



Lecture #7 of 12

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Linear Free Energy Relationships (LFERs)

Marcus–Hush (1950s–1960s)

theoretical (semiclassical) rate constant equation

Brønsted–Pedersen (1924)

empirical LFER for proton transfer

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

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

Brønsted slope...

... most people use α ...

... but I prefer β

... like in EChem

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

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

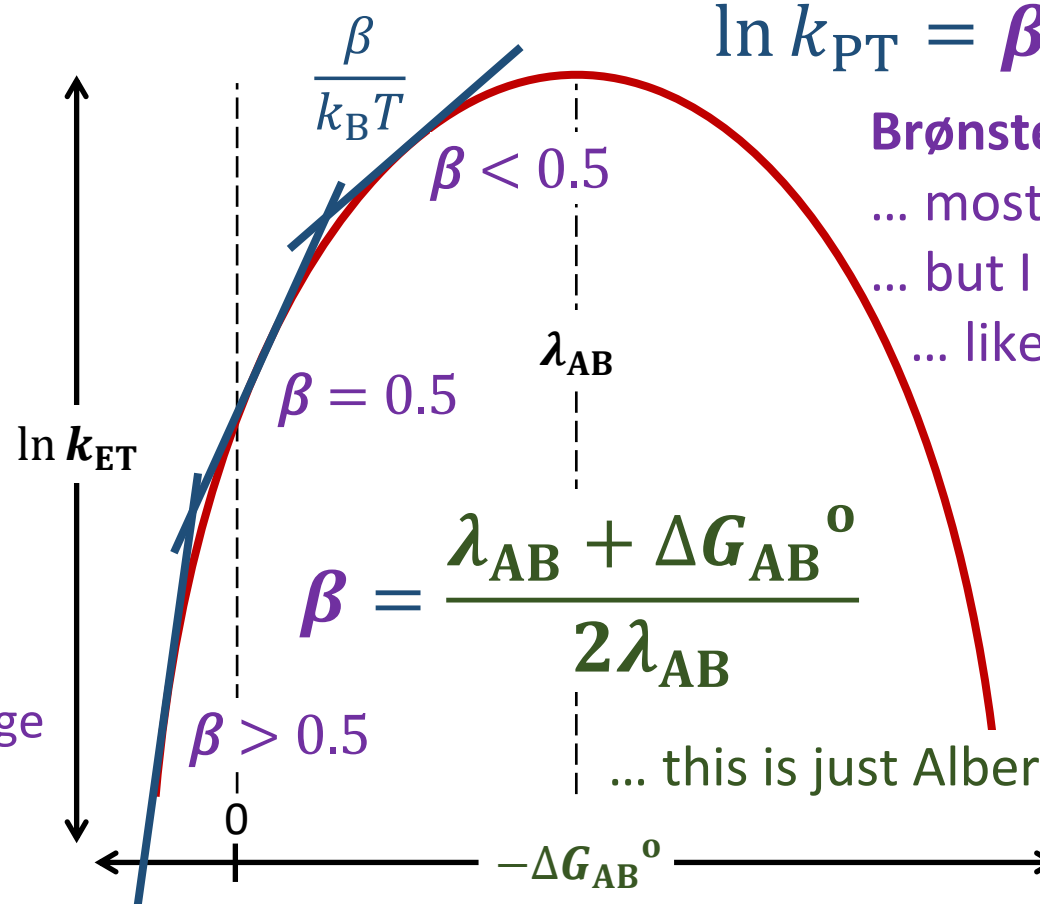
A linear correlation between the logarithm of a [rate constant](#) or [equilibrium constant](#) for one series of reactions and the logarithm of the [rate constant](#) or [equilibrium constant](#) for a related series of reactions. Typical examples of such relations (also known as linear Gibbs energy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

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

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

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

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

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

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

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 $E_{eq} = E^{o'} - \frac{RT}{nF} \ln \frac{c_R^*}{c_O^*}$

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

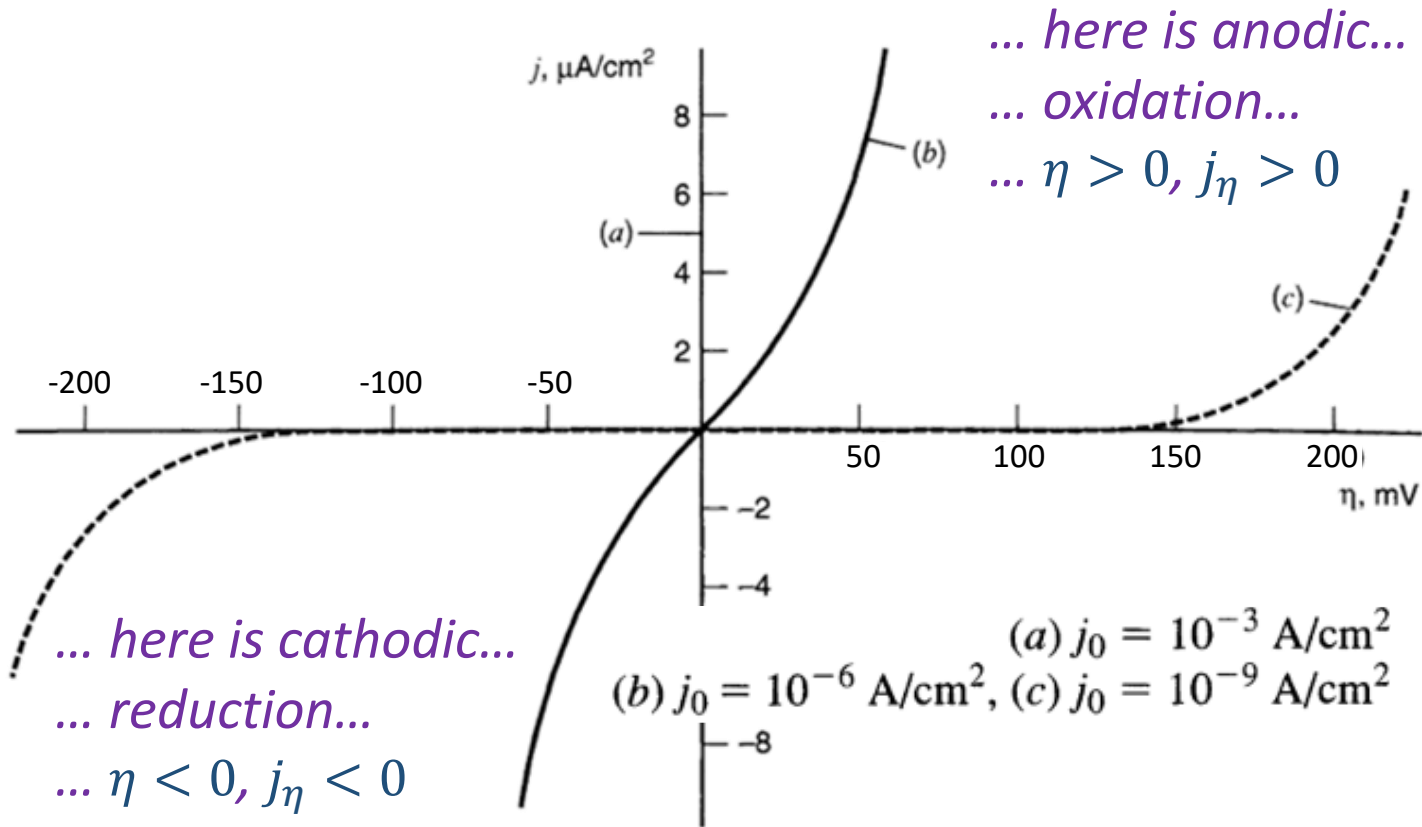
... assuming a rapidly stirred solution

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

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

Butler–Volmer equation

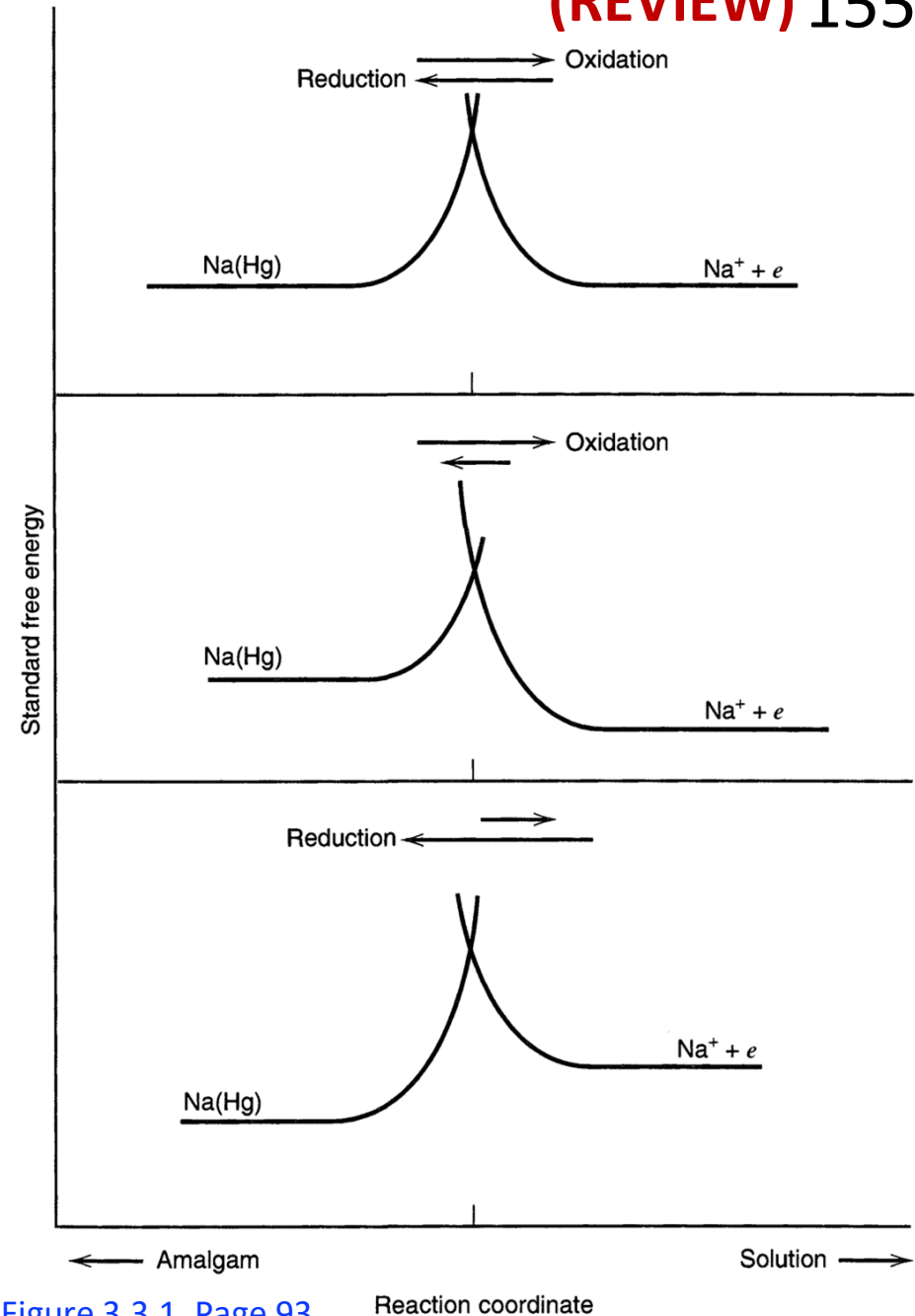
... let's examine effects of j_0 (or k^0)...



