Lecture #7 of 12

Prof. Shane Ardo
Department of Chemistry
University of California Irvine

Linear Free Energy Relationships (LFERs)

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

linear free-energy relation

Also contains definition of: linear Gibbs energy relation

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

The name arises because the logarithm of an equilibrium constant (at constant temperature and pressure) is proportional to a 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

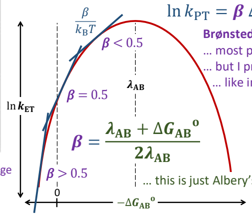
… trend looks linear over a small enough $\Delta G_{\mathrm{AB}}{}^{\mathrm{o}}$ range

Brønsted–Pedersen (1924)
empirical LFER for proton transfer

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

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

Brønsted slope…
… most people use $\boldsymbol{\alpha}$…
… but I prefer $\boldsymbol{\beta}$
… like in EChem



$$\boldsymbol{\beta} = \frac{\boldsymbol{\lambda}_{\mathbf{AB}} + \Delta \boldsymbol{G}_{\mathbf{AB}}{}^{\mathbf{o}}}{2\boldsymbol{\lambda}_{\mathbf{AB}}}$$

… this is just Albery's Equation 8

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

Butler–Volmer equation

$$n\mathrm{e}^{-,\mathrm{M}} + \mathrm{O} \rightleftarrows \mathrm{R}^{n-}$$

$j_E = nF\left(\boldsymbol{k'}_{\boldsymbol{b},\boldsymbol{E}} c_{\mathrm{R},z_{\mathrm{o}}} - \boldsymbol{k'}_{\boldsymbol{f},\boldsymbol{E}} c_{\mathrm{O},z_{\mathrm{o}}}\right)$ … for this example, let's assume that $n = 1$…

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

Current–Potential Characteristic

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

$$\boldsymbol{\eta} = \left(\boldsymbol{E} - \boldsymbol{E}_{\mathbf{eq}}\right) = \boldsymbol{E}_{\mathbf{app}}$$

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

Current–Overpotential Equation

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

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

Butler–Volmer Equation

… assuming a rapidly stirred solution

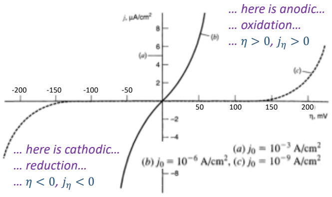
Tafel Slopes

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

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

Butler–Volmer equation

… let's examine effects of $\boldsymbol{j_o}$ (or $\boldsymbol{k^0}$)…

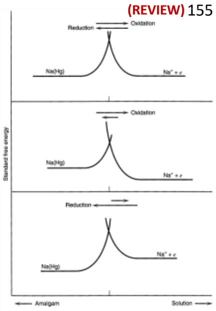


… here is anodic…
… oxidation…
… $\eta > 0,\ j_\eta > 0$

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

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

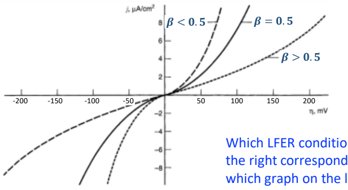
… recall that… $\boldsymbol{\eta} = (\boldsymbol{E} - \boldsymbol{E}_{\mathbf{eq}}) = \boldsymbol{E}_{\mathbf{app}} = \frac{\Delta G^{\mathrm{o}}}{-nF}$



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

Butler–Volmer equation

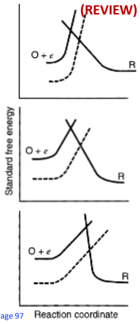
… let's examine effects of $\boldsymbol{\beta}$ (or Tafel slope)…



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

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

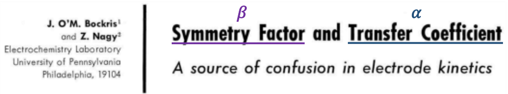
… recall that… $\boldsymbol{\eta} = (\boldsymbol{E} - \boldsymbol{E}_{\mathbf{eq}}) = \boldsymbol{E}_{\mathbf{app}} = \frac{\Delta G^{\mathrm{o}}}{-nF}$



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

* "Frumkin" non-idealities for Henderson–Hasselbalch pH titration curves result in similar behavior as the analogous "Hill" equation

Charge Transfer across Electrified Interfaces



J. O'M. Bockris[1]
and Z. Nagy[2]
Electrochemistry Laboratory
University of Pennsylvania
Philadelphia, 19104

β α

Symmetry Factor and Transfer Coefficient

A source of confusion in electrode kinetics

Symmetry factor ($\boldsymbol{\beta}$): change in the activation free energy of the cathodic elementary reaction step, expressed as a fraction of $\boldsymbol{E}_{\mathbf{app}}$

