4/27/2023

UCI CHEM267 – Photochemistry, Spring 2023   122

Lecture #6 of 12
{80 min away from being halfway through… tear}

Prof. Shane Ardo
Department of Chemistry
University of California Irvine

UCI CHEM267 – Photochemistry, Spring 2023   123

Thermal (Dark) Reactions

Prof. Shane Ardo
Department of Chemistry
University of California Irvine

Marcus–Hush Theory

(REVIEW) 124

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

… but how is this a first-order reaction (s^{-1})?… more on this later…

$$\underset{A}{D + A} \rightleftarrows \underset{B}{D^+ + A^-}$$

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

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

$$A \rightleftarrows X^{\neq} \rightleftarrows B$$

Eyring–Polanyi–Evans (1930s)
theoretical rate constant equation (from **transition-state theory / activated complex theory**)

$$k_f = \kappa\nu K^{\neq} = \frac{\kappa k_BT}{h}K^{\neq} \dots \text{ with } \textbf{transmission coefficient}, \kappa, \text{ and } \textbf{vibrational frequency}, \nu \text{ (s}^{-1})$$

$$\dots \text{ and } R = N_A k_B \dots \text{ and } \frac{\kappa k_BT}{h} \text{ has units of s}^{-1}$$

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

… what is the largest predicted pre-exponential factor at 25 °C? **(161 fs)$^{-1}$ = (1.61 x 10^{-13} s)$^{-1}$**

1

Marcus–Hush Theory

$$D + A \rightleftarrows D^+ + A^-$$
$$_{A} _{B}$$

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

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

quantum adiabatic electronic coupling   classical nuclear free-energy dependence

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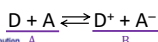
$$\Delta G_{AB}^{\neq} = \frac{(\lambda_{AB}+\Delta G_{AB}{}^o)^2}{4\lambda_{AB}}$$

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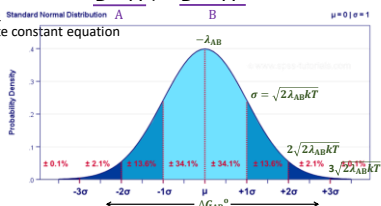

Marcus–Hush Theory

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

Marcus–Hush (1950s–1960s) Standard Normal Distribution   A   B $\mu = 0 \,|\, \sigma = 1$
theoretical (semiclassical) rate constant equation

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

$-\lambda_{AB}$ $\sigma = \sqrt{2\lambda_{AB}kT}$ $2\sqrt{2\lambda_{AB}kT}$ $3\sqrt{2\lambda_{AB}kT}$

±0.1% ±2.1% ±13.6% ±34.1% ±34.1% ±13.6% ±2.1% ±0.1%

-3σ -2σ -1σ μ $+1\sigma$ $+2\sigma$ $+3\sigma$ $\Delta G_{AB}{}^o$

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

Inner *versus* Outer Sphere Reactions

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

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

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 ($2H_{DA} > \lambda_{AB}$)
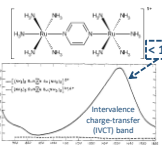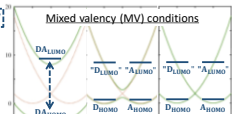... so what is $2H_{DA}$ for Class III [C–T]$^{5+}$?

Creutz–Taube ion (1969)

< 1 eV

Intervalence charge-transfer (IVCT) band

Mixed valency (MV) conditions

DA_{LUMO} "D_{LUMO}" "A_{LUMO}"   "D_{LUMO}" "A_{LUMO}"
DA_{HOMO} D_{HOMO} A_{HOMO} D_{HOMO} A_{HOMO}

C. Creutz & H. Taube, *J. Am. Chem. Soc.*, **1969**, *91*, 3988–3989
B. S. Brunschwig, C. Creutz & N. Sutin, *Chem. Soc. Rev.*, **2002**, *31*, 168–184

