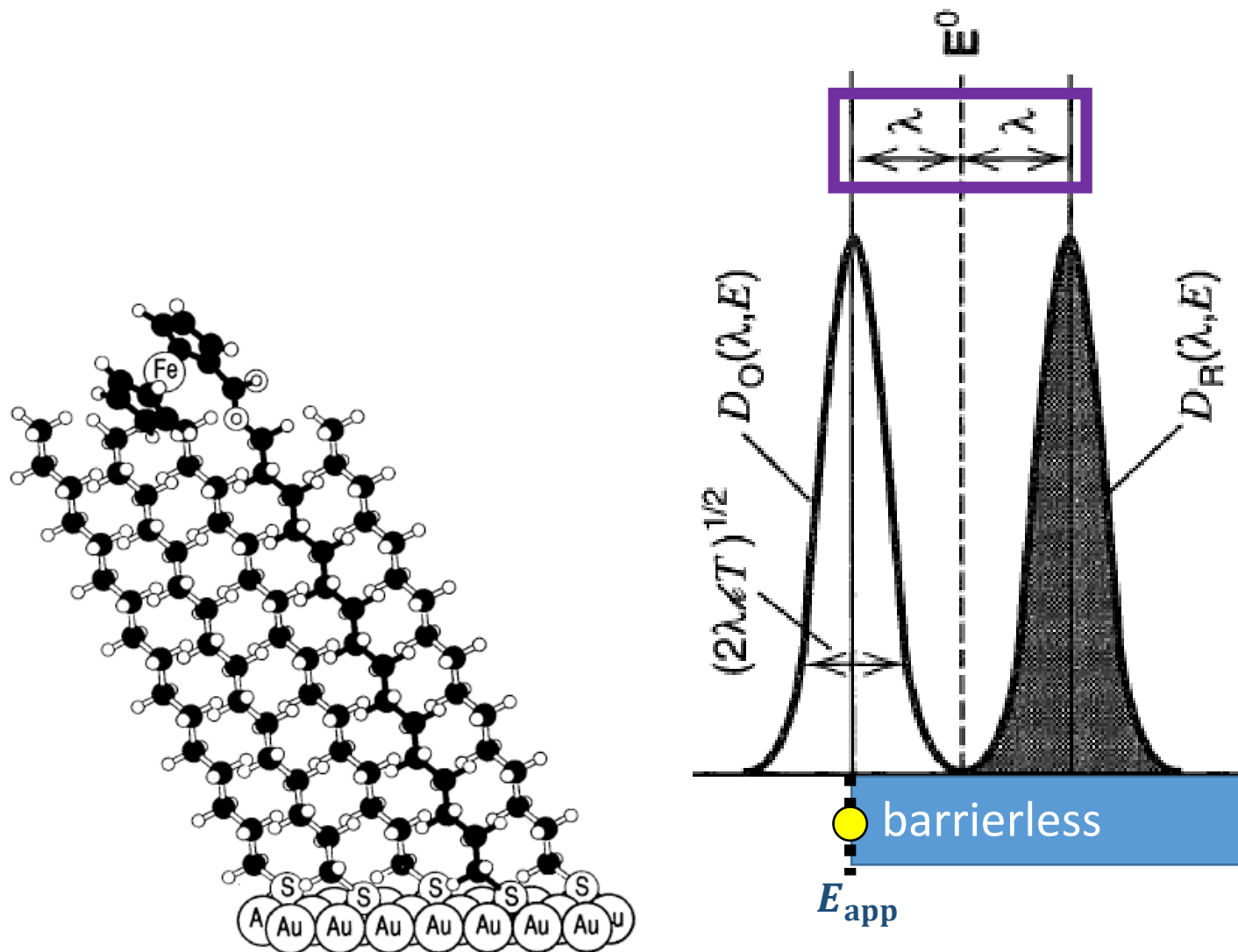
C. E. D. Chidsey, *Science*, **1991**, 251, 919–922

