

Lecture #19 of 20+

In conclusion, with the Guoy–Chapman–Stern Model we have a semi-quantitative understanding of this interface with some predictive power...

... but don't forget my questions from the start of this series of lectures on the double layer...

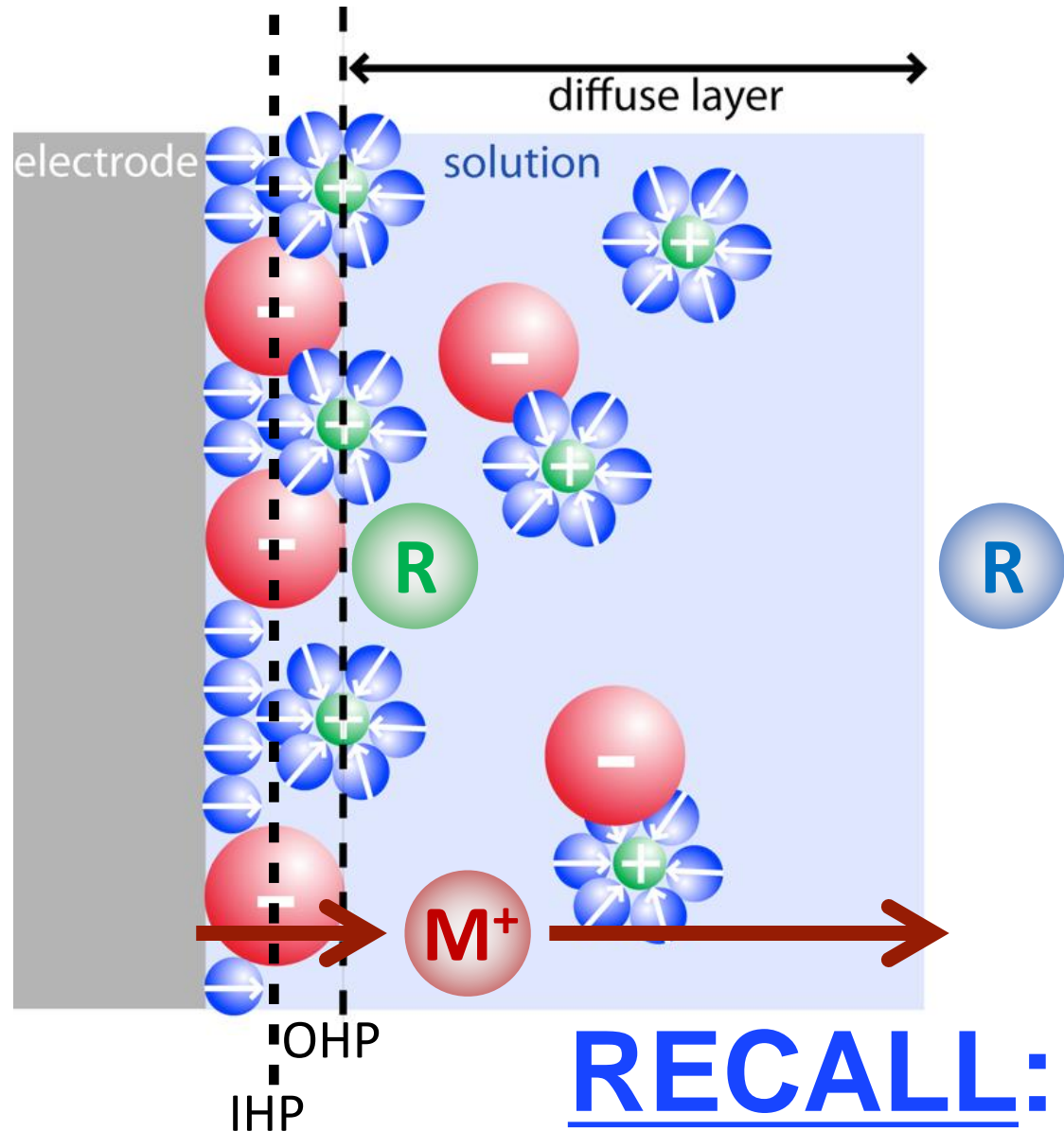
... What is the potential difference between the two sides?

E_{app}

What is the potential difference between one side and near the middle?

$\sim E_{app}/2$

NEW QUESTION: Can anyone explain how a corrosion reaction can be potential dependent when the electron never transfers across the metal|solution interface?



RECALL:

An ion transfers across the double layer... mind = blown, again!

In conclusion, with the Guoy–Chapman–Stern Model we have a semi-quantitative understanding of this interface with some predictive power...