Huang–Rhys Factor

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

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

$$\equiv \nu_n(r)\kappa_{el}(r)\kappa_n(r)$$

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

… separable due to the Born–Oppenheimer approximation

If $\hbar\omega_j \gg k_B T$, only $v_j = 0$ is appreciably populated
and

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

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

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 ($\hbar\omega \gg k_B T$), and[a,b,1,2,13,131]

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

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.[99,103]

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

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…

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

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

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

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_{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

$$k_{es} = 4\pi X_G X_p (\Delta\nu)^2/(W_{Gp} - X_p W_p - X_G W_G)C_{tot} \quad (1)$$

where k_{es} is the rate of electron exchange, X_G 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_{Gp} is the peak width at half height of the signal of interest for the mixture, W_G 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!
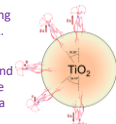
S. Ardo & G. J. Meyer, *J. Am. Chem. Soc.*, **2011**, *133*, 15384–15396

Marcus Cross Relations

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

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

$$\Delta G_{AB}^{\neq} = \frac{(\lambda_{AB} + \Delta G_{AB}{}^o)^2}{4\lambda_{AB}}$$

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

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

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

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

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

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

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

$\Delta G_{II,H}^{\ddagger} = \frac12\Delta G_{I,\ell}^{\ddagger}+\frac12\Delta G_{II,H}^{\ddagger}+\frac14\Delta G^{\neq} + \frac{(\Delta G^{\neq})^2}{8(\Delta G_{I,\ell}^{\ddagger}+\Delta G_{II,H}^{\ddagger})}$

J. Albery, *Ann. Rev. Phys. Chem.*, **1980**, *31*, 227–263
R. A. Marcus & N. Sutin, *Biochim. Biophys. Acta*, **1985**, *811*, 265–322


Today's Critical Guiding Question

*Since **Marcus–Hush** theory is sufficient to predict <u>all</u> rate constants (with knowledge of only $\Delta G_{AB}{}^o$, 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
$\bar\mu_i^\alpha = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_{j\neq i}}$ **(REVIEW)** 133

$Si_{CB}(h^+) + Si_{VB}(e^-) \rightleftharpoons Si_{CB}(e^-) + Si_{VB}(h^+)$
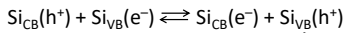
At equilibrium,
$\bar\mu_{CB(h^+)}^{Si} + \bar\mu_{VB(e^-)}^{Si} = \bar\mu_{CB(e^-)}^{Si} + \bar\mu_{VB(h^+)}^{Si}$

As reference states, it is useful to define
$\bar\mu_{CB(h^+)}^{Si} = \bar\mu_{VB(e^-)}^{Si} = 0$

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

Anyway... therefore,
$\bar\mu_{CB(e^-)}^{Si} = -\bar\mu_{VB(h^+)}^{Si}$
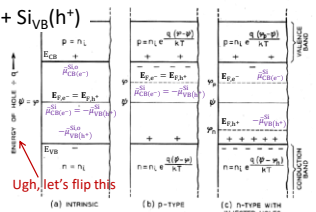
$E_{F,e^-} = \bar\mu_{e^-}$
$E_{F,h^+} = -\bar\mu_{h^+}$
$E_{F,e^-} = E_{F,h^+}$

Ugh, let's flip this

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

4

Charge Transfer across Electrified Interfaces

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

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

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

I did not include primes here, for simplicity

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

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

… R_O is a rate… with units of M/s (= mol dm^{-3} s^{-1})
… k_f (s^{-1}) is an inverse time constant!