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

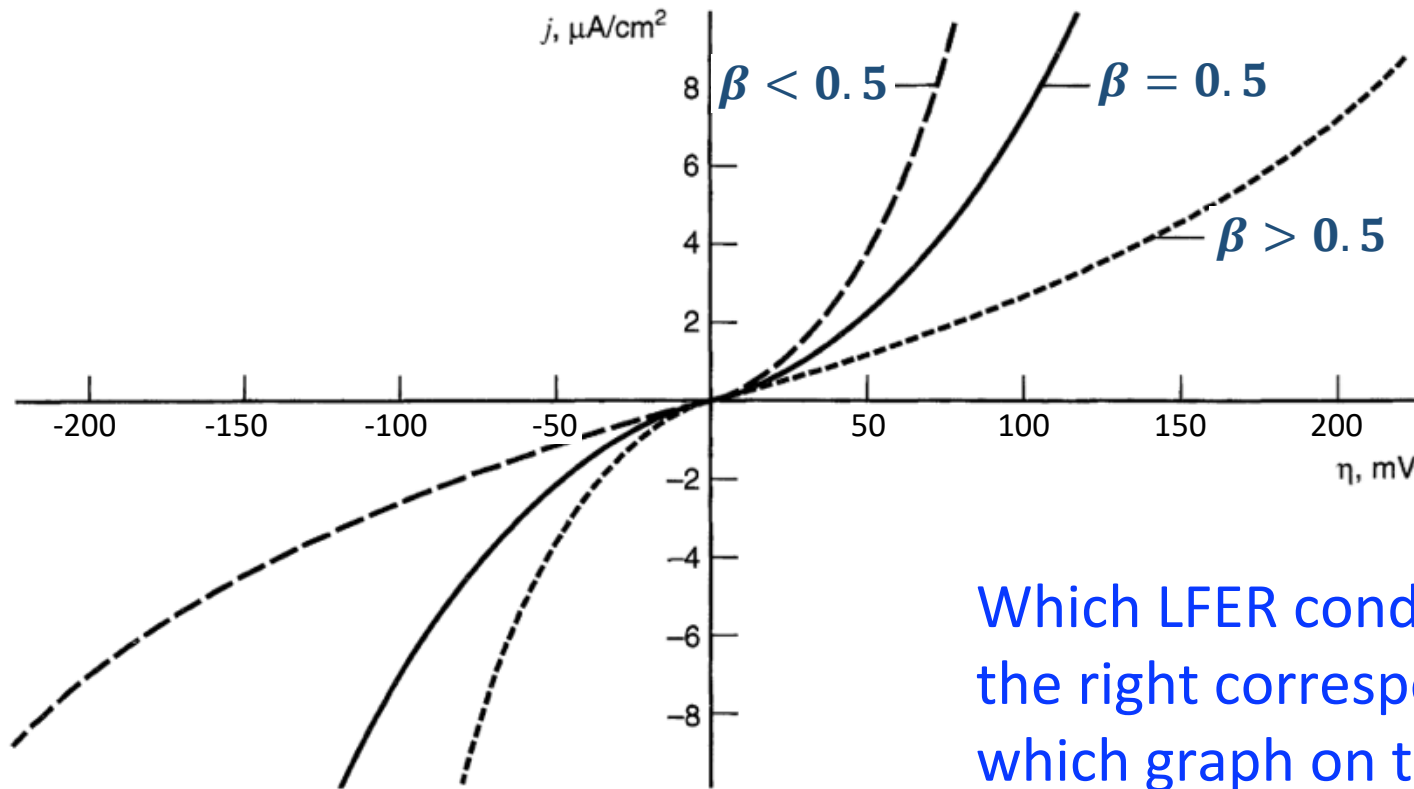
... recall that... $\eta = (E - E_{\text{eq}}) = E_{\text{app}} = \frac{\Delta G^0}{-nF}$

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



Butler–Volmer equation

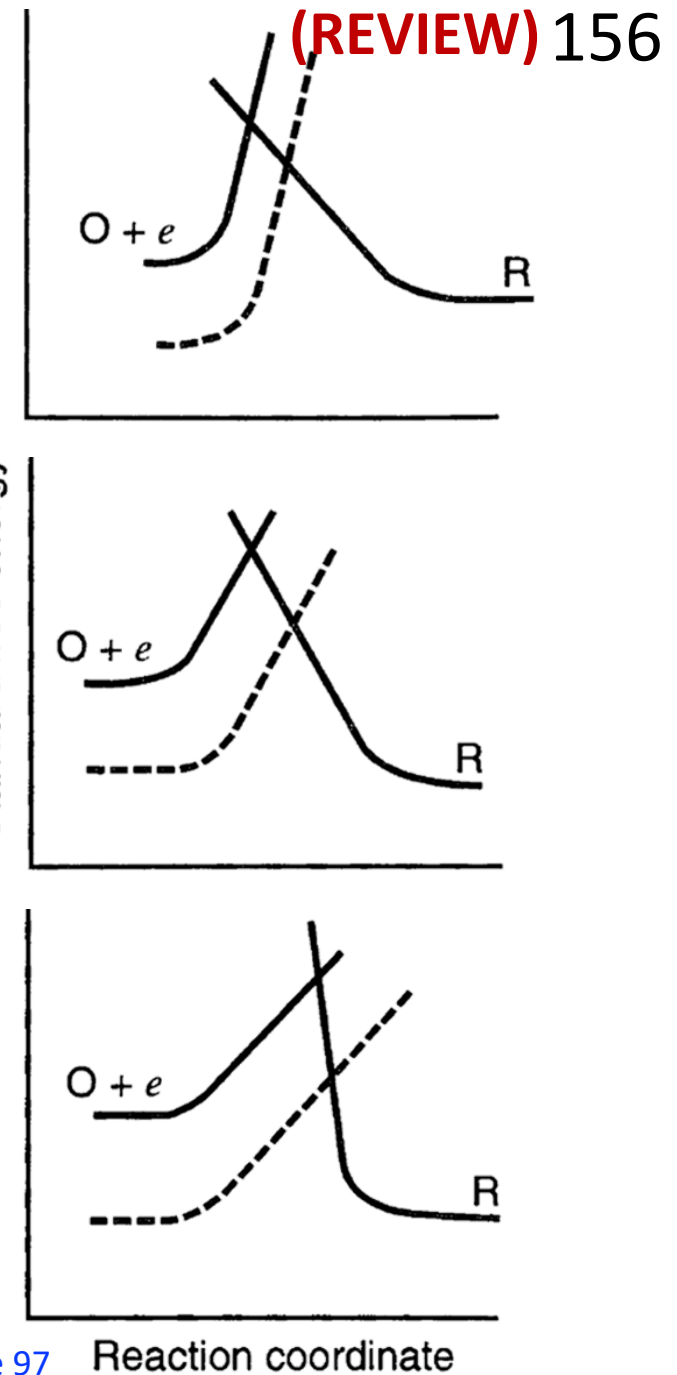
... let's examine effects of β (or Tafel slope)...



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



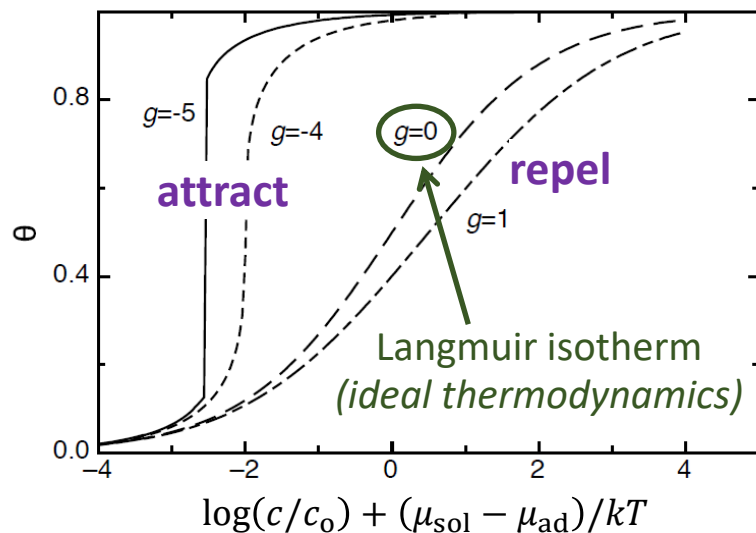
Which LFER condition on the right corresponds to which graph on the left?

Charge Transfer across Electrified Interfaces

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Frumkin isotherms



* g is a lateral interaction term

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}

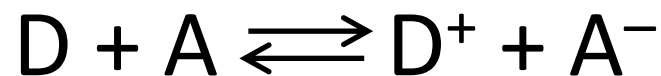
Do the two transfer coefficients always have to sum to one?

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

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

Rate-Determining Step (RDS)

Poisson's Equation (from Gauss's law)



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

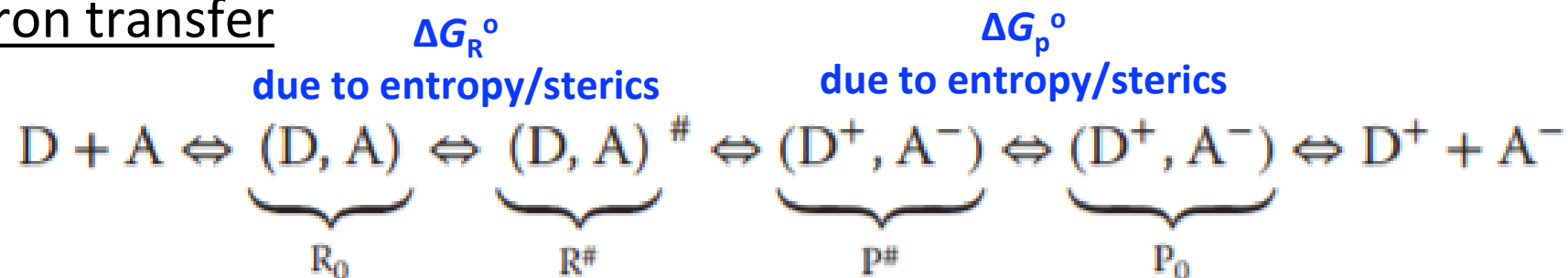
$$E = -\frac{\partial \phi(x)}{\partial x}$$

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

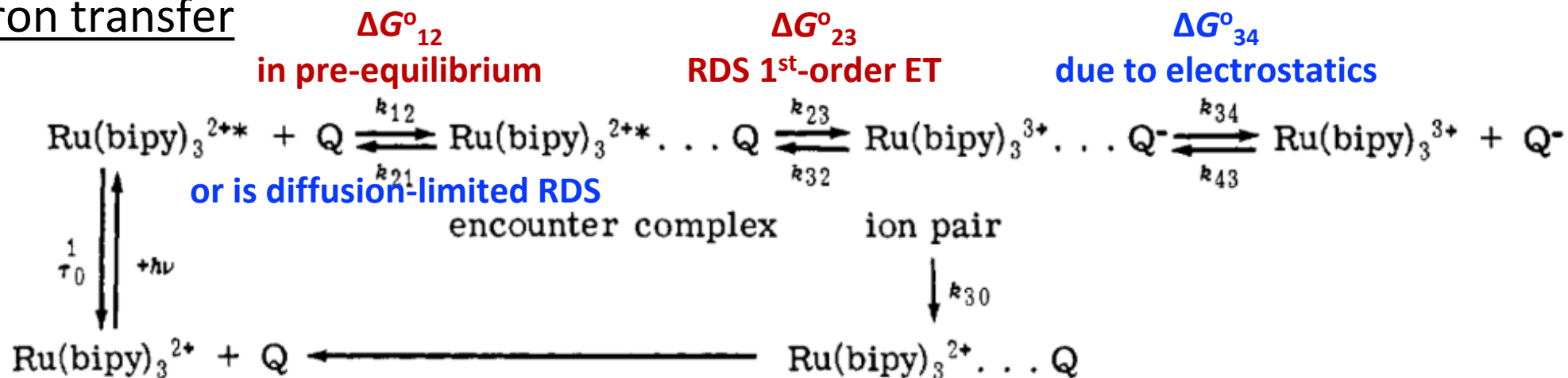
But wait... is this the elementary reaction step for electron transfer between a (D)onor and an (A)ceptor in solution?