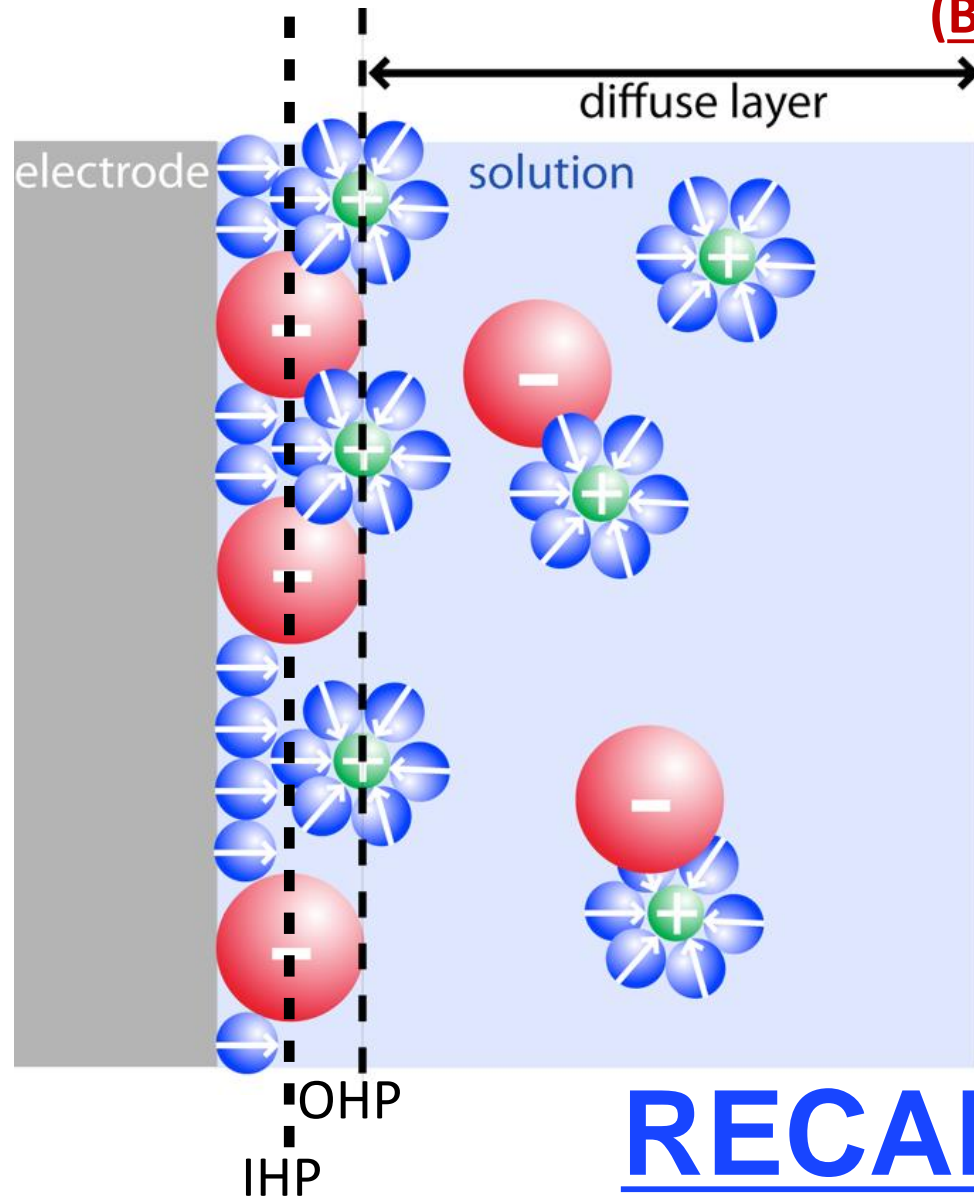
(BRIEFLY)

Now what about starting with this approximate behavior (an active area of research)...

... plus adding in Faradaic charge-transfer reaction kinetics?!?!?!?

... Oh yeah!!! ... Now we're talking!

... still don't forget about the location of the reactants and products within/outside of the double layer during Faradaic charge transfer



RECALL:

Interfacial Charge-Transfer Kinetics

Chapter 3

Q: What's in this set of lectures?

A: B&F Chapter 3 main concepts:

- Sections 3.1 & 3.6: Homogeneous Electron-Transfer (ET) (Arrhenius, Eyring, Transition-State Theory (Activated Complex Theory), Marcus Theory)
- Sections 3.2, 3.3, 3.4 & 3.6: Heterogeneous ET (Butler–Volmer Equation, Tafel Equation, Volcano Plot, Gerischer Theory, Quantum Mechanical Tunneling)
- Section 3.5: Multistep ET Mechanisms

RECALL... since the continuity of mass equation is “better than” the conservation of mass law, and it is highly relevant to electrochemistry and in fact all science and engineering fields, we better know it...