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

… as a specific case choose $E^{0\prime}$… and thus, $j_{E^{0\prime}} = nF\left(-k'_{f,E^{0\prime}} c_{O,z_o} + k'_{b,E^{0\prime}} c_{R,z_o}\right)$

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

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

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

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

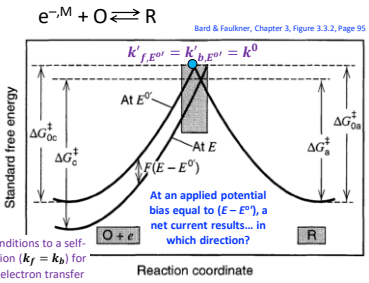$$\eta = (E - E_{eq}) = E_{app} = \frac{\Delta G^o}{-nF}$$ … where η (V) is overpotential

… 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 $\Delta G_A^o = \bar{\mu}_e^M + \bar{\mu}_O^o$)**

- *The derivation here assumes that the electrode is inert, e.g. not like battery electrodes*

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

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

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

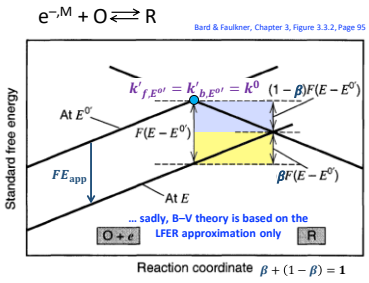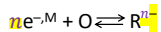At an applied potential bias equal to $(E - E^o)$, a net current results… in which direction?

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 $\Delta G_A^o = \bar{\mu}_e^M + \bar{\mu}_O^o$)**

- 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?**

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

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

$$k'_{f,E^{0\prime}} = k'_{b,E^{0\prime}} = k^0$$ $(1-\beta)F(E-E^{0\prime})$

$F(E-E^{0\prime})$

$\beta F(E-E^{0\prime})$

… sadly, B–V theory is based on the LFER approximation only

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

Butler–Volmer equation

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

$$j_E = nF\left(k'_{b,E} c_{R,z_o} - k'_{f,E} c_{O,z_o}\right) \qquad \text{... for this example, let's assume that } n = 1...$$

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

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

... c^* means bulk concentration... conversion is trivial using $E_{eq} = E^{o\prime} - \frac{RT}{nF} \ln \frac{c_R^*}{c_O^*}$
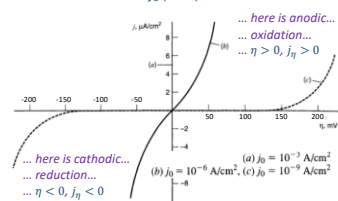
$$j_E = j_o \left\{ \exp\left(\frac{(1-\beta)F\eta}{RT}\right) - \exp\left(\frac{-\beta F\eta}{RT}\right)\right\} \quad \begin{matrix}\text{Butler–}\\\text{Volmer}\\\text{Equation}\end{matrix}$$

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

... assuming a rapidly stirred solution

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

Butler–Volmer equation

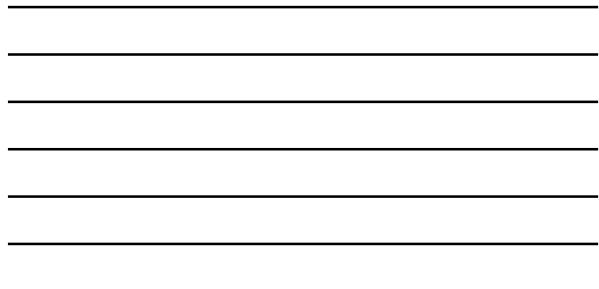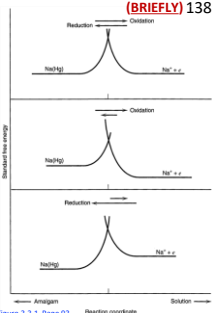... let's examine effects of j_o (or k^0)...

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

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

(a) $j_0 = 10^{-3}$ A/cm^2
(b) $j_0 = 10^{-6}$ A/cm^2, (c) $j_0 = 10^{-9}$ A/cm^2