Nope!

Ground-state electron transfer

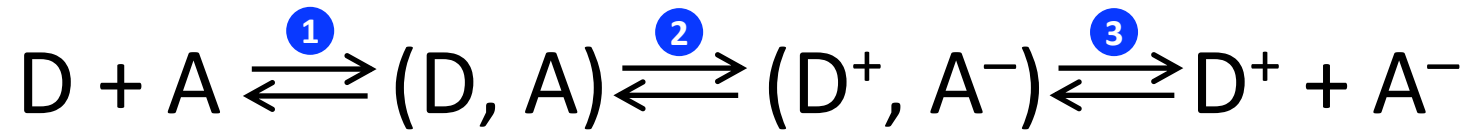


Excited-state electron transfer



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 reciprocate



... 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 dominate the observed rate when it is the slowest step

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

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

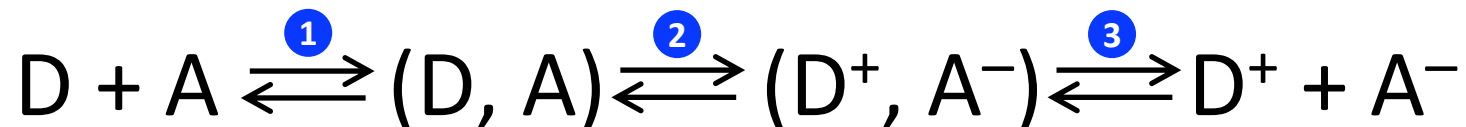
... and for completion, what if 3 (same-order) reactions occur simultaneously, i.e. **in parallel**?

... 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

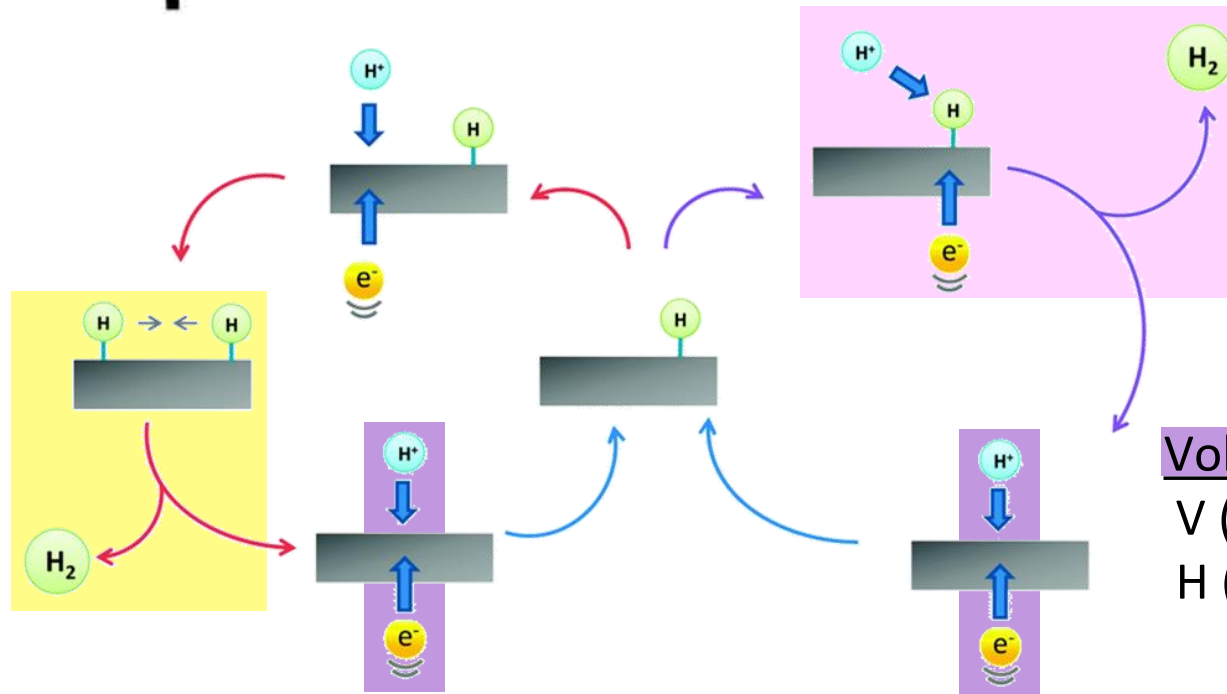
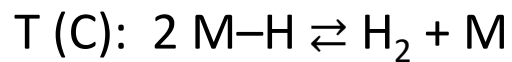
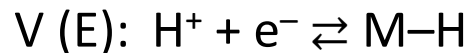
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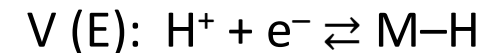
β Symmetry Factor and α Transfer Coefficient

A source of confusion in electrode kinetics

Volmer–Tafel mechanism



Volmer–Heyrovsky mechanism



Charge Transfer across Electrified Interfaces

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Symmetry Factor and Transfer Coefficient

A source of confusion in electrochemistry

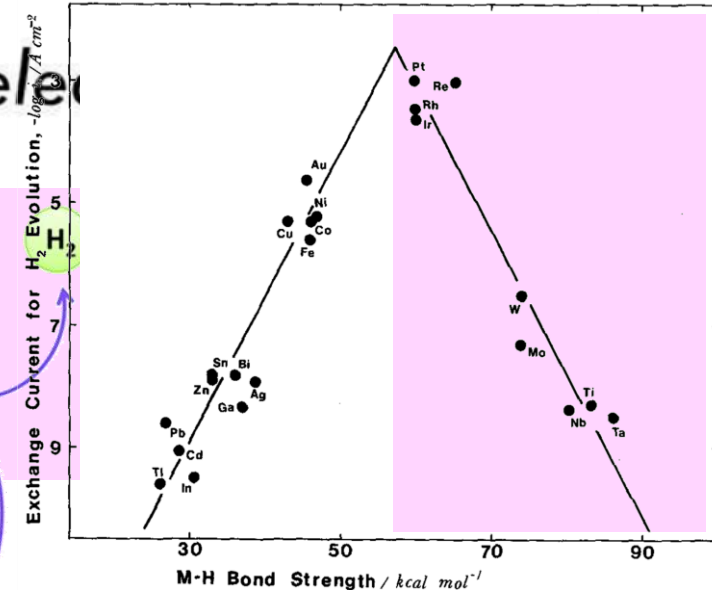
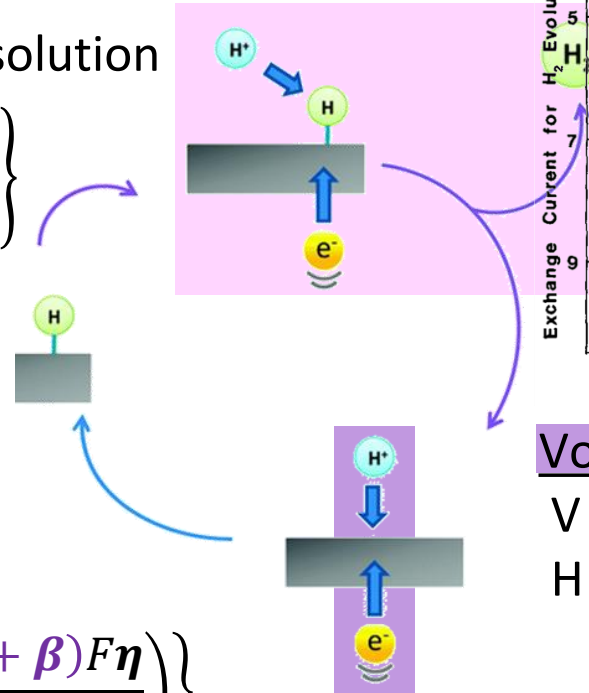
Case 1: V = pre-equilibrium; H = RDS; E = E_{eq} ; rapidly stir solution

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

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

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

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



Volmer–Heyrovsky mechanism



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

Charge Transfer across Electrified Interfaces

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β Symmetry Factor and α Transfer Coefficient

A source of confusion in electrochemistry

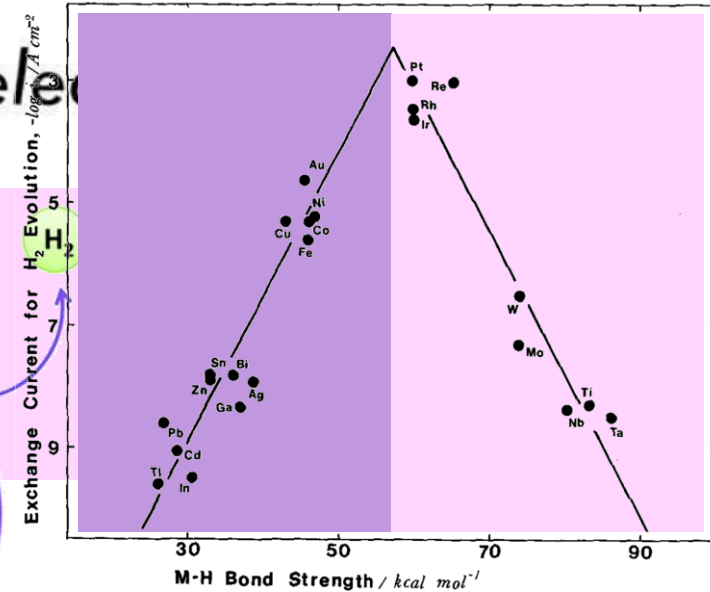
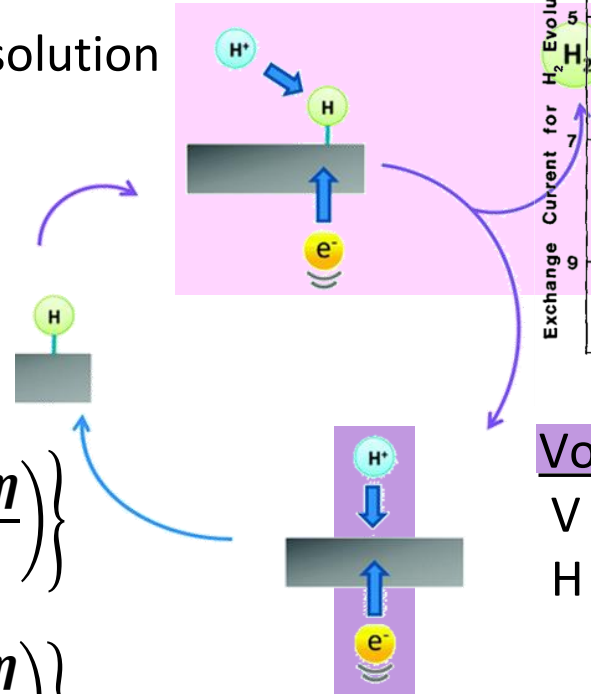
Case 2: V = RDS; H = pre-equilibrium; $E = E_{eq}$; rapidly stir solution

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

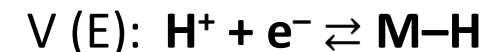
$$j_E = 2j_0 \left\{ \theta_{M-H} \exp\left(\frac{(1-\beta)F\eta}{RT}\right) - \exp\left(\frac{-\beta F\eta}{RT}\right) \right\}$$

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

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



Volmer–Heyrovsky mechanism



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



Photophysical Processes

Prof. Shane Ardo

Department of Chemistry

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Today's Critical Guiding Question

What continuity/conservation laws are most important for photophysical processes like absorption and emission of photons?