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



Marcus–Gerischer Theory



Marcus–Gerischer Theory

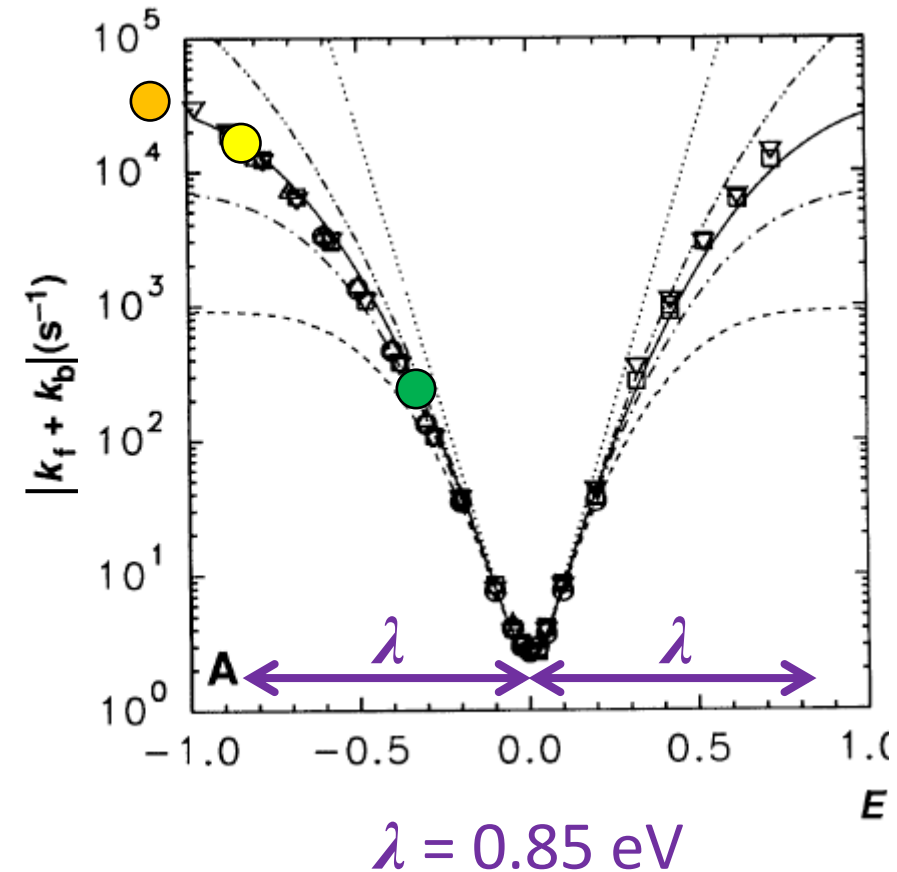
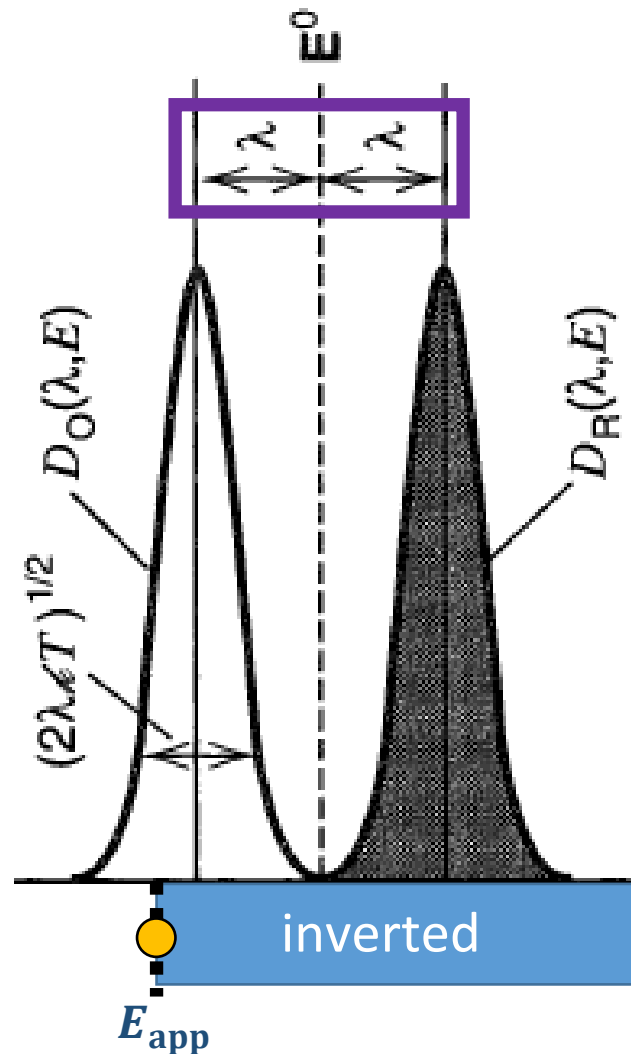
- It is easy to sweep/vary the driving force, ΔG_{AB} , by simply changing the electrochemical potential of electrons (e^-) in the (M)etal working electrode, $\bar{\mu}_e^M$, through variations in E_{app}

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

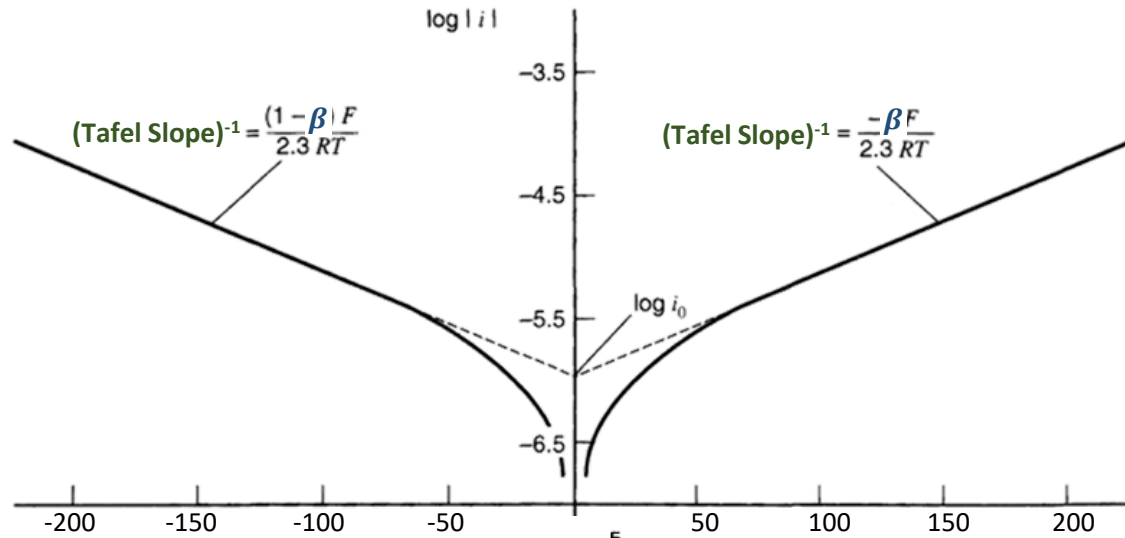
... what if Chidsey had plotted the derivative of his data on the right?

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

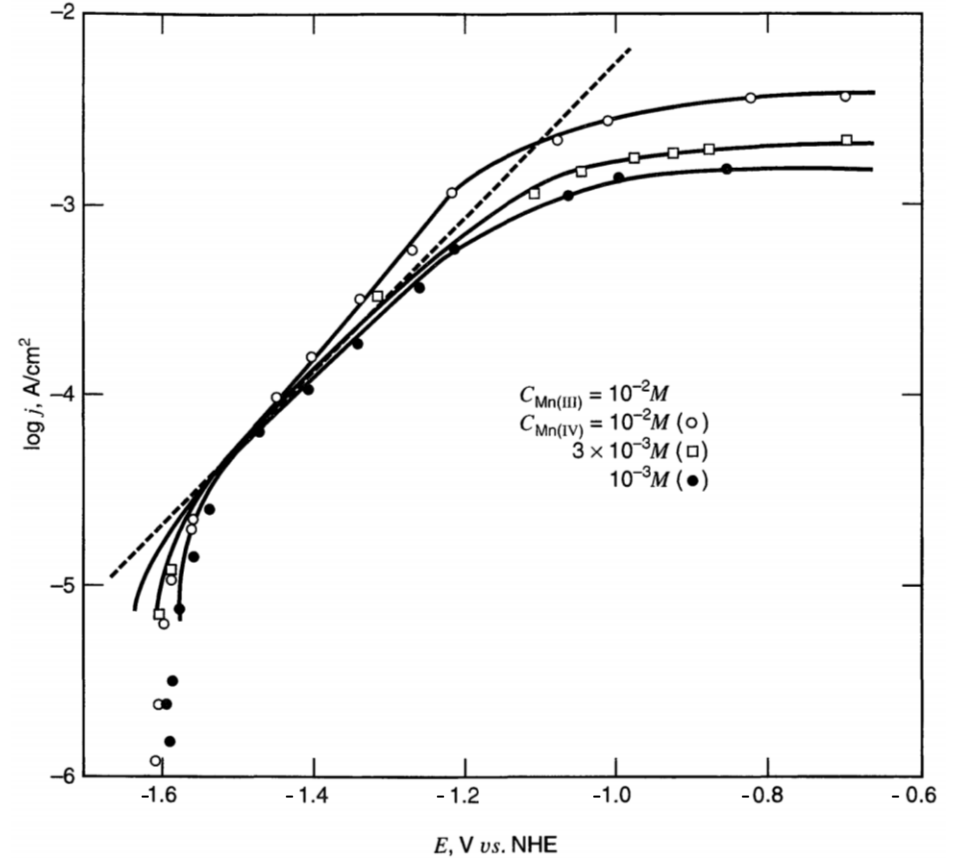
... I wish he had done that!