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

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

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

Butler–Volmer equation

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

$\beta < 0.5$ $\beta = 0.5$

$\beta > 0.5$

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

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

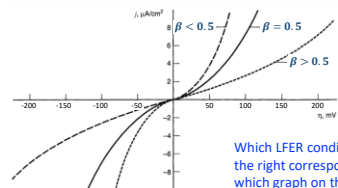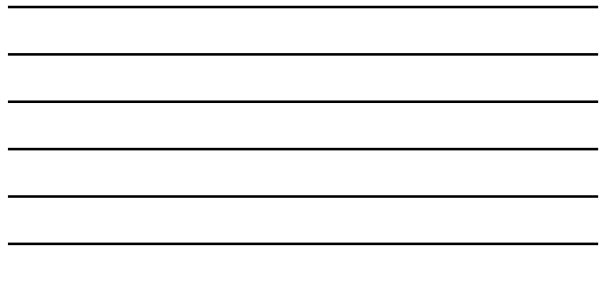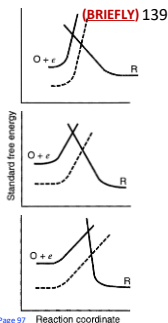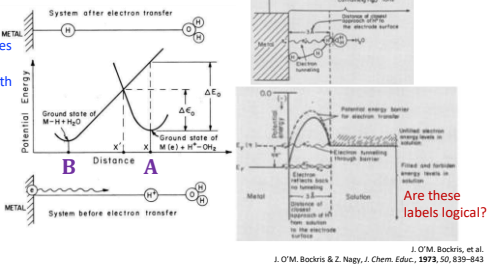... recall that... $\eta = (E - E_{eq}) = E_{app} = \frac{\Delta G^o}{-nF}$

Bard & Faulkner, Chapter 3, Figure 3.3.4, Page 97   Reaction coordinate
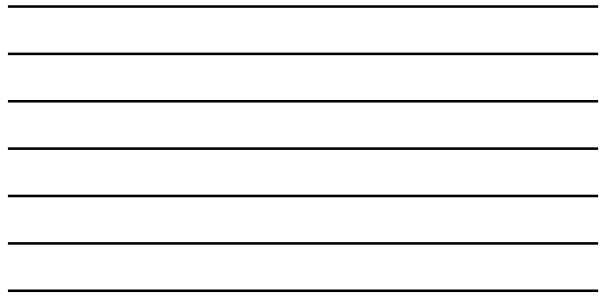
Charge Transfer across Electrified Interfaces (BRIEFLY) 140

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?

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

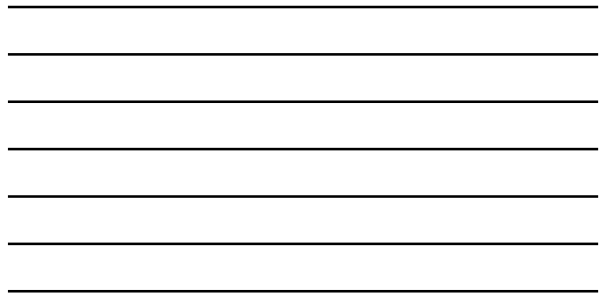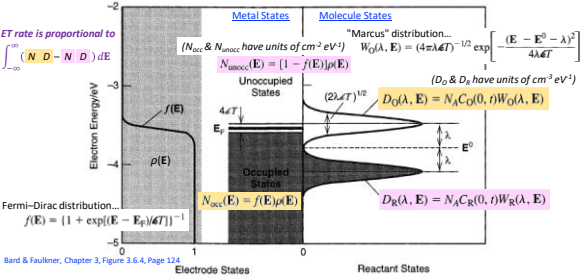## Fermi's (Second) Golden Rule (BRIEFLY) 141

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

k'_j (cm s^{-1})… a velocity!