... it is introduced to most undergraduate students studying chemical engineering, materials science, and physics, but only partially to chemists (first half) and mechanical engineers (second half)...

... anyway, here it is for species A along dimension x ... Enjoy!

$$\frac{\partial c_A}{\partial t} = \sum_i R_{A,i} - \frac{\partial N_A}{\partial x}$$

rate of change of the (c)oncentration of species A with respect to (t)ime

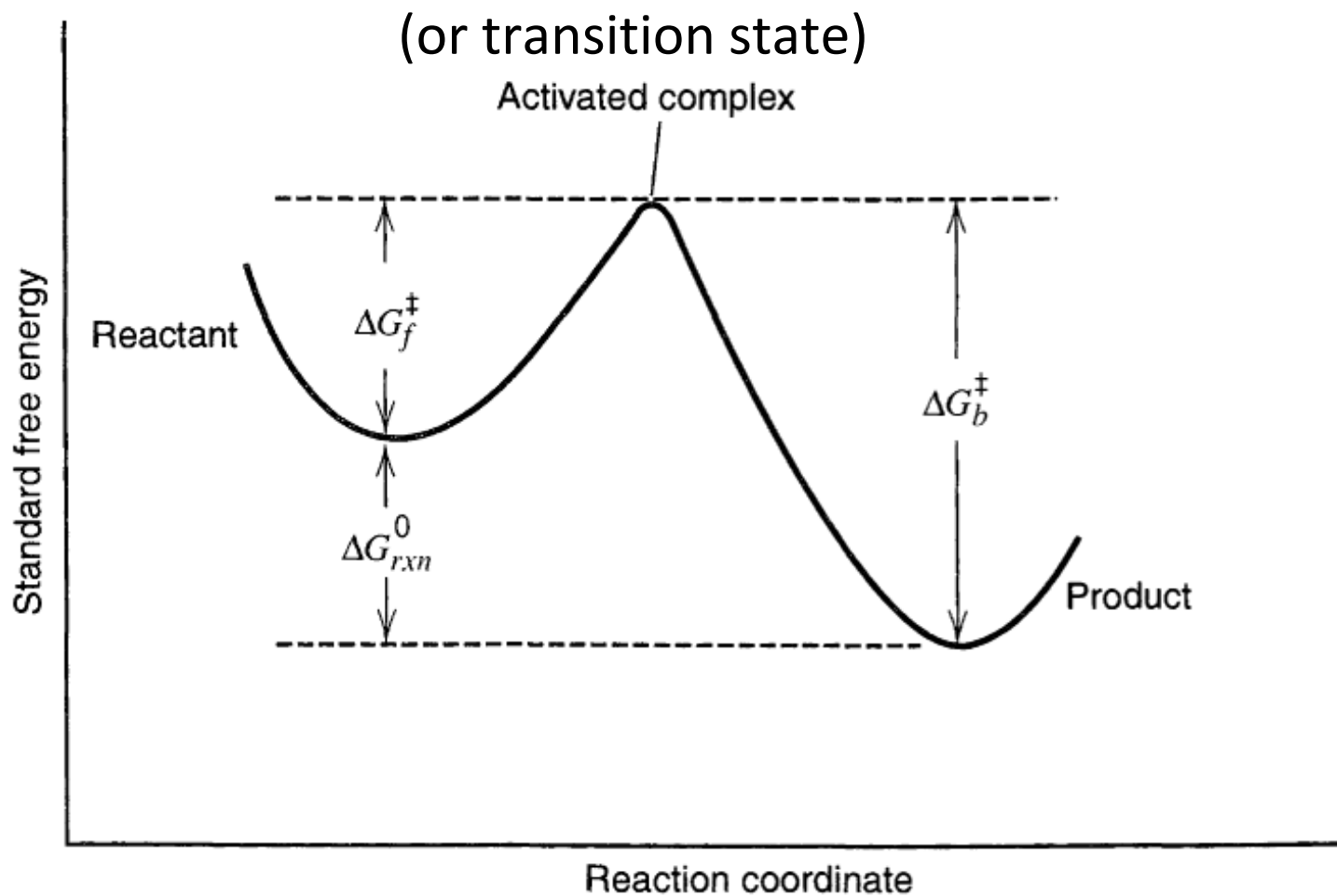
mass action (R)ate laws that effect species A,
e.g. $R_A = k_2[A][B]$

rate of change of the flux (N) of species A with respect to position (x)

... differences in chemical potential, μ_i , drive (R)eactions... differences in electrochemical potential, $\bar{\mu}_i$, drive fluxes (dN/dx)

https://en.wikipedia.org/wiki/Continuity_equation

From transition state theory (TST) (activated complex theory (ACT)), ⁸²⁵ the *standard Gibb's free energy of activation*, ΔG^\ddagger is defined as follows... and electron-transfer reactions exhibit unique behavior...