Photophysical Processes

- **Blackbody radiation, Photon properties, Light–Matter interactions, Conservation laws, Einstein coefficients**
- Jablonski diagram, Spin multiplicity, Internal conversion, Intersystem crossing, Thexi state, Kasha–Vavilov rule, Stokes shift, PL
- Born–Oppenheimer approximation, Franck–Condon principle, Transition dipole moment operator, Franck–Condon factors, Beer–Lambert law, Absorption coefficient, Oscillator strength, Absorptance
- Luminescence processes, Selection rules, Charge-transfer transitions, Spin–Orbit coupling, Heavy-atom effect, E – k diagrams, Jortner energy gap law, Conical intersections, Energy transfer, Exciplex/Excimer
- Photoluminescence spectrometer, Emission/Excitation spectra, Inner filter effects, Anisotropy, Excited-state lifetime, Emission quantum yield

Schrödinger Equation

Elegant master equation that allows one to determine internal energies, E_n , of a system

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

... but this is not good enough for photochemists where **time-varying** oscillating electromagnetic fields often interact with matter...

$$E = h\nu = \hbar\omega \text{ (Planck)}$$

$$E = mc^2 = pc \text{ (Einstein)}$$

$$p = \frac{h\nu}{c} = \frac{h}{\lambda} = h\bar{\nu} = \hbar k \text{ (de Broglie)}$$

$$\hat{H}\Psi_n(x, t) = i\hbar \frac{\partial}{\partial t} \Psi_n(x, t)$$

... so, how does one solve either of these Schrödinger equations?... We need to know \hat{H} !

$$\hat{H} = \hat{T} + \hat{V}$$

... um... well that didn't really help us at all... anyway, so instead, we need to know \hat{T} and \hat{V} ?

$$\hat{T}(x) = \text{KE} = \frac{1}{2}m\hat{v}^2 = \frac{\hat{p}^2}{2m} \dots \text{with } (\hat{p})\text{momentum} = (m)\text{mass} \times (\hat{v})\text{velocity} = -i\hbar \frac{\partial}{\partial x} \dots \text{Wow, right?}$$

$$\hat{V}(x) = \text{PE} = 0 \dots \text{for particle-in-a-box...}$$

$$\hat{V}(x) = \frac{1}{2}k_f x^2 = \frac{1}{2}m\omega^2 x^2 \dots \text{for harmonic oscillator, with } k_f \text{ (force const), } \omega \text{ (angular freq)...}$$

$$\hat{V}(r) = -\frac{q^2}{4\pi\epsilon_0 r} \dots \text{for Hydrogen atom, with } F = qN_A \text{ (Faraday const), } \epsilon_0 \text{ (vacuum permittivity)}$$

Schrödinger Equation

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

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

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

Poisson's Equation (from Gauss's law)

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

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

for a point charge...
look familiar?

... and that under most chemical conditions, potential energy, $\hat{V}(x)$, is **electrostatic**, $\phi(x)$

... which is actually not so limiting because there are only 4-ish forces of Nature

... and while we're at it, let's (re)learn **overlap integral** (S_{nm}), **expectation value** ($\langle p_n \rangle$), **bra-ket notation** ($\langle \psi_n | \psi_m \rangle$), and exponential **tunneling probability**...

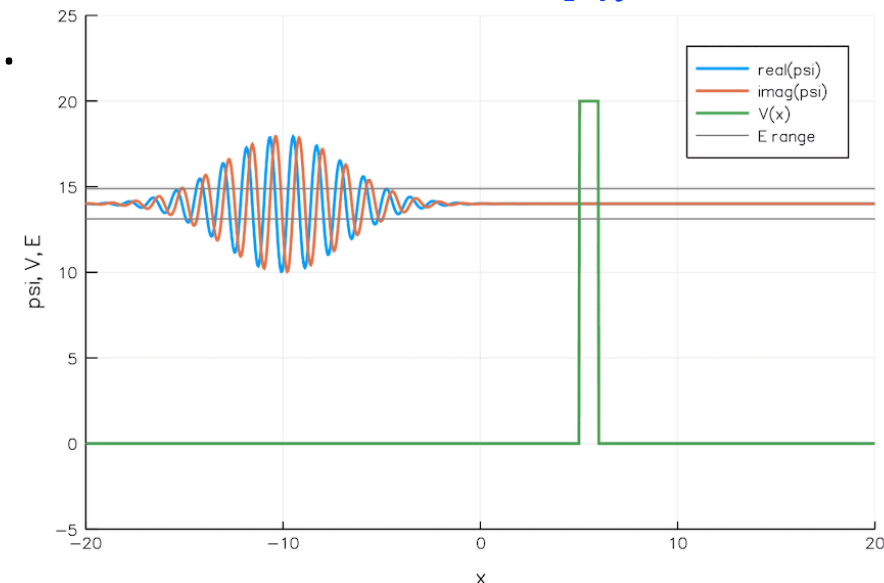
$$\text{Probability Density}(x) = |\psi_n(x)|^2 = \psi_n^*(x)\psi_n(x)$$

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

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

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

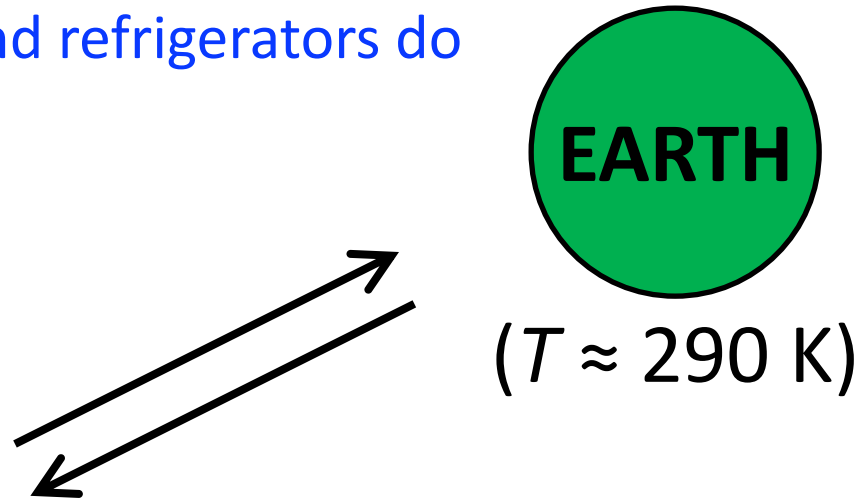
$$\text{Mean Energy, } \langle E_n \rangle = \frac{\int_{-\infty}^{\infty} \Psi_n^*(x,t)\hat{H}\Psi_n(x,t)dx}{\int_{-\infty}^{\infty} \Psi_n^*(x,t)\Psi_n(x,t)dx} = \langle \Psi_n | \hat{H} | \Psi_n \rangle = \langle \hat{H} \rangle$$



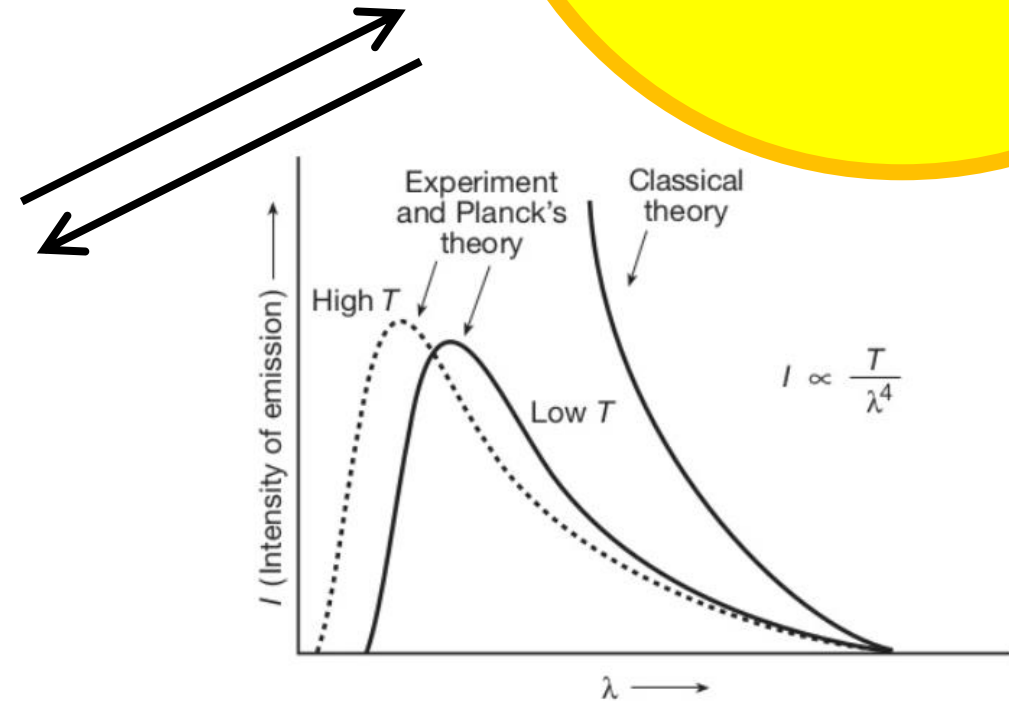
Blackbody Radiation

Carnot efficiency limit, $\eta = \frac{w}{Q_H} = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H} = 1 - \frac{T_C}{T_H}$

... light-driven processes between two blackbodies
 ... interconvert energy and work,
 like heat engines and refrigerators do



UNIVERSE
 ($T \approx 3$ K)



... if any two bodies are that the same temperature
 ... and they only interact via radiation, i.e., photons (e.g., not chemical)
 ... then no work can be performed due to these photon exchanges
 ... and electrochemical potentials do not change due to them

Turro, Chapter 4, Figure 4.1, Page 171

Photon Properties & Conservation Laws

Where does light come from?