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

Recall M–H… $k_{ET} = \frac{2\pi}{h}|H_{DA}|^2 \frac{1}{\sqrt{4\pi\lambda_{AB}kT}}\exp\left(-\frac{\Delta G_{AB}^0}{kT}\right)$

Transition probability   *Matrix element for the interaction*   *Density of final states* (DoS)

… divide the DoS term by c_{i,z_o} …

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

frequency factor (s^{-1})

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

proportionality function (cm^3 eV)   applied potential   R. Memming, Chapter 6, Semiconductor Electrochemistry

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

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

energy

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

Marcus–Gerischer Theory (BRIEFLY) 142

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

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

Unoccupied States

$(2\lambda kT)^{1/2}$

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

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

$4kT$ E_F λ E^0 λ

$f(E)$ $\rho(E)$

Occupied States

Fermi–Dirac distribution…
$$f(E) = \{1 + \exp[(E - E_F)/kT]\}^{-1}$$

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

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

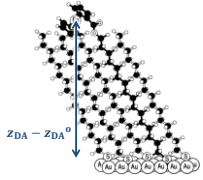Bard & Faulkner, Chapter 3, Figure 3.6.4, Page 124
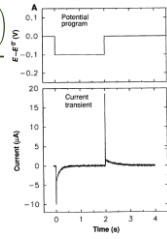
Electrode States   Reactant States

Marcus–Gerischer Theory

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

quantum adiabatic electronic coupling   classical nuclear free-energy dependence

$z_{DA} - z_{DA}{}^o$

... 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

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

Marcus–Gerischer Theory

145

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

Marcus–Gerischer Theory

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

$\lambda = 0.85$ eV

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

Today's Critical Guiding Question

*Since **Marcus–Hush** theory is sufficient to predict all rate constants (with knowledge of only ΔG_{AB}^{o}, 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

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

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

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

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

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

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

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

... assuming a rapidly stirred solution

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

Butler–Volmer equation

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

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

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

(a) $j_0 = 10^{-3}$ A/cm^2,
(b) $j_0 = 10^{-6}$ A/cm^2, (c) $j_0 = 10^{-9}$ A/cm^2

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

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

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

Butler–Volmer equation

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

$\beta < 0.5$ $\beta = 0.5$

$\beta > 0.5$

j, μA/cm²

η, mV

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

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

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

Standard free energy

$O + e$ R

$O + e$ R

$O + e$ R

Reaction coordinate

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"?

$E_{\text{app}} \ll \dfrac{\lambda_{AB}}{2}$

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

System after electron transfer

METAL

Ground state of M−H+H₂O

Ground state of M(e)+H⁺=OH₂

ΔE_0

$\Delta \varepsilon_0$

B   Distance   A

METAL

System before electron transfer

Potential Energy

Are these labels logical?

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

Fermi's (Second) Golden Rule

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

k'_j (cm s⁻¹)... a velocity!

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

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

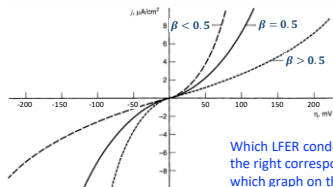Transition probability   Matrix element for the interaction   Density of final states (DoS)

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

frequency factor (s⁻¹)

$k_f = \nu \displaystyle\int_{-\infty}^{\infty} \varepsilon_{\text{red}}(E)W_O(\lambda, E)f(E)\rho(E)dE$
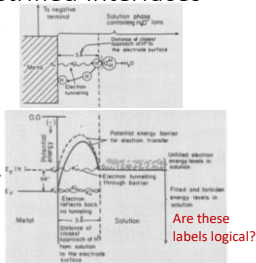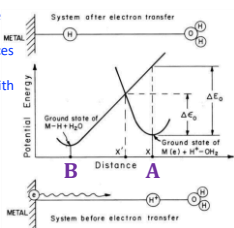
proportionality function (cm³ eV)

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

applied potential

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

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

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

energy

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

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

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

R. Memming, Chapter 6, Semiconductor Electrochemistry

4/27/2023

Marcus–Gerischer Theory

ET rate is proportional to
$$\int_{-\infty}^{\infty} (N_O D_R - N_R D_O)\, dE$$

Metal States | Molecule States

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

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

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

Unoccupied States

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

$(2\lambda kT)^{1/2}$ $D_O(\lambda, E) = N_A C_O(0, t) W_O(\lambda, E)$

$4kT$

E_F

$\rho(E)$

Occupied States

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

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

Fermi–Dirac distribution…
$$f(E) = \{1 + \exp[(E - E_F)/kT]\}^{-1}$$

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

Electrode States   Reactant States

Marcus–Gerischer Theory

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

quantum adiabatic electronic coupling   classical nuclear free-energy dependence

$z_{DA} - z_{DA}^0$

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

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

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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