... Marcus Theory... the idea...

- Has anyone ever told you that the overall thermodynamics of a reaction are not related to the kinetics of the reaction? ... Well, **this is not true for (at least) electron-transfer reactions!**
- What we know
 - **KINETICS**: Kinetics of a reaction are dependent on the activation energy, and temperature, by the empirical Arrhenius equation... and are related to the free energy of the transition state by the Eyring equation and transition-state theory (activated-complex theory):

$$k_{ET} = A e^{-\frac{E_a}{RT}} \quad k_{ET} = \frac{\kappa k_B T}{h} e^{-\frac{\Delta G^\ddagger}{RT}}$$

- **THERMODYNAMICS**: A reaction is spontaneous if the ΔG is negative, and thus $\Delta E (E_{\text{cell}})$ is positive
- What is new?

The kinetics of an electron-transfer reaction (k_{ET}) **are dependent** on the driving force for the overall reaction (i.e. $\Delta G^0 (\Delta E^0, E^0_{\text{cell}})$)
... Marcus Theory (Nobel Prize in Chemistry in 1992)

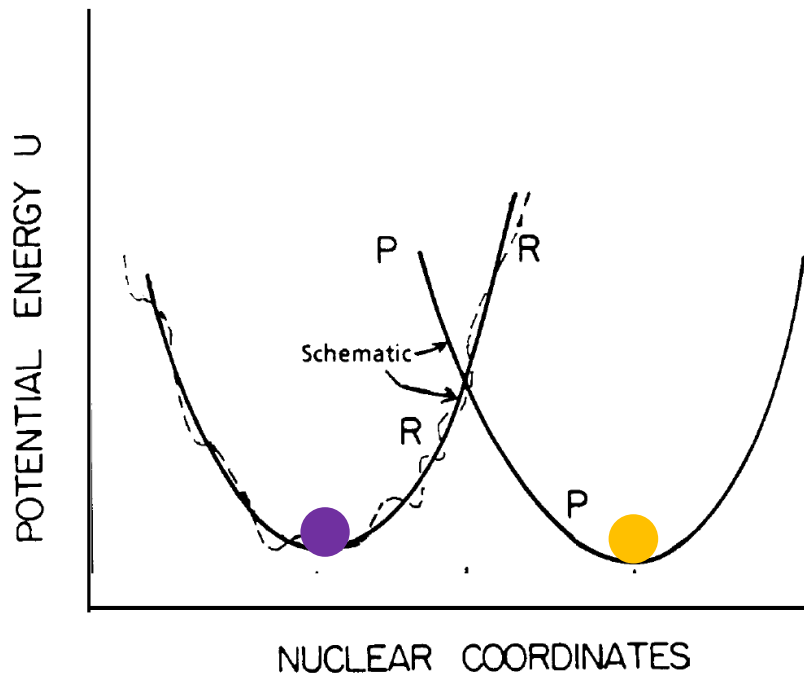


... Marcus Theory... the idea...

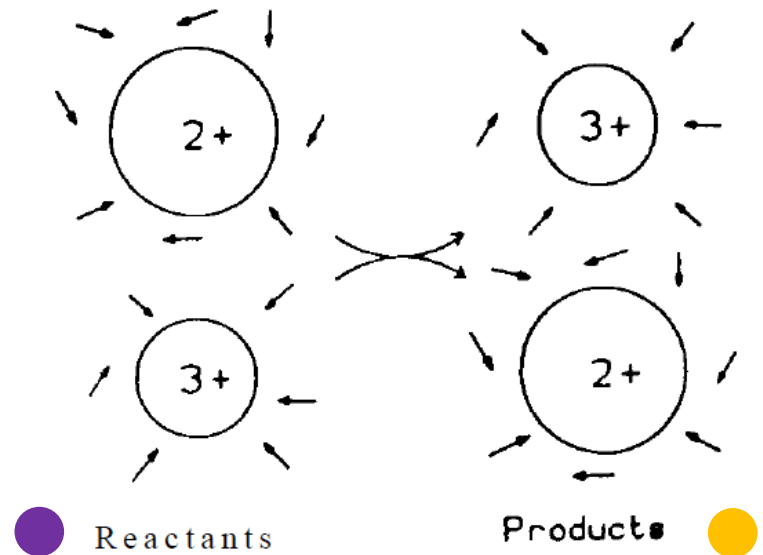
Rudy asked: For an electron-transfer event, how does one satisfy the Franck–Condon principle and the conservation of energy?