Transfer coefficient ($\boldsymbol{\alpha}_{\boldsymbol{j}}$): change in the (cath)odic/(an)odic reaction rate expressed as a change in the activation free energy as a fraction of $\boldsymbol{E}_{\mathbf{app}}$

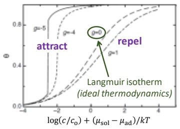
$$\mathrm{TS_{cath}}^{-1} = \left(\frac{d(\log|j_E|)}{d|\boldsymbol{\eta}|}\right)_{\mathrm{cath}} = \frac{-\boldsymbol{\alpha}_{\mathbf{cath}}F}{2.303RT}$$

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

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

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

Frumkin isotherms



* *g* is a lateral interaction term

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

Rate-Determining Step (RDS)

$$\mathrm{D + A \rightleftarrows D^+ + A^-}$$

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!**

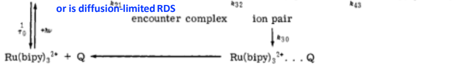
Ground-state electron transfer

$\Delta G_R{}^o$ due to entropy/sterics **$\Delta G_p{}^o$ due to entropy/sterics**

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

Excited-state electron transfer

$\Delta G^o{}_{12}$ in pre-equilibrium **$\Delta G^o{}_{23}$ RDS 1st-order ET** **$\Delta G^o{}_{34}$ due to electrostatics**



or is diffusion-limited RDS

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

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

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

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

… 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…

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

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

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

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…

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

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

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

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

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

… since $\frac{\partial[\mathrm{D^+}]}{\partial t} = \frac{\partial[\mathrm{A^-}]}{\partial t} = k_{3f}[(\mathrm{D^+, A^-})]$… 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… consistent!

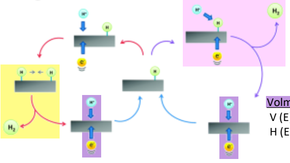
Charge Transfer across Electrified Interfaces

J. O'M. Bockris[1]
and **Z. Nagy**[2]
Electrochemistry Laboratory
University of Pennsylvania
Philadelphia, 19104

β α

Symmetry Factor and Transfer Coefficient

A source of confusion in electrode kinetics



Volmer–Tafel mechanism
V (E): $H^+ + e^- \rightleftarrows M{-}H$
T (C): $2\ M{-}H \rightleftarrows H_2 + M$

Volmer–Heyrovsky mechanism
V (E): $H^+ + e^- \rightleftarrows M{-}H$
H (E): $M{-}H + e^- + H^+ \rightleftarrows H_2 + M$

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S. Trasatti, *J. Electroanal. Chem. Interfacial Electrochem.*, **1972**, *39*, 163–184

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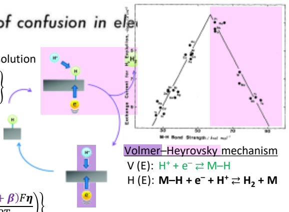
Case 1: V = pre-equilibrium; H = **RDS**; $E = E_{\mathrm{eq}}$; rapidly stir solution

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

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

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

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



Volmer–Heyrovsky mechanism
V (E): $H^+ + e^- \rightleftarrows M{-}H$
H (E): $\mathbf{M{-}H + e^- + H^+ \rightleftarrows H_2 + M}$

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

S. Trasatti, *J. Electroanal. Chem. Interfacial Electrochem.*, **1972**, *39*, 163–184

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J. O'M. Bockris[1]
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Philadelphia, 19104

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A source of confusion in ele

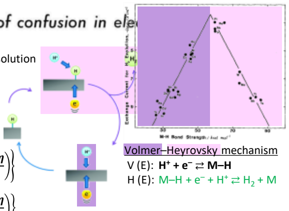
Case 2: V = **RDS**; H = pre-equilibrium; $E = E_{\mathrm{eq}}$; rapidly stir solution

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

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

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

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



Volmer–Heyrovsky mechanism
V (E): $\mathbf{H^+ + e^- \rightleftarrows M{-}H}$
H (E): $M{-}H + e^- + H^+ \rightleftarrows H_2 + M$

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

Photophysical Processes

Prof. Shane Ardo
Department of Chemistry
University of California Irvine

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

(REVIEW) 167

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

$$\boldsymbol{\hat{H}}\psi_n(x) = \mathbf{E}_{\boldsymbol{n}}\psi_n(x)$$

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

$\mathrm{E} = h\nu = \hbar\omega$ (Planck)
$\mathrm{E} = mc^2 = pc$ (Einstein)
$p = \frac{h\nu}{c} = \frac{h}{\lambda} = h\bar{\nu} = \hbar k$ (de Broglie)

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

… 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 $\hat{V}$?