E^0

λ λ

$D_O(\lambda, E)$ $D_R(\lambda, E)$

$(2\lambda kT)^{1/2}$

normal

E_{app}

$\lambda = 0.85$ eV

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

Marcus–Gerischer Theory

λ = 0.85 eV

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

Marcus–Gerischer Theory

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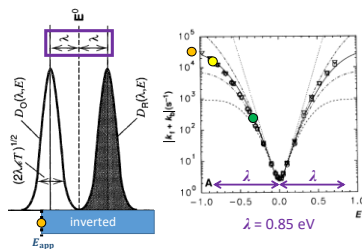
- **But evidence of the inverted region is a little challenging to clearly observe**

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

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

… I wish he had done that!

λ = 0.85 eV

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

Limiting Processes

160

B–V theory
(Current–Overpotential Equation)

M–G theory

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

λ = 0.85 eV
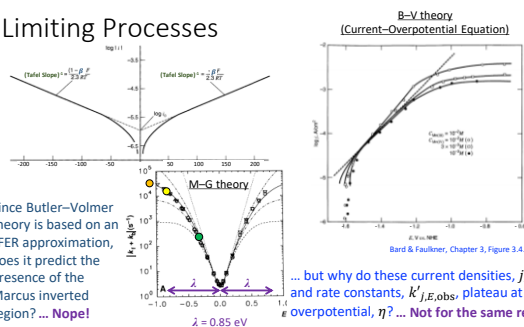
Bard & Faulkner, Chapter 3, Figure 3.4.5, Page 104

… 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!**

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

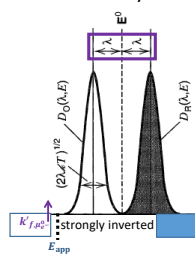- But one cannot alter the driving force, $\Delta G_{AB}°$, by simply changing the electrochemical potential of electrons (e⁻) in the (S)emi(C)onductor working electrode, $\bar{\mu}_{e^-}^{SC}$, through variations in E_{app}, because instead that changes the concentration of e⁻

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

Think solution studies… vary the molecule!

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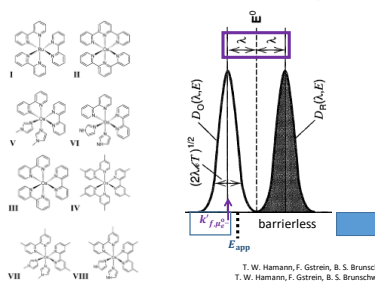
T. W. Hamann, F. Gstrein, B. S. Brunschwig & N. S. Lewis, *J. Am. Chem. Soc.*, **2005**, *127*, 7815–7824
T. W. Hamann, F. Gstrein, B. S. Brunschwig & N. S. Lewis, *J. Am. Chem. Soc.*, **2005**, *127*, 13949–13954

Marcus–Gerischer Theory

λ = 0.67 eV

k_{IET} (cm⁴ s⁻¹)… a second-order rate constant!

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

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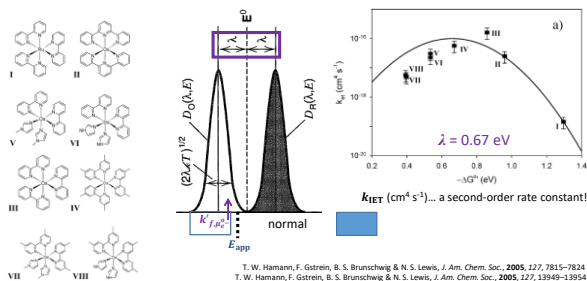
Charge Transfer across Electrified Interfaces

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

Frumkin isotherms

attract   repel

Langmuir isotherm
(ideal thermodynamics)