- Franck–Condon principle: Nuclei are fixed during electron-transfer between orbitals (IUPAC Gold Book); Born–Oppenheimer approximation is relevant

Potential Energy Surfaces, Profile



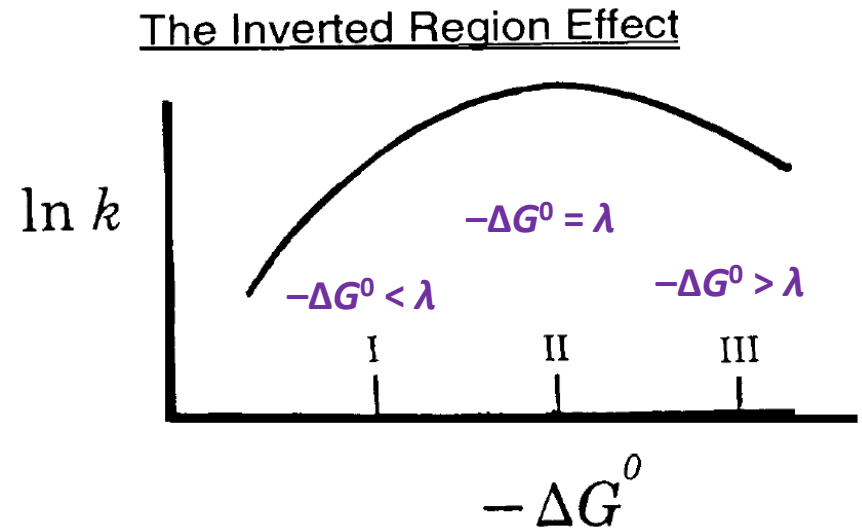
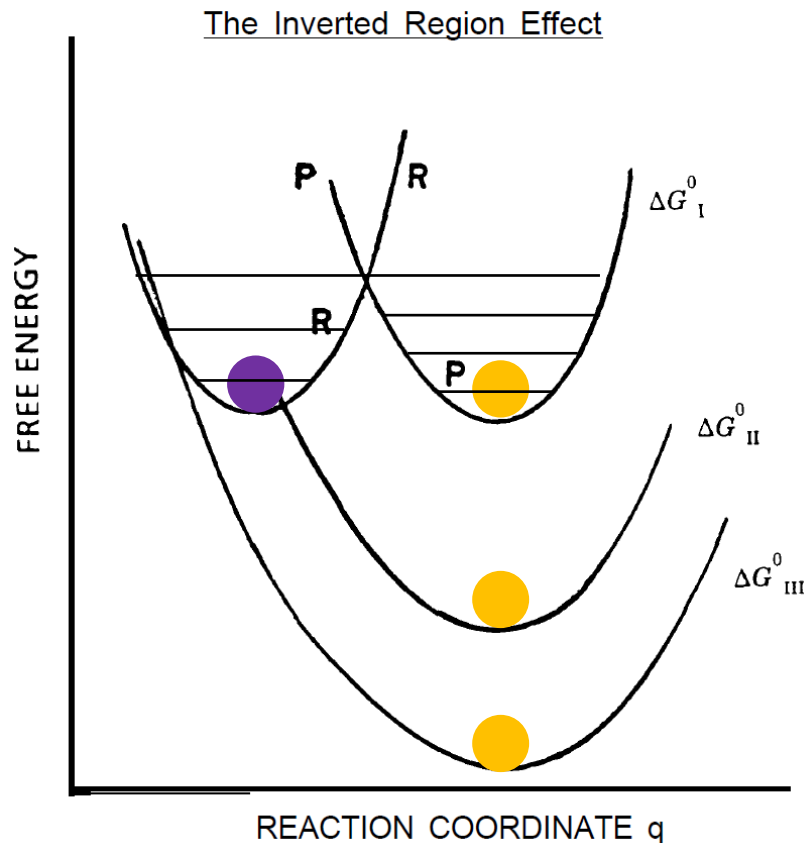
Electron Transfer in Solution



... Marcus Theory... the idea...

- Minor assumptions to go from internal (potential) energy to free energy ($\Delta G = \Delta H - T\Delta S$)
- Three regions of electron transfer: (I) Normal, (II) Barrierless, (III) Inverted

The nuclear reorganization energy, λ , is the free energy required to reorganize the solvent (outer) and bonds (inner) when the electron moves from the reactant to the product potential-energy surface, while at the nuclear arrangement of the reactant (and $\Delta G^0 = 0$)