Particle Type: Boson

Mass: 0

Charge: 0

Energy: $E = h\nu = \hbar\omega$

Linear Velocity: $\frac{c}{n} = \left(\frac{\lambda}{n}\right)\nu = \lambda'\nu$

Linear Momentum: $p = \frac{h}{\lambda'} = \frac{nh\nu}{c} \approx 0$

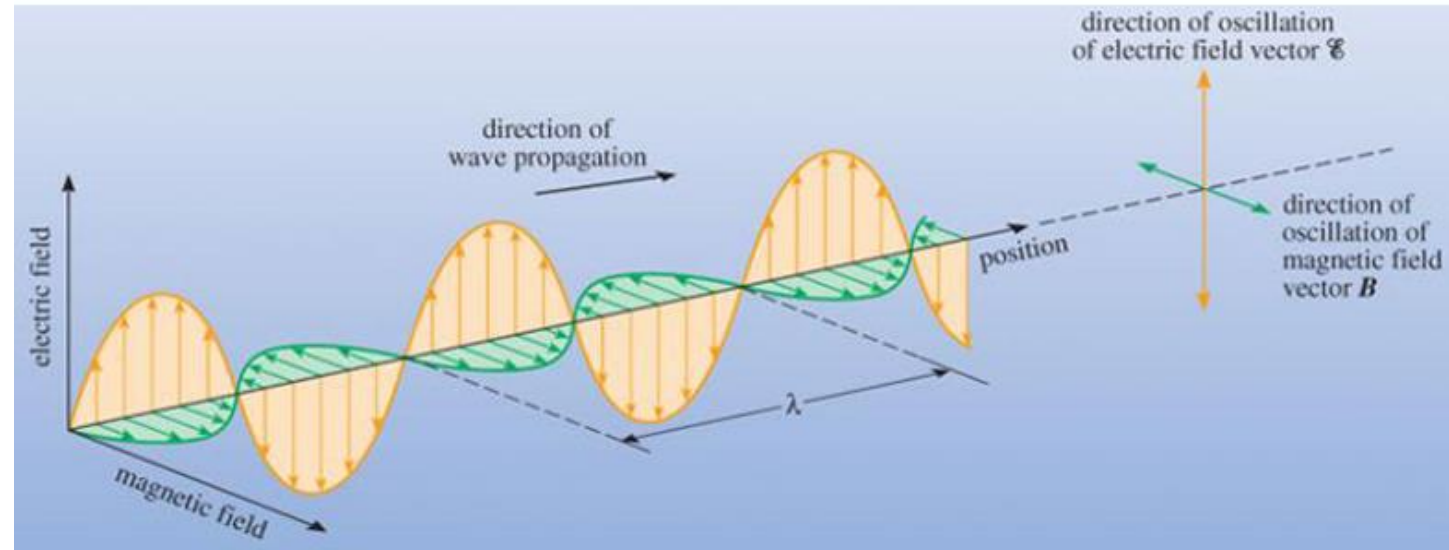
Linear Polarization: \vec{E} and \vec{B}

z-Direction Angular Momentum / Circular Polarization / Chirality / Helicity / Spin: $\pm\hbar = \pm\frac{h}{2\pi}$

Wait... is a light a wave or a particle?

... I mean, is matter a wave or particle?

... I mean, doesn't everything exhibit wave-like and particle-like properties?



With what matter does light interact?

Fermion Angular Momentum (Orbital, Spin)

Magnitude: $\hbar\sqrt{J(J+1)}$

z-Direction: $m_J\hbar$, $m_J = [-J, J]$ in steps of 1

Multiplicity/Degeneracy, $g_J: 2J + 1$

Today's Critical Guiding Question

What continuity/conservation laws are most important for photophysical processes like absorption and emission of photons?

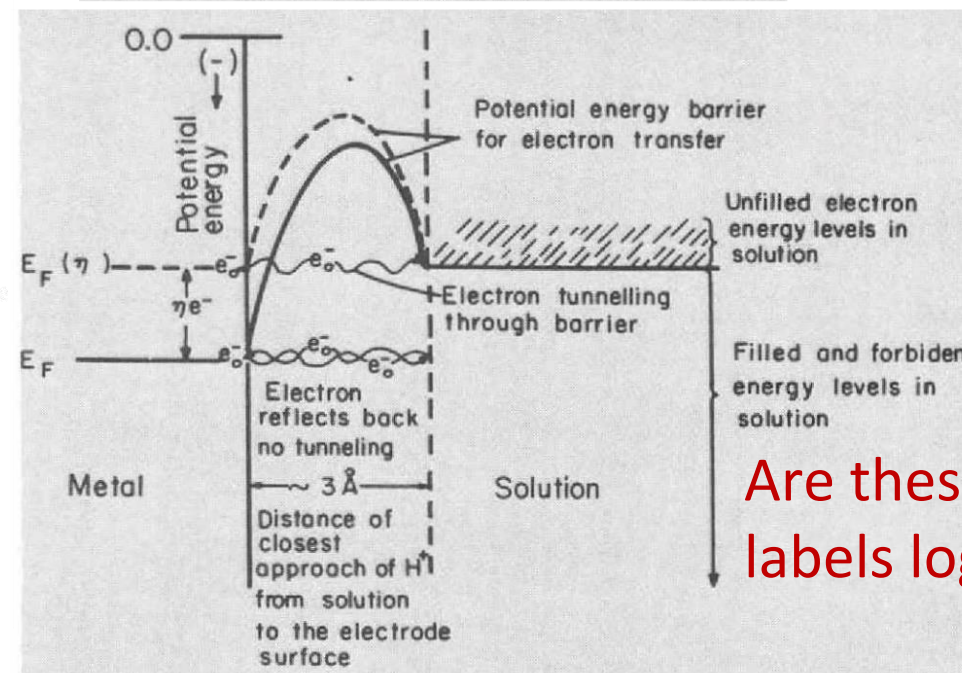
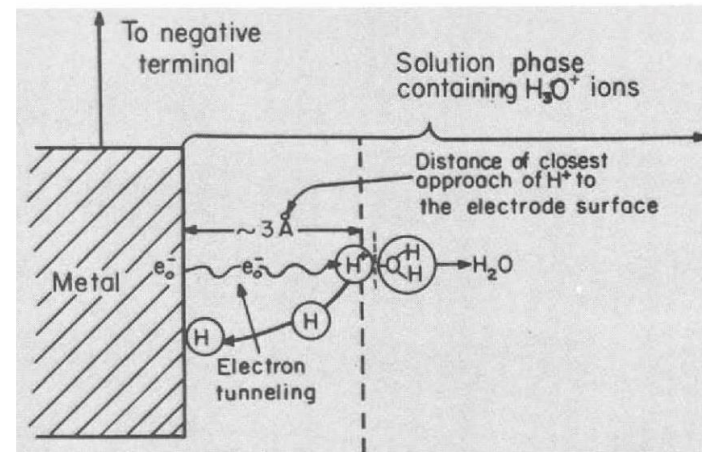
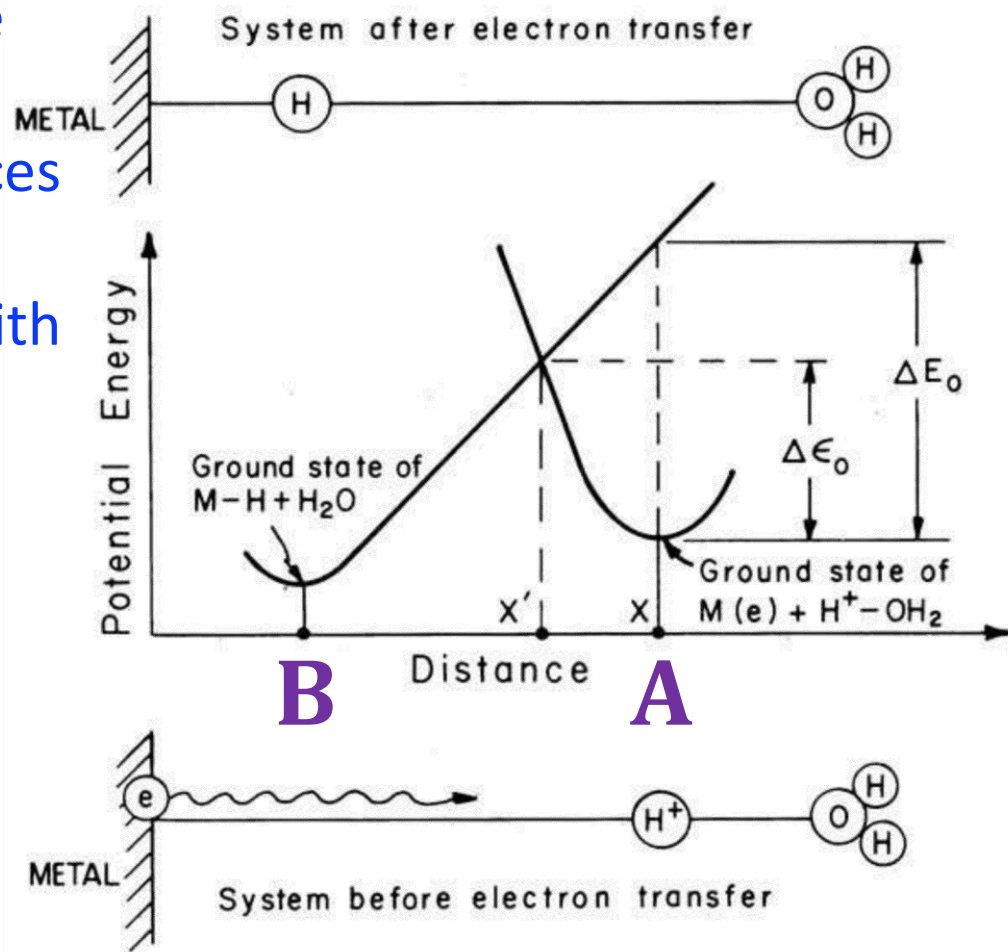
DISCUSSION SESSION TOPICS

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)

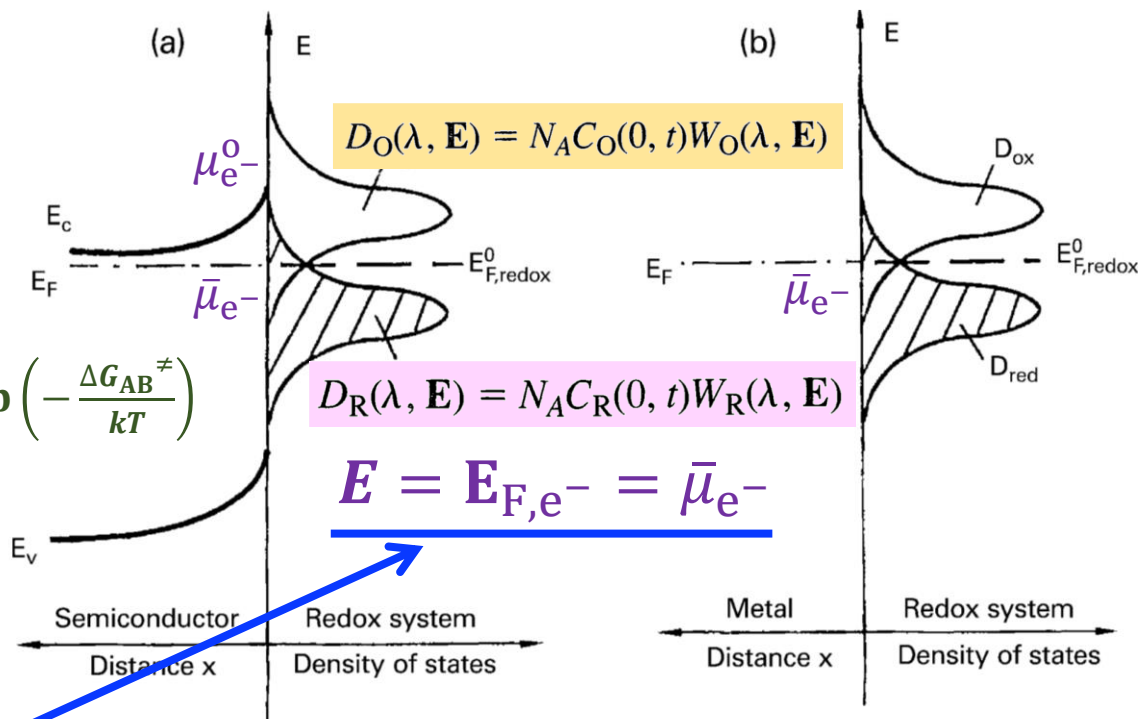
$$k_b = \nu \int_{-\infty}^{\infty} \epsilon_{ox}(\mathbf{E}) W_R(\lambda, \mathbf{E}) [1 - f(\mathbf{E})] \rho(\mathbf{E}) d\mathbf{E}$$