$\hat{T}(x) = \mathrm{KE} = \frac{1}{2}m\hat{v}^2 = \frac{\hat{p}^2}{2m}$… with ($\boldsymbol{\hat{p}}$)momentum = ($m$)ass x ($\hat{v}$)elocity = $-\boldsymbol{i}\hbar\frac{\boldsymbol{\partial}}{\boldsymbol{\partial x}}$… Wow, right?

$\hat{V}(x) = \mathrm{PE} = 0$… for particle-in-a-box…

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

$\hat{V}(r) = -\frac{q^2}{4\pi\varepsilon_0 r}$… for Hydrogen atom, with $F = qN_\mathrm{A}$ (Faraday const), ε_0 (vacuum permittivity)

Schrödinger Equation

(REVIEW) 168

Poisson's Equation (from Gauss's law)

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

for a point charge… look familiar? $\phi(r) = \frac{q}{4\pi\varepsilon r}$

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

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

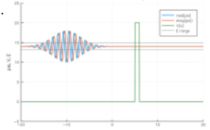
… we need to fill **internal energies**, E_n, with particles… okay.

… 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

Blackbody Radiation

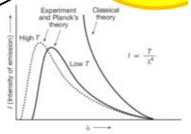
169

Carnot efficiency limit, $\eta = \frac{w}{Q_\mathrm{H}} = \frac{Q_\mathrm{H}-Q_\mathrm{C}}{Q_\mathrm{H}} = 1 - \frac{Q_\mathrm{C}}{Q_\mathrm{H}} = 1 - \frac{T_\mathrm{C}}{T_\mathrm{H}}$

(T ≈ 5790 K)
SUN

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

EARTH
(T ≈ 290 K)



UNIVERSE
(T ≈ 3 K)

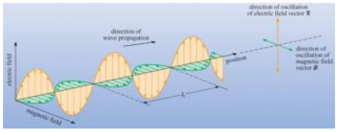
… if any two bodies are that the same temperature
… and they only interact via radiation, i.e., photons (e.g., not chemical)
… then no work can be performed due to these photon exchanges
… and electrochemical potentials do not change due to them

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: $\vec{\mathrm{E}}$ and $\vec{\mathrm{B}}$



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

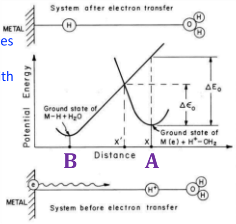
(REVIEW) 173

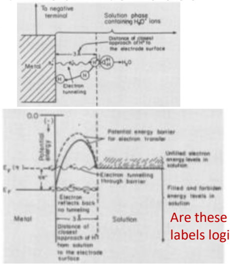
Charge Transfer across Electrified Interfaces

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

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

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





Are these labels logical?

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

(REVIEW) 174

Fermi's (Second) Golden Rule

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

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

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

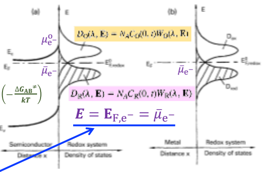
Transition probability

Matrix element for the interaction

Density of final states (DoS)

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

… divide the DoS term by c_{i,z_o}…



$D_\mathrm{O}(\lambda, \mathbf{E}) = N_A C_\mathrm{O}(0, t) W_\mathrm{O}(\lambda, \mathbf{E})$

$D_\mathrm{R}(\lambda, \mathbf{E}) = N_A C_\mathrm{R}(0, t) W_\mathrm{R}(\lambda, \mathbf{E})$

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

R. Memming, Chapter 6, Semiconductor Electrochemistry

frequency factor (s^{-1})

$$k_\mathrm{f} = \nu \int_{-\infty}^{\infty} \varepsilon_{\mathrm{red}}(\mathbf{E}) W_\mathrm{O}(\lambda, \mathbf{E}) f(\mathbf{E}) \rho(\mathbf{E}) d\mathbf{E}$$

proportionality function (cm^3 eV)

$$k_\mathrm{b} = \nu \int_{-\infty}^{\infty} \varepsilon_{\mathrm{ox}}(\mathbf{E}) W_\mathrm{R}(\lambda, \mathbf{E})[1 - f(\mathbf{E})] \rho(\mathbf{E}) d\mathbf{E}$$

applied potential

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

energy

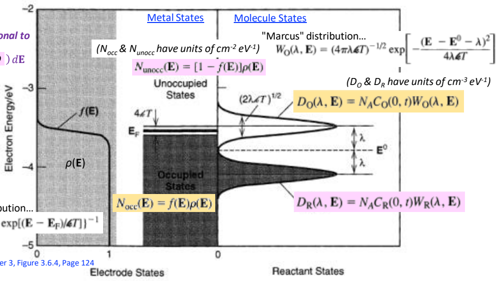
$$j_{E,\mathrm{obs}} = nF\left(-\boldsymbol{k'}_{\boldsymbol{f,E,\mathrm{obs}}} c_{\mathrm{O},z_\mathrm{o}} + \boldsymbol{k'}_{\boldsymbol{b,E,\mathrm{obs}}} c_{\mathrm{R},z_\mathrm{o}}\right)$$