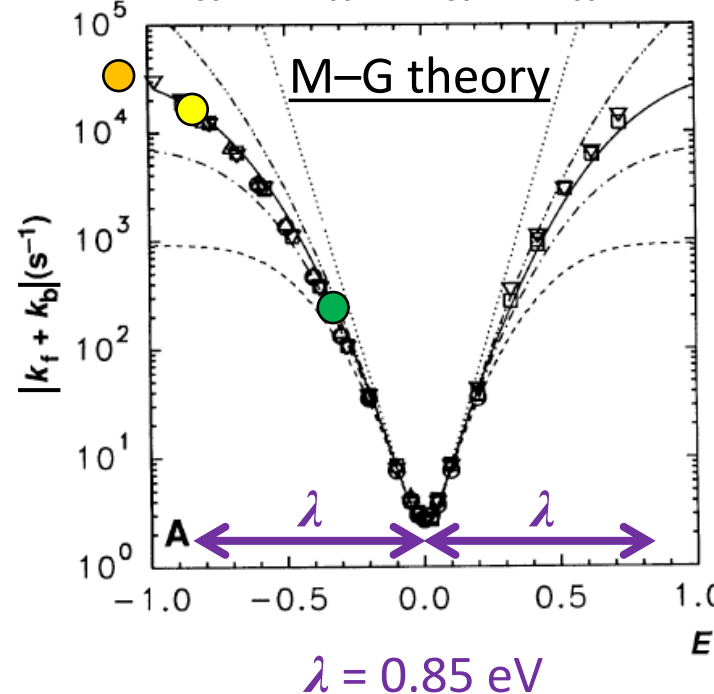
Limiting Processes



B-V theory (Current-Overpotential Equation)



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

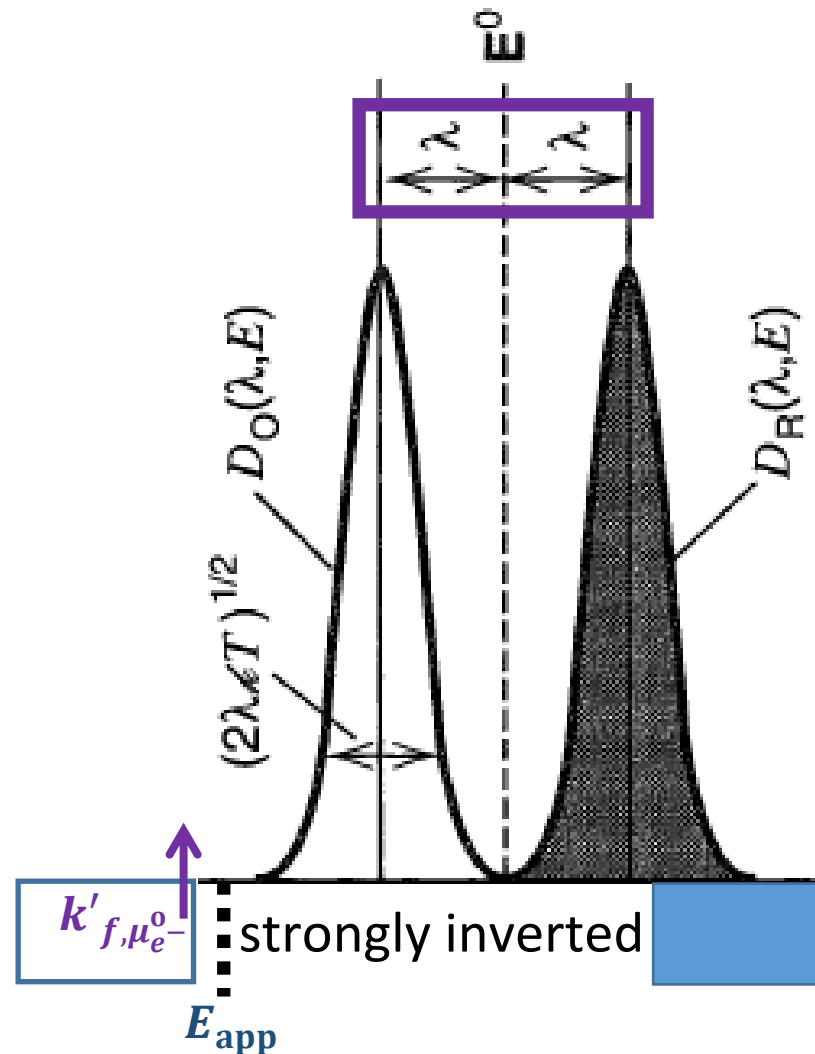


... but why do these current densities, j_E , and rate constants, $k'_{j,E,obs}$, plateau at large overpotential, η ? ... **Not for the same reasons!**

Since Butler-Volmer theory is based on an LFER approximation, does it predict the presence of the Marcus inverted region? ... **Nope!**