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

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

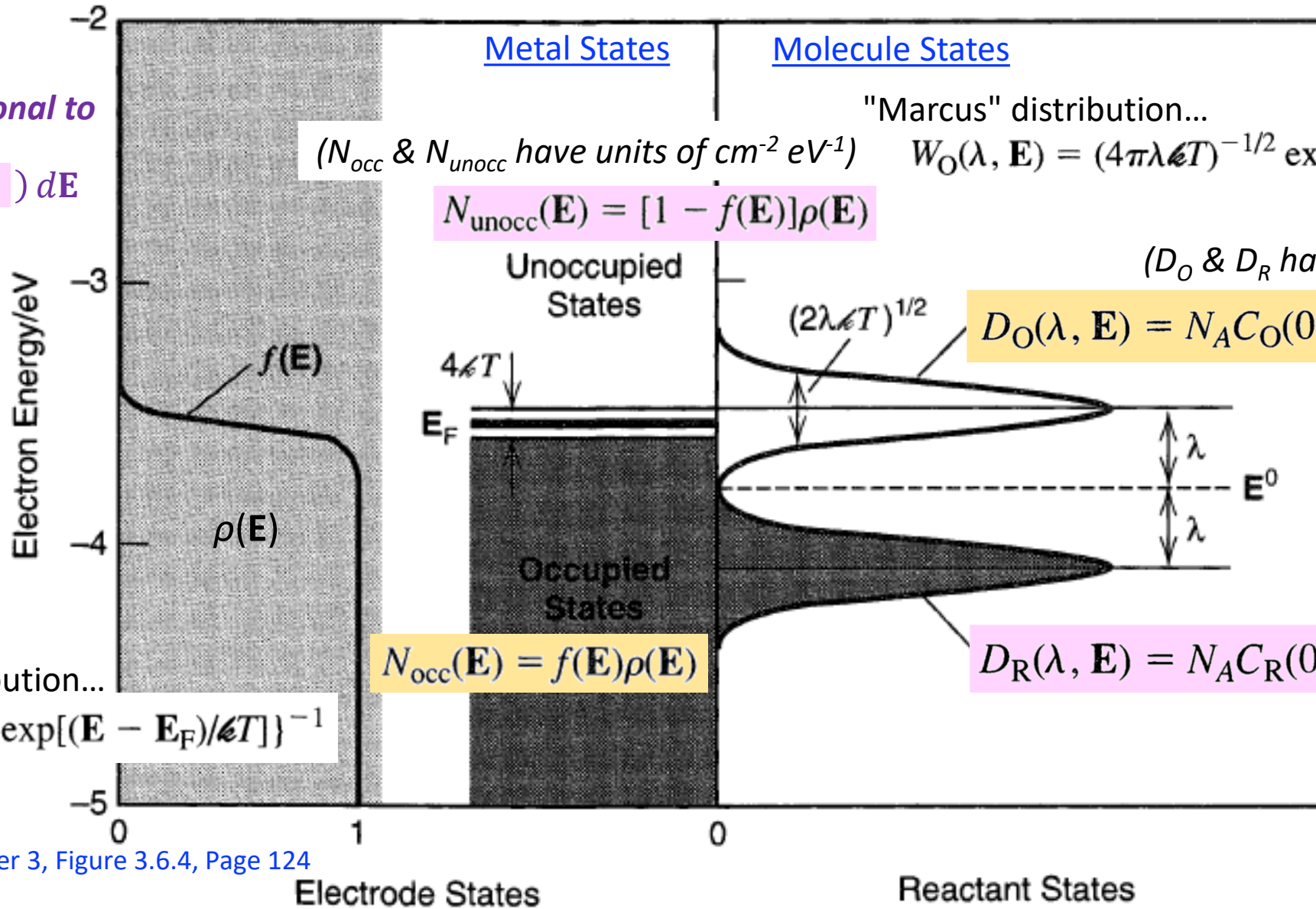


R. Memming, Chapter 6, Semiconductor Electrochemistry

Marcus–Gerischer Theory

ET rate is proportional to

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



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

"Marcus" distribution... $W_O(\lambda, E) = (4\pi\lambda\epsilon T)^{-1/2} \exp\left[-\frac{(E - E^0 - \lambda)^2}{4\lambda\epsilon T}\right]$

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

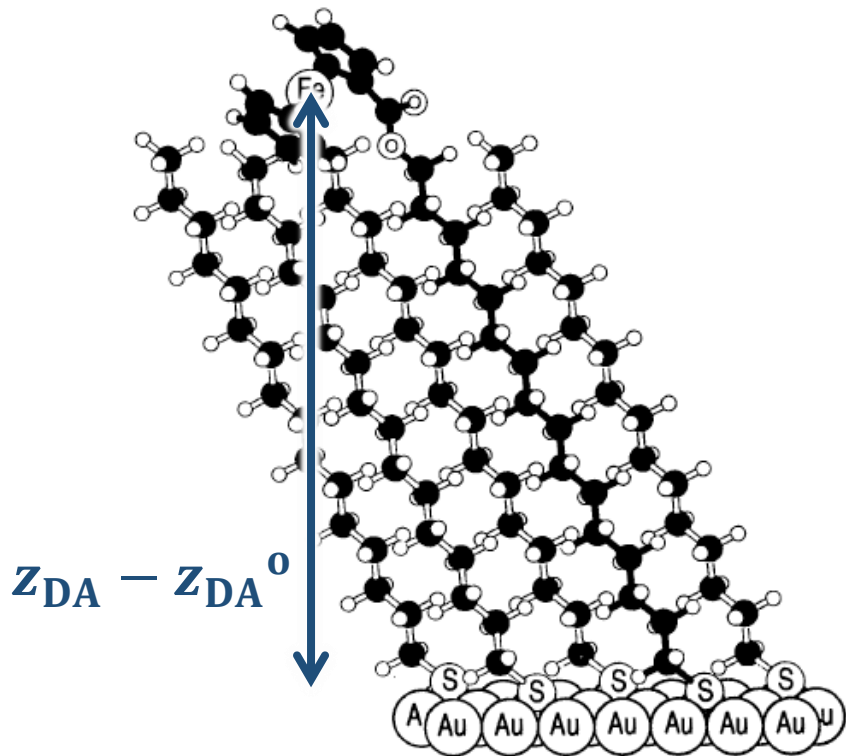
Fermi-Dirac distribution...

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

Marcus–Gerischer Theory

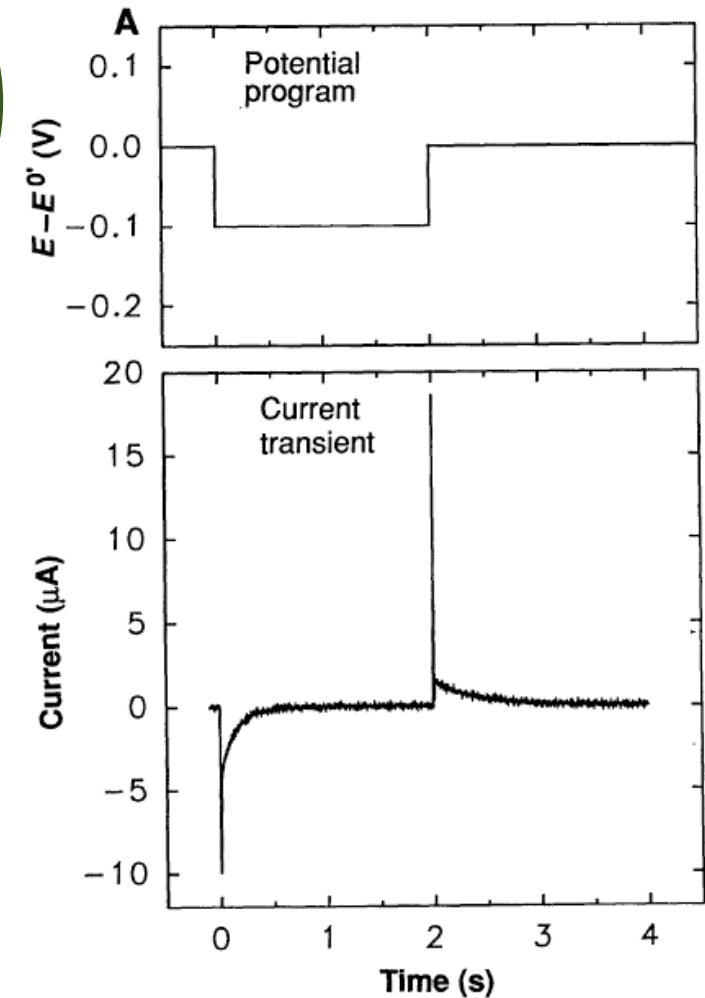
$$k_{\text{ET}} = \frac{2\pi}{\hbar} |H_{\text{DA}}^0|^2 e^{-2\beta(z_{\text{DA}} - z_{\text{DA}}^0)} \frac{1}{\sqrt{4\pi\lambda_{\text{AB}}kT}} \exp\left(-\frac{(\lambda_{\text{AB}} + \Delta G_{\text{AB}}^0)^2}{4\lambda_{\text{AB}}kT}\right)$$