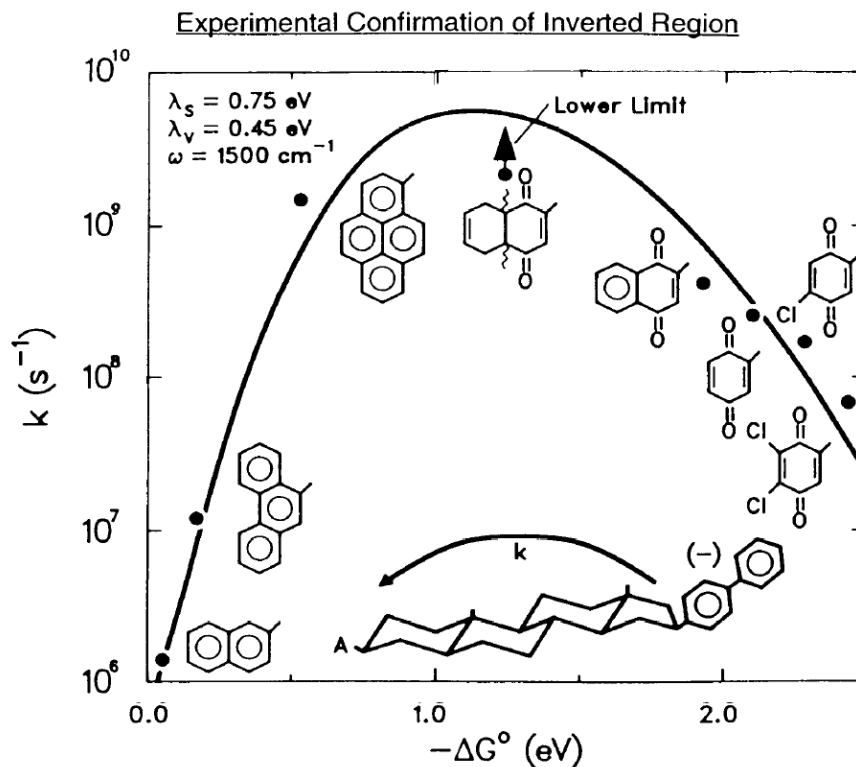


$$k_{et} = \frac{2\pi}{\hbar} |H_{AB}|^2 \frac{1}{\sqrt{4\pi\lambda k_b T}} \exp\left(-\frac{(\lambda + \Delta G^0)^2}{4\lambda k_b T}\right)$$

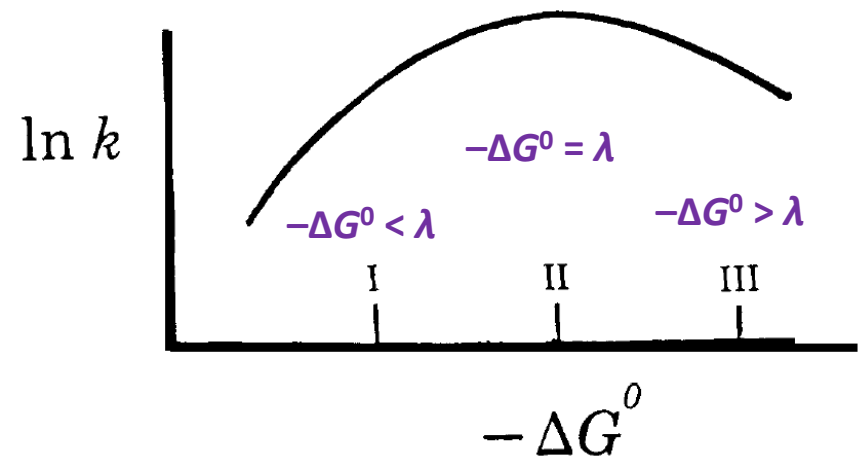
... Marcus Theory... **Experimental Confirmation!**

- Minor assumptions to go from internal (potential) energy to free energy ($\Delta G = \Delta H - T\Delta S$)
- Three regions of electron transfer: (I) Normal, (II) Barrierless, (III) Inverted

The nuclear reorganization energy, λ , is the free energy required to reorganize the solvent (outer) and bonds (inner) when the electron moves from the reactant to the product potential-energy surface, while at the nuclear arrangement of the reactant (and $\Delta G^0 = 0$)



The Inverted Region Effect



$$k_{et} = \frac{2\pi}{\hbar} |H_{AB}|^2 \frac{1}{\sqrt{4\pi\lambda k_b T}} \exp\left(-\frac{(\lambda + \Delta G^0)^2}{4\lambda k_b T}\right)$$