(REVIEW) 175

Marcus–Gerischer Theory

ET rate is proportional to

$$\int_{-\infty}^{\infty} (N\ D - N\ D)\, d\mathbf{E}$$



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

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

"Marcus" distribution…

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

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

$D_\mathrm{O}(\lambda, \mathbf{E}) = N_A C_\mathrm{O}(0, t) W_\mathrm{O}(\lambda, \mathbf{E})$

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

$D_\mathrm{R}(\lambda, \mathbf{E}) = N_A C_\mathrm{R}(0, t) W_\mathrm{R}(\lambda, \mathbf{E})$

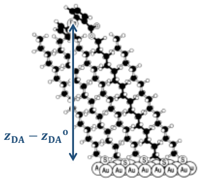
Fermi–Dirac distribution…

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

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

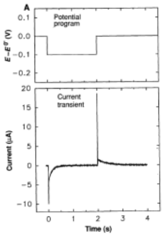
Marcus–Gerischer Theory

$$k_{\mathrm{ET}} = \underbrace{\frac{2\pi}{\hbar}\left|H_{\mathrm{DA}}{}^{\mathrm{o}}\right|^2 e^{-2\beta(z_{\mathrm{DA}}-z_{\mathrm{DA}}{}^{\mathrm{o}})}}_{\text{quantum adiabatic electronic coupling}} \underbrace{\frac{1}{\sqrt{4\pi\lambda_{\mathrm{AB}}kT}}\exp\left(-\frac{\left(\lambda_{\mathrm{AB}}+\Delta G_{\mathrm{AB}}{}^{\mathrm{o}}\right)^2}{4\lambda_{\mathrm{AB}}kT}\right)}_{\text{classical nuclear free-energy dependence}}$$



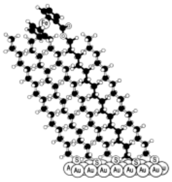
… as an aside… why is the data biphasic for the Current?

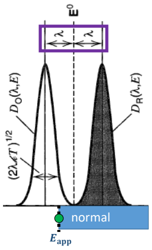
… RC-circuit double layer charging… followed by 1st-order ET kinetics

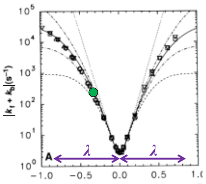


C. E. D. Chidsey, *Science*, **1991**, *251*, 919–922
H. D. Sikes, J. F. Smalley, S. P. Dudek, A. R. Cook, M. D. Newton, C. E. D. Chidsey & S. W. Feldberg, *Science*, **2001**, *291*, 1519–1523

Marcus–Gerischer Theory



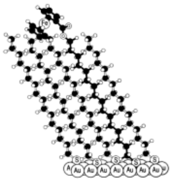


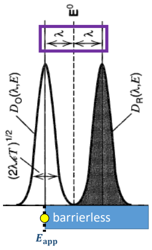


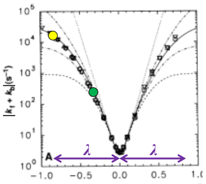
λ = 0.85 eV

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

(REVIEW/UPDATED) 179

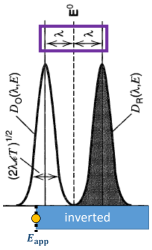
- It is easy to sweep/vary the driving force, ΔG_{AB}, by simply changing the electrochemical potential of electrons (e^-) in the (M)etal working electrode, $\bar{\mu}_e^{\mathrm{M}}$, through variations in E_{app}
- **But evidence of the inverted region is a little challenging to clearly observe**

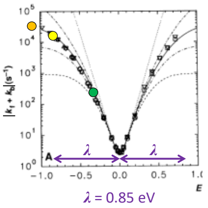
… what if Chidsey had plotted the derivative of his data on the right?

… what do you expect that would have looked like?

… a nice Marcus parabola!

… I wish he had done that!





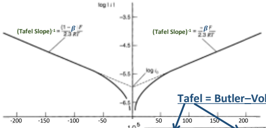
λ = 0.85 eV

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

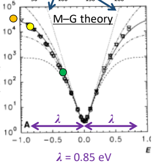
C. E. D. Chidsey, *Science*, **1991**, *251*, 919–922

Limiting Processes

180



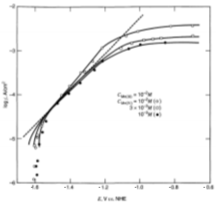
Tafel = Butler–Volmer



λ = 0.85 eV

Since Butler–Volmer theory is based on an LFER approximation, does it predict the presence of the Marcus 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!**