Marcus–Gerischer Theory

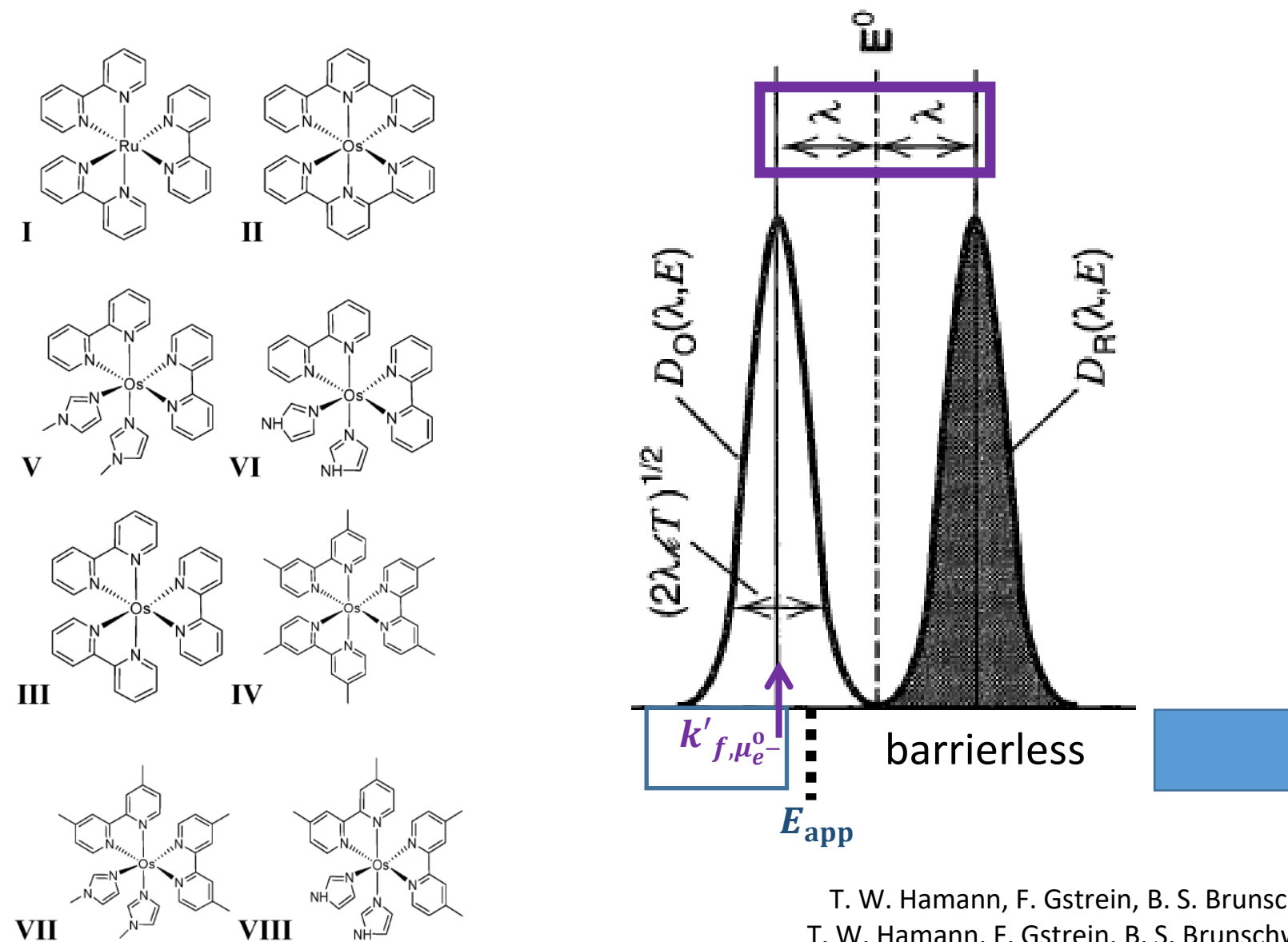
- Use of a semiconductor limits the electronic states to those with (approximately) a single $\mu_{e^-}^0$, which makes analysis of data simpler, i.e. one does not need to consider a distribution of states in the electrode
- But one cannot alter the driving force, ΔG_{AB}^0 , by simply changing the electrochemical potential of electrons (e^-) in the (S)emi(C)onductor working electrode, $\bar{\mu}_{e^-}^{SC}$, through variations in E_{app} , because instead that changes the concentration of e^-