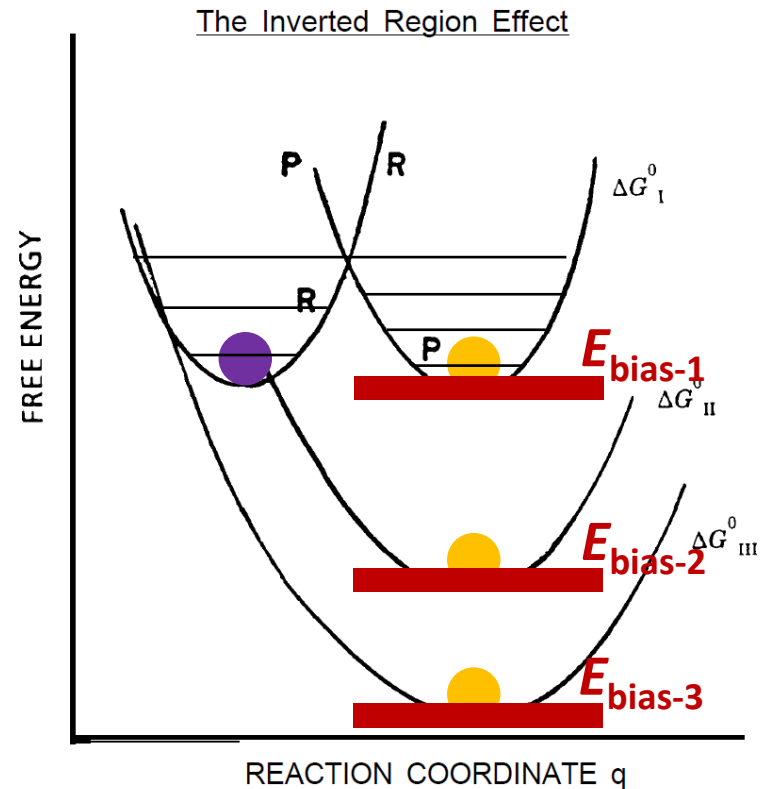
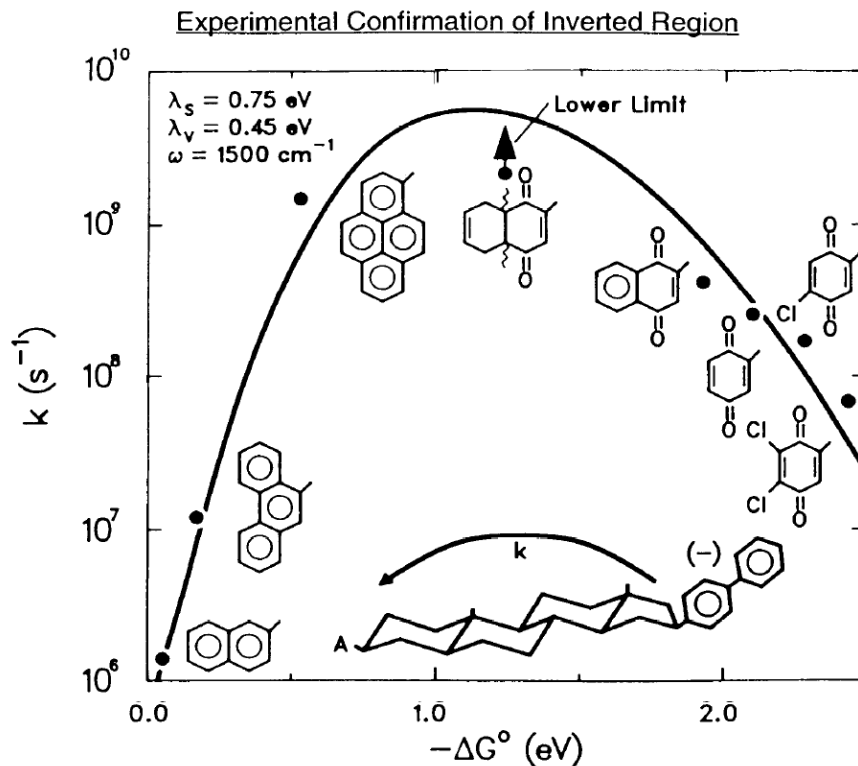
Closs & Miller, *Science*, 1988, 240, 440

http://www.nobelprize.org/nobel_prizes/chemistry/laureates/1992/marcus-lecture.pdf

... Marcus Theory... Experimental Confirmation!

- Minor assumptions to go from internal (potential) energy to free energy ($\Delta G = \Delta H - T\Delta S$)
- Three regions of electron transfer: (I) Normal, (II) Barrierless, (III) Inverted

Foreshadowing...



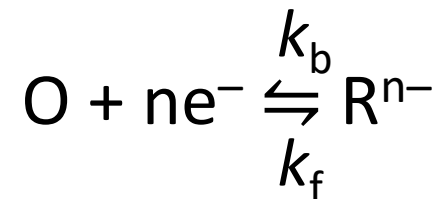
Closs & Miller, *Science*, 1988, 240, 440

http://www.nobelprize.org/nobel_prizes/chemistry/laureates/1992/marcus-lecture.pdf

Electrochemical kinetics:

The Butler–Volmer Reaction (current as a function of potential)

Derivation... start with the generic reaction:



the rate of the forward and backward reactions are:

$$v_f = k_f C_{\text{O}}(0, t) = \frac{-i_c}{nFA}$$

$$v_b = k_b C_{\text{R}}(0, t) = \frac{i_a}{nFA}$$

The units of v are moles $\text{cm}^{-2} \text{s}^{-1}$, and that means k_b , and k_f , have units of...
... cm s^{-1} (a velocity!)