quantum adiabatic electronic coupling classical nuclear free-energy dependence



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

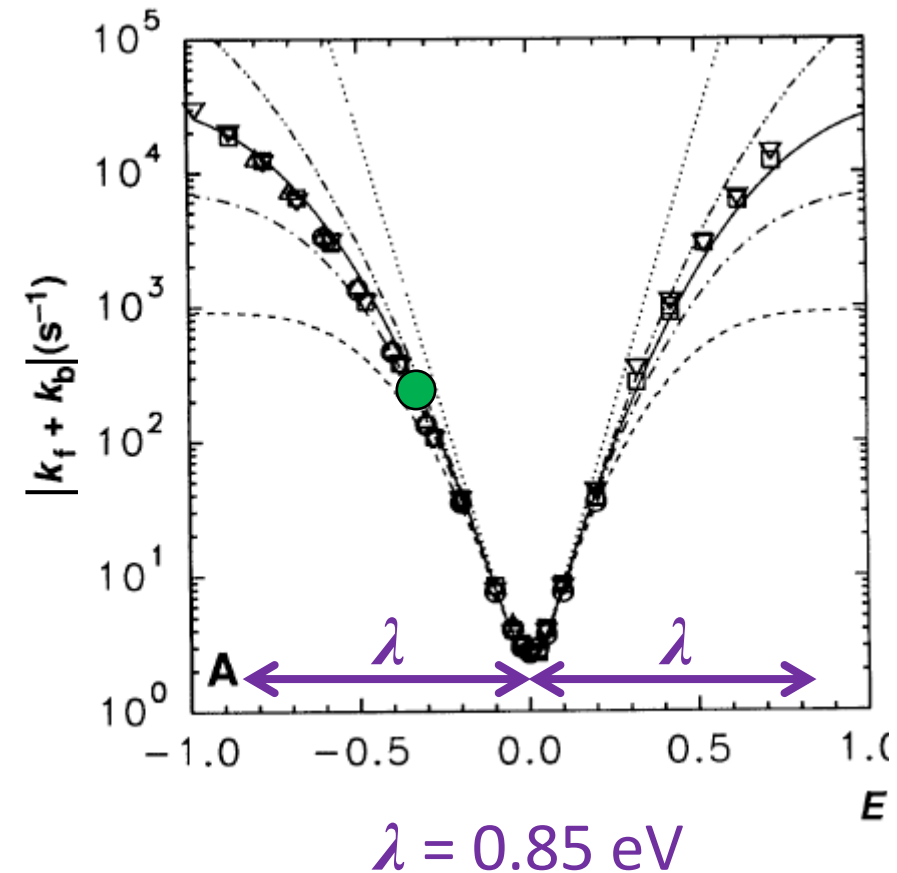
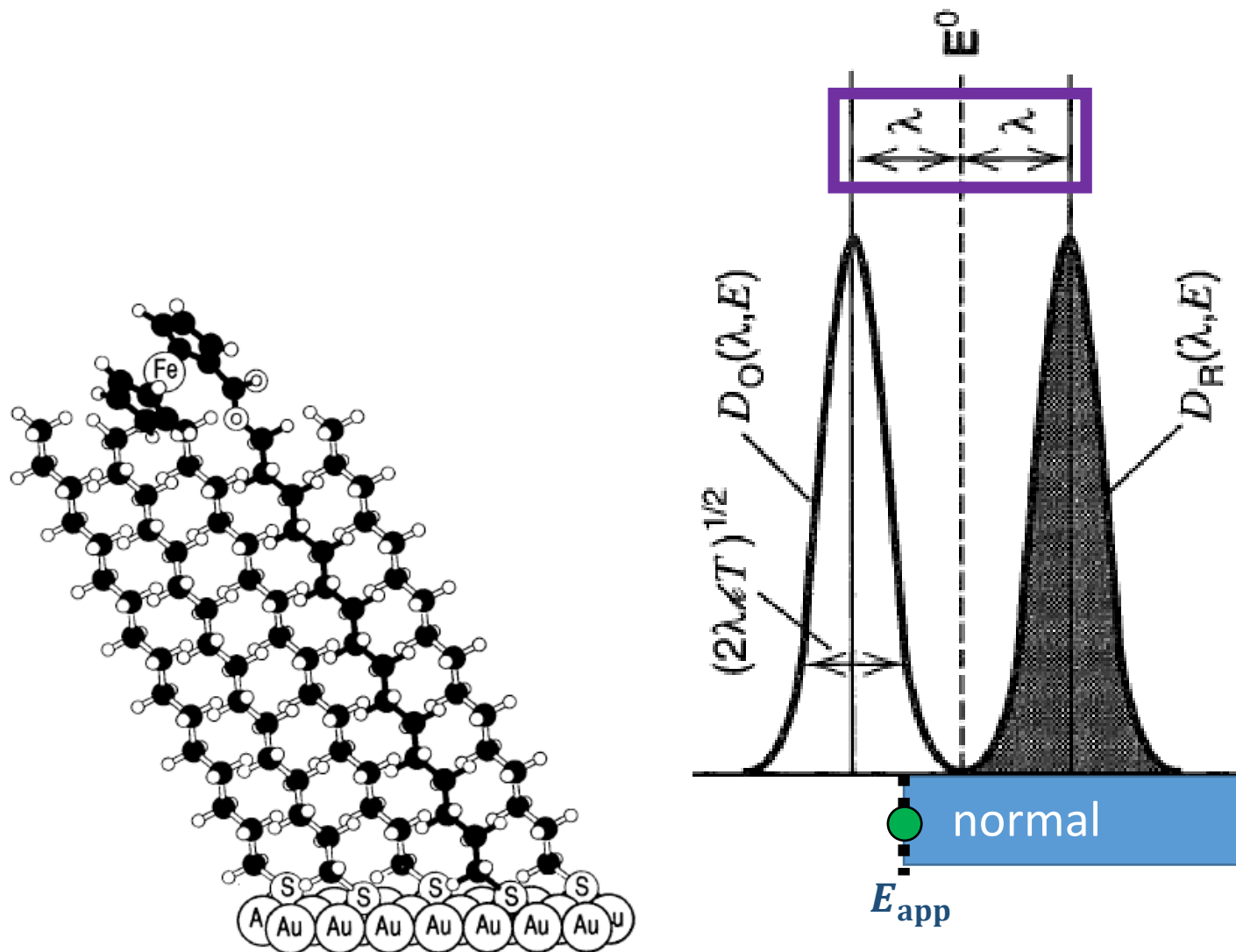
... RC-circuit double layer charging... followed by 1st-order ET kinetics



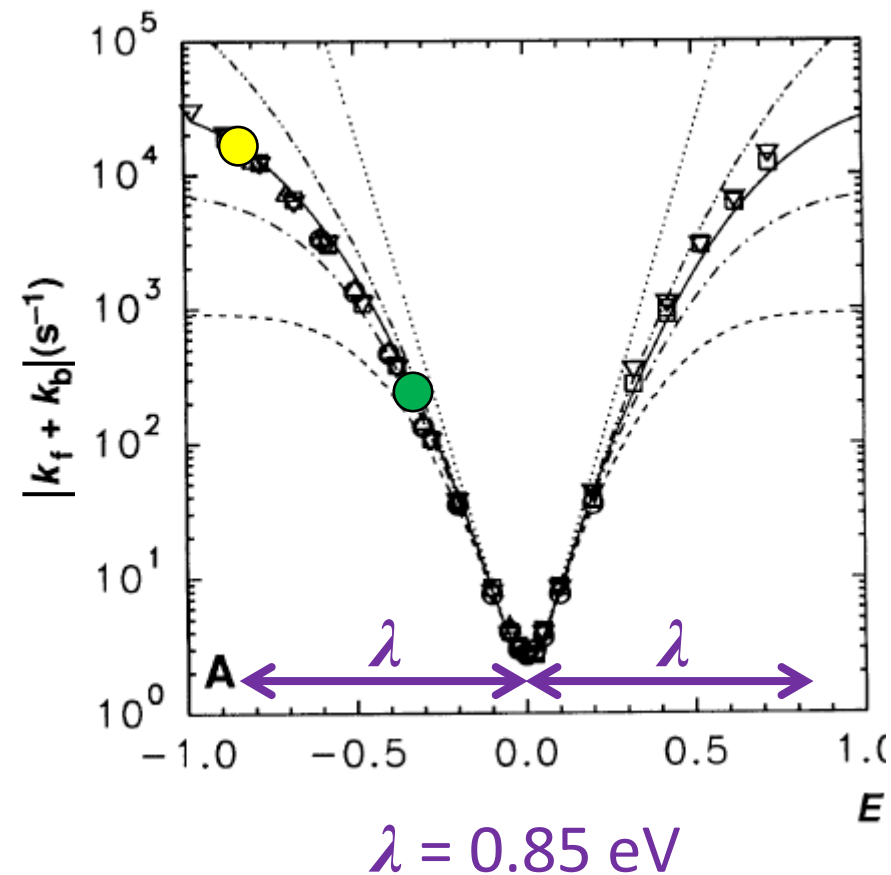
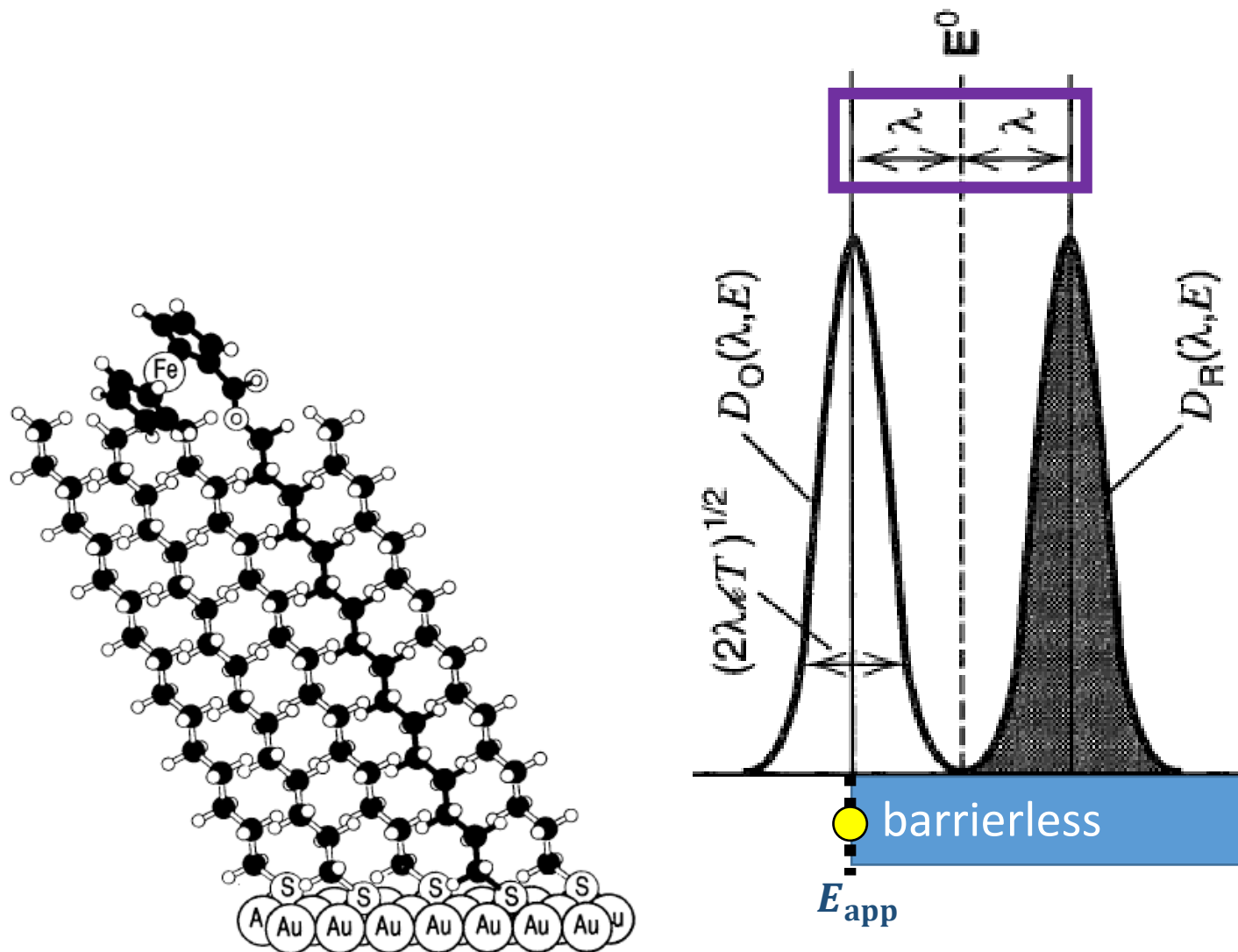
C. E. D. Chidsey, *Science*, **1991**, 251, 919–922