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

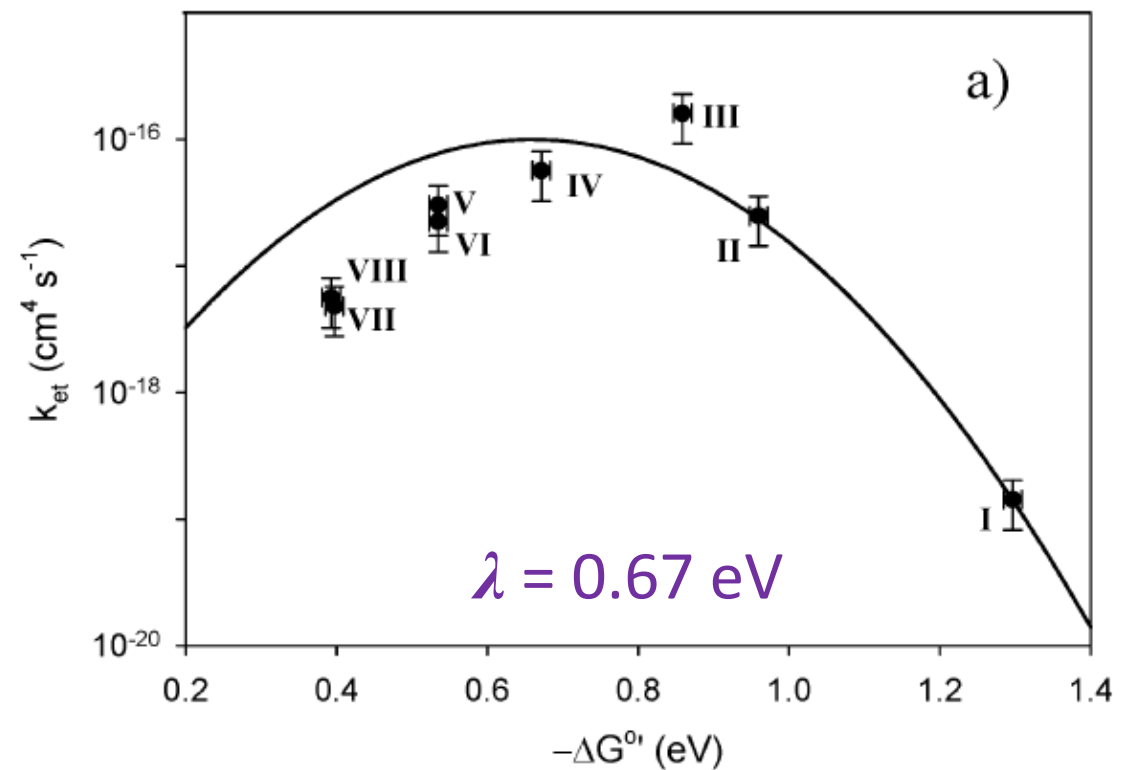
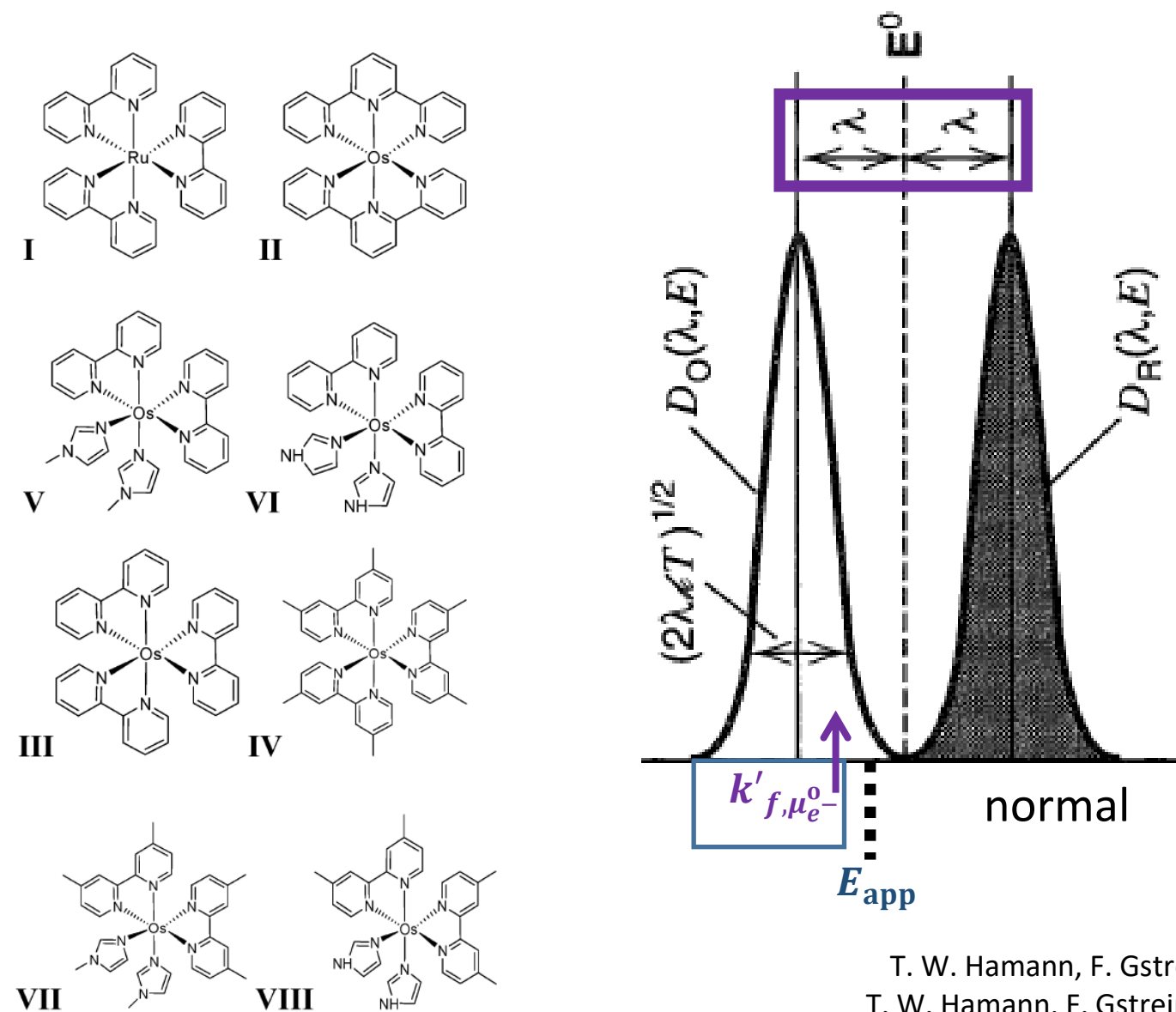
Think solution studies...
vary the molecule!

Marcus–Gerischer Theory



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

Marcus–Gerischer Theory



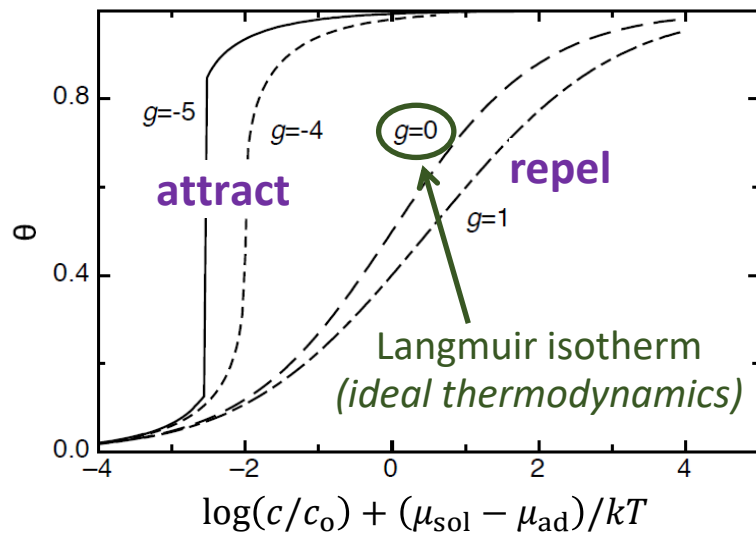
$k_{IET} \text{ (cm}^4 \text{ s}^{-1}\text{)} \dots$ a second-order rate constant!