$\log(c/c_s) + (\mu_{sol} - \mu_{ad})/kT$

* g is a lateral interaction term

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

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): change in the (cath)odic/(an)odic reaction rate expressed as a change in the activation free energy as a fraction of E_{app}

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

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

$$TS_{an}^{-1} = \left(\frac{d(\log j_E)}{d\eta}\right)_{an} = \frac{\alpha_{an}F}{2.303RT}$$
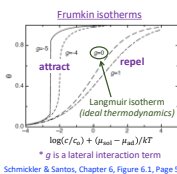
J. O'M. Bockris & Z. Nagy, *J. Chem. Educ.*, **1973**, *50*, 839–843

Rate-Determining Step (RDS)

$$D + A \rightleftharpoons D^+ + A^-$$

Poisson's Equation (from Gauss's law)

$$\frac{\partial^2 \phi(x)}{\partial x^2} = -\frac{\rho}{\varepsilon} \qquad E = -\frac{\partial \phi(x)}{\partial x}$$
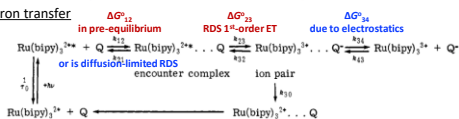
$$\phi(r) = \frac{q}{4\pi \varepsilon r}$$
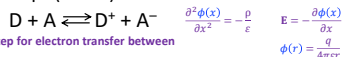
But wait... is this the elementary reaction step for electron transfer between a (D)onor and an (A)cceptor in solution? **Nope!**

Ground-state electron transfer

ΔG_e° due to entropy/sterics ΔG_p° due to entropy/sterics

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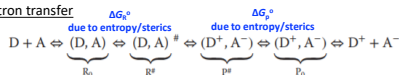
Excited-state electron transfer

ΔG°_{12} in pre-equilibrium ΔG°_{23} RDS 1st-order ET ΔG°_{34} due to electrostatics

$$Ru(bipy)_3^{2+}* + Q \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} Ru(bipy)_3^{2+}* \cdots Q \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} Ru(bipy)_3^{3+} \cdots Q^- \underset{k_{43}}{\overset{k_{34}}{\rightleftharpoons}} Ru(bipy)_3^{3+} + Q^-$$

or is diffusion-limited RDS

encounter complex   ion pair

$\frac{1}{\tau_0}$ $h\nu$ k_{10}

$$Ru(bipy)_3^{2+} + Q \longleftarrow Ru(bipy)_3^{2+}* \cdots Q$$

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

$$D + A \overset{1}{\rightleftharpoons} (D, A) \overset{2}{\rightleftharpoons} (D^+, A^-) \overset{3}{\rightleftharpoons} D^+ + A^-$$
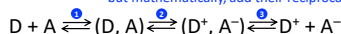
... so how does one determine the **observed** rate constant for 3 reactions **in series**?

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

... 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...

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

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

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

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 $k_{f,\text{obs}} = k_{1f}$ then?… not always…

$$D + A \overset{①}{\rightleftharpoons} (D, A) \overset{②}{\rightleftharpoons} (D^+, A^-) \overset{③}{\rightleftharpoons} D^+ + A^-$$
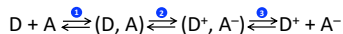
Assume that the middle steps come and go quickly… so each has a small steady-state conc…

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

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

… 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 $k_{f,\text{obs}} = k_{1f}$

… 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): $H^+ + e^- \rightleftharpoons M–H$
T (C): $2\,M–H \rightleftharpoons H_2 + M$

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

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

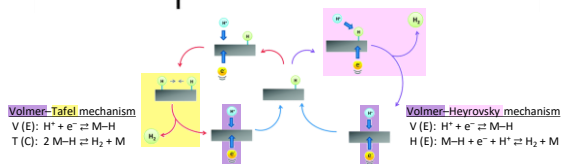S. Trasatti, *J. Electroanal. Chem. Interfacial Electrochem.*, **1972**, *39*, 163–184

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 ele...

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

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

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

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

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

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

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

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

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

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

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

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

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

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