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}

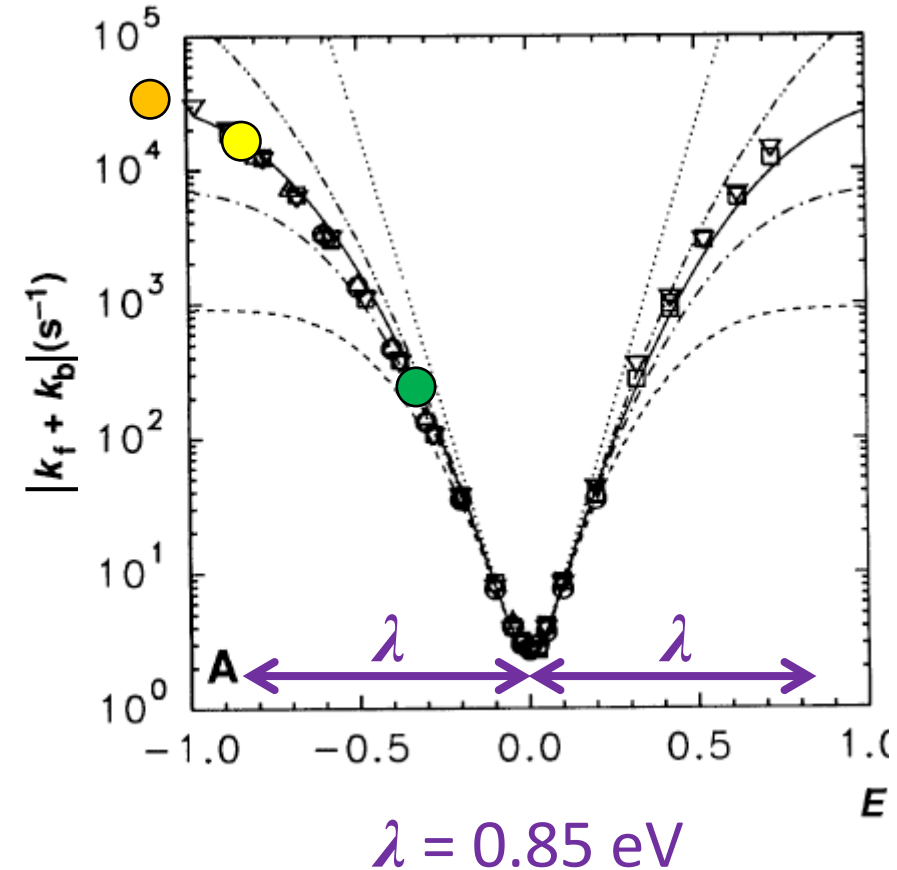
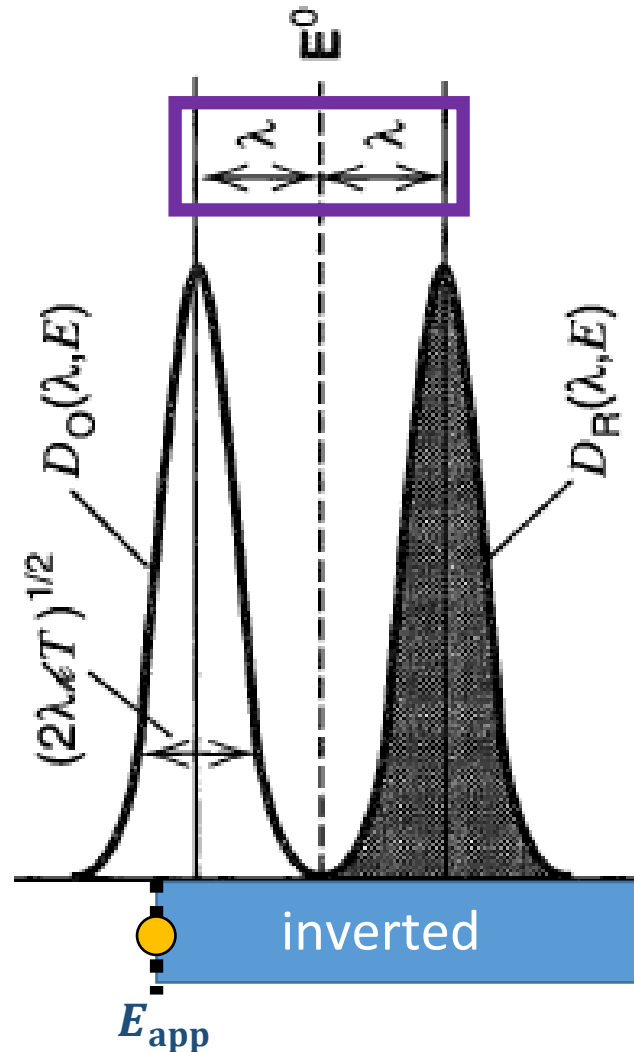
- But evidence of the inverted region is a little challenging to clearly observe

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

... what do you expect that would have looked like?

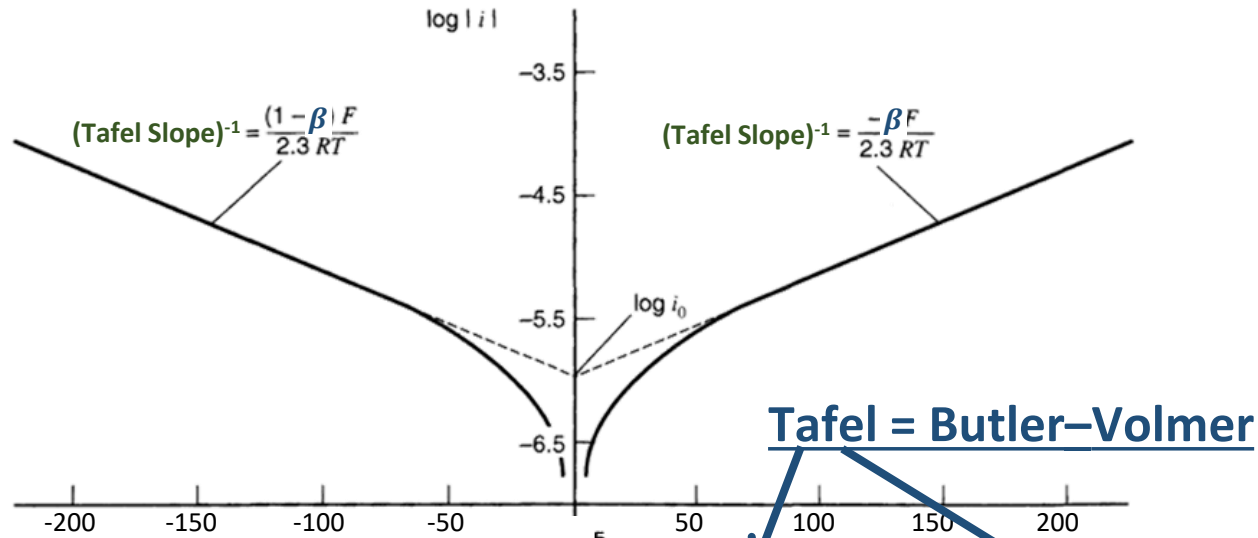
... a nice Marcus parabola!

... I wish he had done that!

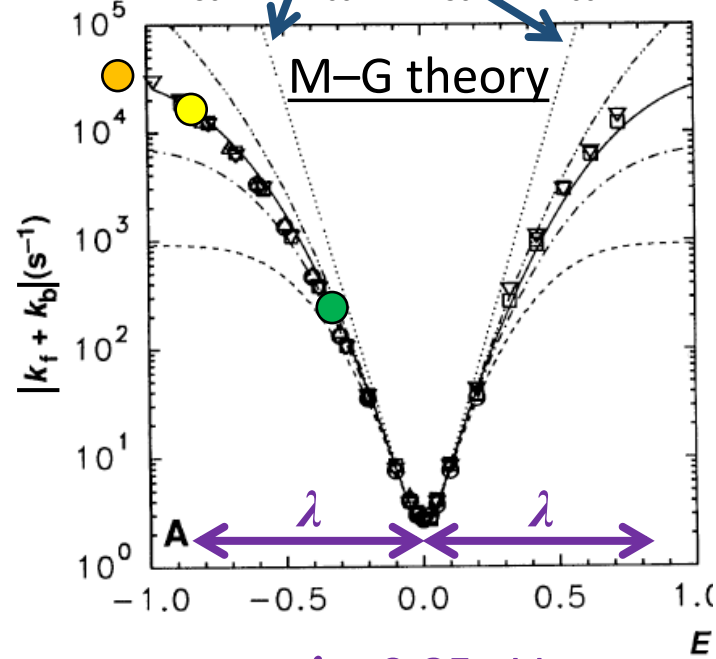


... anyway... why is λ so small in water? ... think about the metal!

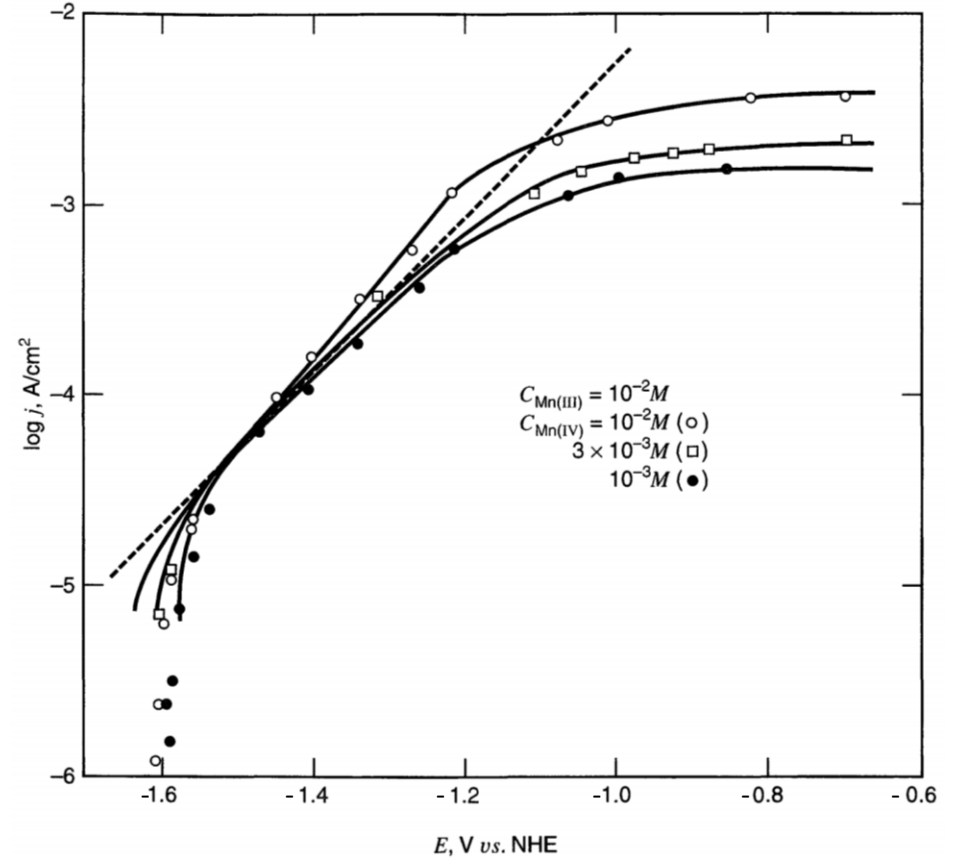
Limiting Processes



Tafel = Butler–Volmer



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!**