Charge Transfer across Electrified Interfaces

J. O'M. Bockris¹
and Z. Nagy²

Electrochemistry Laboratory
University of Pennsylvania
Philadelphia, 19104

Frumkin isotherms



* g is a lateral interaction term

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

β Symmetry Factor and α 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 (cath)odic/(an)odic reaction rate expressed as a change in the activation free energy as a fraction of E_{app}

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

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

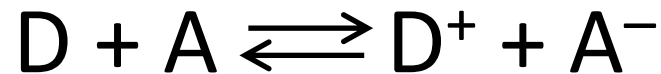
$$TS_{\text{an}}^{-1} = \left(\frac{d(\log j_E)}{d\eta} \right)_{\text{an}} = \frac{\alpha_{\text{an}} F}{2.303RT}$$

Rate-Determining Step (RDS)

Poisson's Equation (from Gauss's law)

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

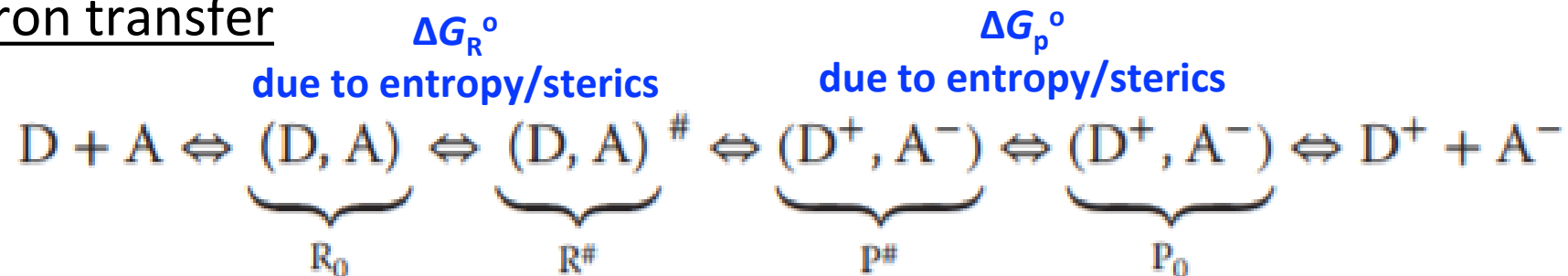
$$\phi(r) = \frac{q}{4\pi\epsilon r}$$



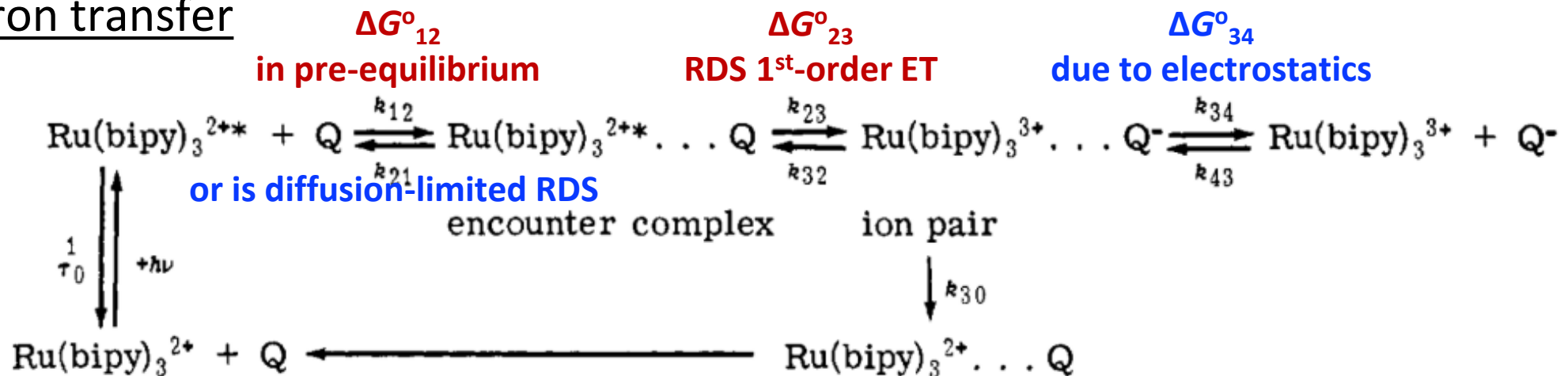
But wait... is this the elementary reaction step for electron transfer between a (D)onor and an (A)cceptor in solution?

Nope!

Ground-state electron transfer

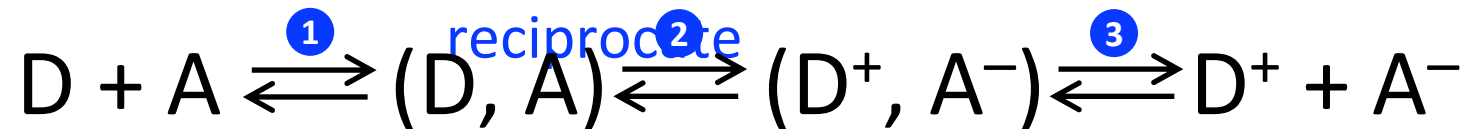


Excited-state electron transfer



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



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

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

... except that Step 2 is preceded by Step 1... and Step 3 is preceded by Steps 1 and 2

... and only one of those Steps 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...

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

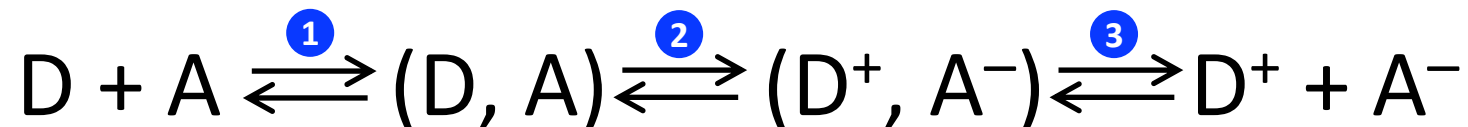
... and for completion, what if 3 (same-order) reactions occur simultaneously, i.e. **in parallel**?

... it's as easy as it seems... $k_{f,obs} = k_{1f} + k_{2f} + k_{3f} = \frac{1}{\tau_{1f}} + \frac{1}{\tau_{2f}} + \frac{1}{\tau_{3f}} = \frac{1}{\tau_{f,obs}}$

RDS: Steady-State Approximation

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

... when all are fast, **except Step 1**, won't $k_{f,obs} = k_{1f}$ then?... not always...



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

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

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

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

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

... which is what the pre-equilibrium approximation would have predicted too, so... consistent!

Charge Transfer across Electrified Interfaces

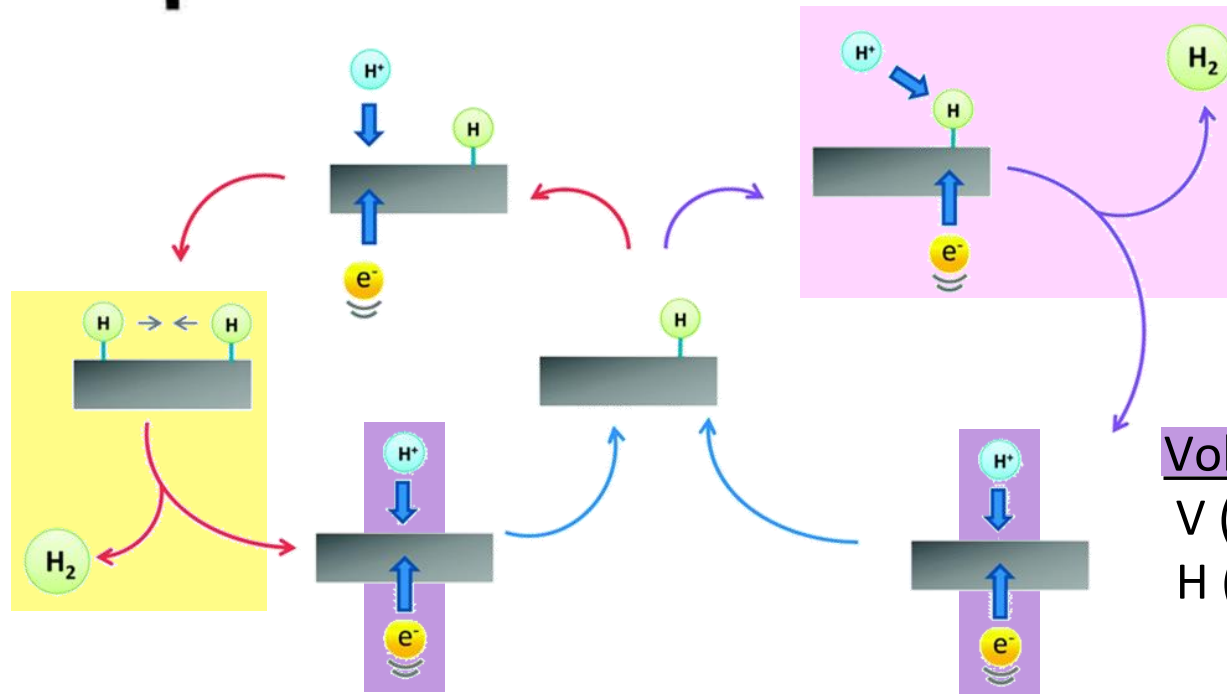
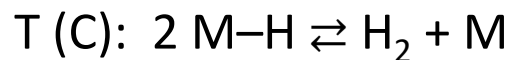
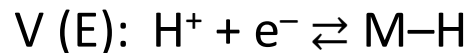
J. O'M. Bockris¹
and Z. Nagy²

Electrochemistry Laboratory
University of Pennsylvania
Philadelphia, 19104

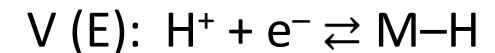
β Symmetry Factor and α Transfer Coefficient

A source of confusion in electrode kinetics

Volmer–Tafel mechanism



Volmer–Heyrovsky mechanism



Charge Transfer across Electrified Interfaces

J. O'M. Bockris¹
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Electrochemistry Laboratory
University of Pennsylvania
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Symmetry Factor and Transfer Coefficient

A source of confusion in electrochemistry

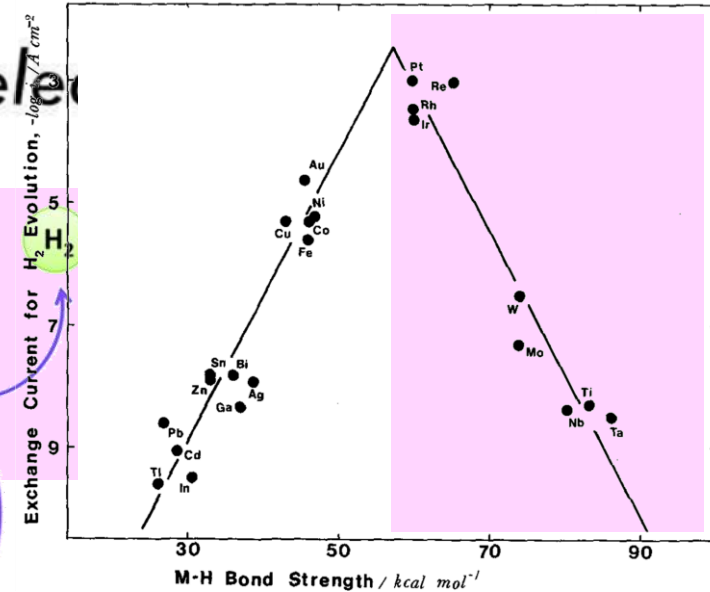
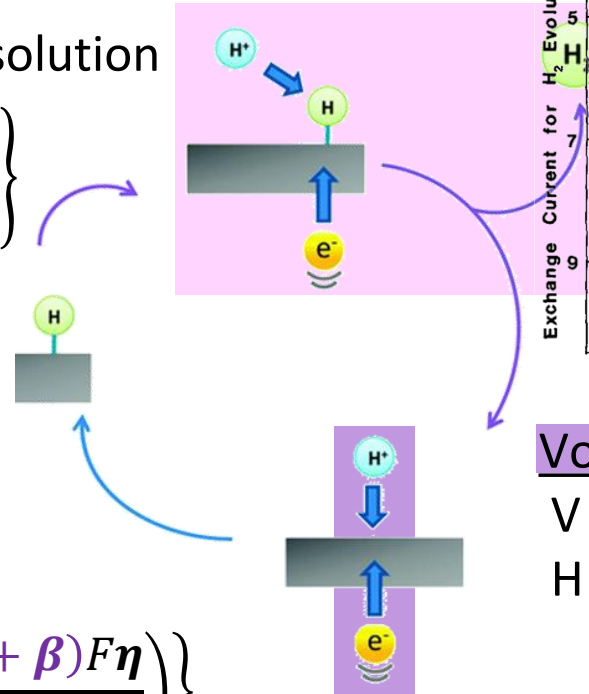
Case 1: V = pre-equilibrium; H = RDS; E = E_{eq} ; rapidly stir solution

$$j_E = 2j_o \left\{ \frac{c_{H_2, z_0}}{c_{H_2}^*} \exp\left(\frac{(1 - \beta)F\eta}{RT}\right) - \frac{c_{M-H, z_0}}{c_{M-H, z_0}^*} \frac{c_{H^+, z_0}}{c_{H^+}^*} \exp\left(\frac{-\beta F\eta}{RT}\right) \right\}$$

$$j_E = 2j_o \left\{ \exp\left(\frac{(1 - \beta)F\eta}{RT}\right) - \theta_{M-H} \exp\left(\frac{-\beta F\eta}{RT}\right) \right\}$$

$$j_E = 2j_o \left\{ \exp\left(\frac{(1 - \beta)F\eta}{RT}\right) - \frac{c_{H^+, z_0}}{c_{H^+}^*} \exp\left(\frac{-F\eta}{RT}\right) \exp\left(\frac{-\beta F\eta}{RT}\right) \right\}$$

$$j_E = 2j_o \left\{ \exp\left(\frac{(1 - \beta)F\eta}{RT}\right) - \exp\left(\frac{-(1 + \beta)F\eta}{RT}\right) \right\}$$



Volmer–Heyrovsky mechanism



$$\alpha_{cath} + \alpha_{an} = (1 + \beta) + (1 - \beta) = 2!$$

Charge Transfer across Electrified Interfaces

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Electrochemistry Laboratory
University of Pennsylvania
Philadelphia, 19104

β Symmetry Factor and α Transfer Coefficient

A source of confusion in electrochemistry

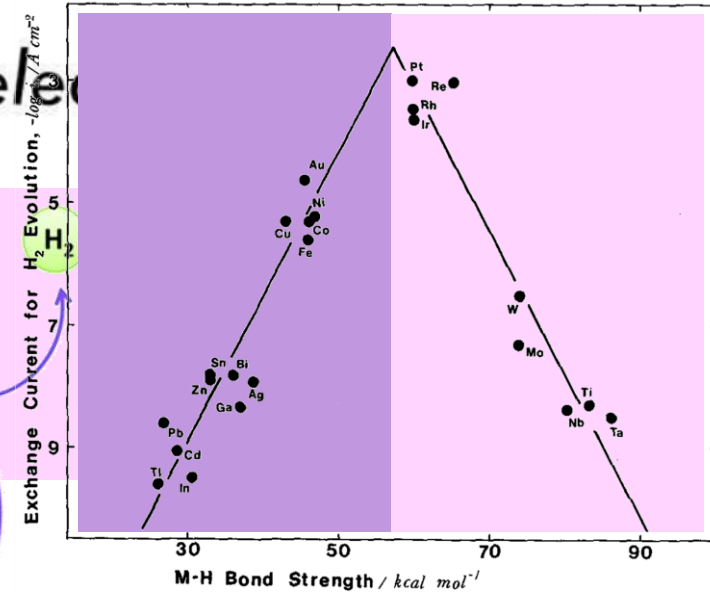
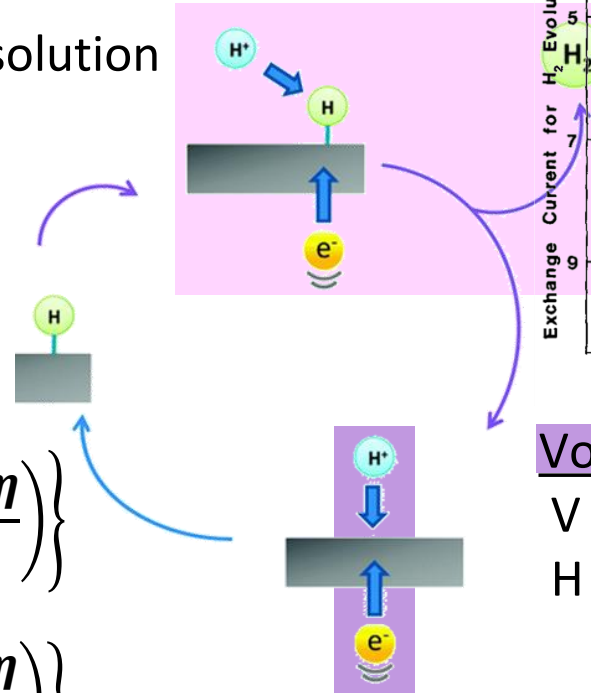
Case 2: V = RDS; H = pre-equilibrium; E = E_{eq} ; rapidly stir solution

$$j_E = 2j_0 \left\{ \frac{c_{M-H,z_0}}{c_{M-H,z_0}^*} \exp\left(\frac{(1-\beta)F\eta}{RT}\right) - \frac{c_{H^+,z_0}}{c_{H^+}^*} \exp\left(\frac{-\beta F\eta}{RT}\right) \right\}$$

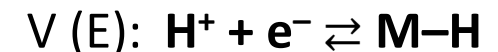
$$j_E = 2j_0 \left\{ \theta_{M-H} \exp\left(\frac{(1-\beta)F\eta}{RT}\right) - \exp\left(\frac{-\beta F\eta}{RT}\right) \right\}$$

$$j_E = 2j_0 \left\{ \frac{c_{H_2,z_0}}{c_{H_2}^*} \frac{c_{H^+}}{c_{H^+,z_0}} \exp\left(\frac{F\eta}{RT}\right) \exp\left(\frac{(1-\beta)F\eta}{RT}\right) - \exp\left(\frac{-\beta F\eta}{RT}\right) \right\}$$

$$j_E = 2j_0 \left\{ \exp\left(\frac{(2-\beta)F\eta}{RT}\right) - \exp\left(\frac{-\beta F\eta}{RT}\right) \right\}$$



Volmer–Heyrovsky mechanism



$$\alpha_{cath} + \alpha_{an} = \beta + (2 - \beta) = 2!$$