The concentration of R at the electrode surface ($x = 0$) as a function of time

the overall (microscopically reversible) reaction rate, v_{net} , is thus given by the difference between the forward and backward rates:

$$v_{\text{net}} = v_f - v_b = k_f C_{\text{O}}(0, t) - k_b C_{\text{R}}(0, t) = \frac{-i}{nFA}$$

or, in terms of the current:

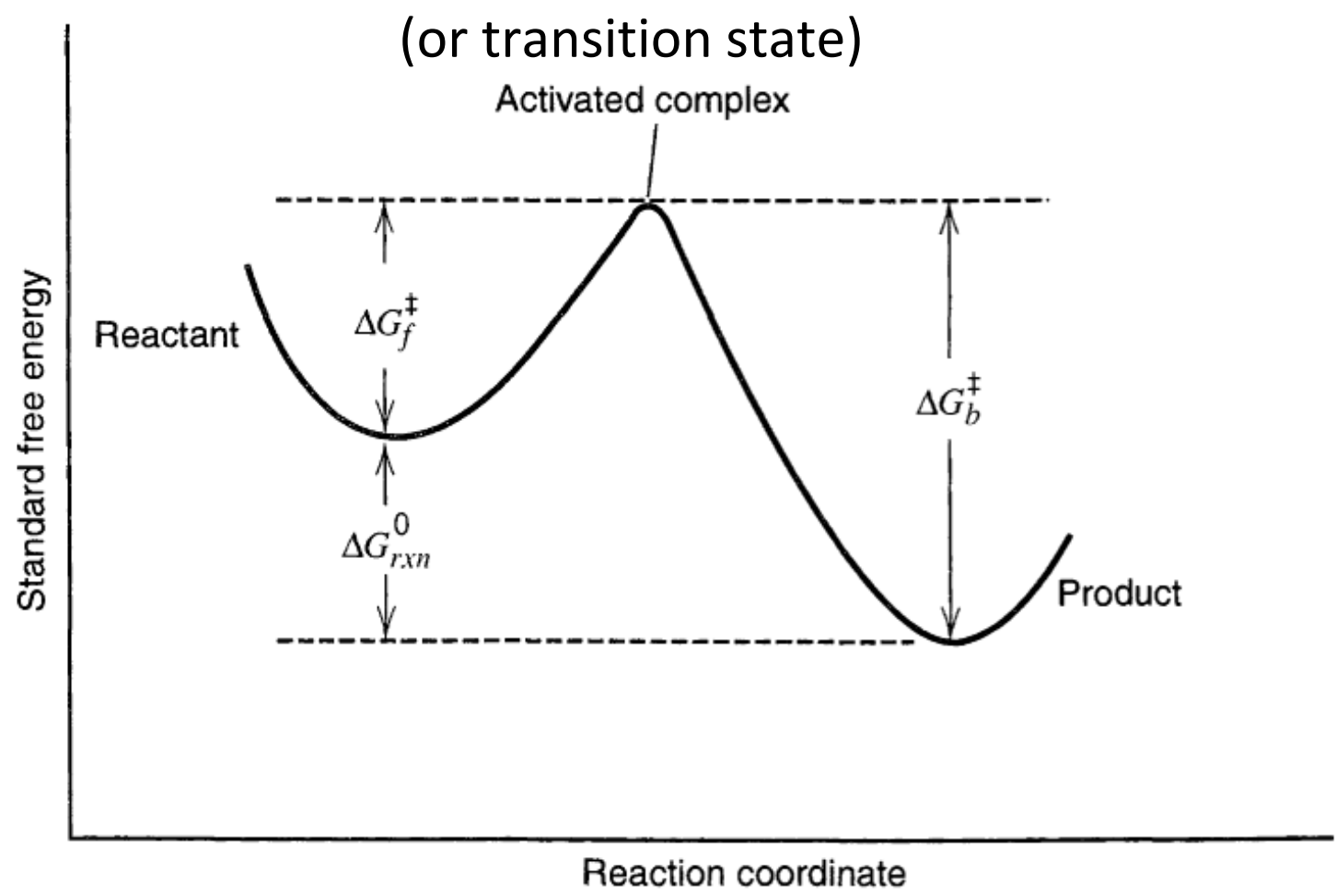
$$i = i_c - i_a = -nFA[k_f C_{\text{O}}(0, t) - k_b C_{\text{R}}(0, t)]$$

(don't forget this... we will come back to it later)

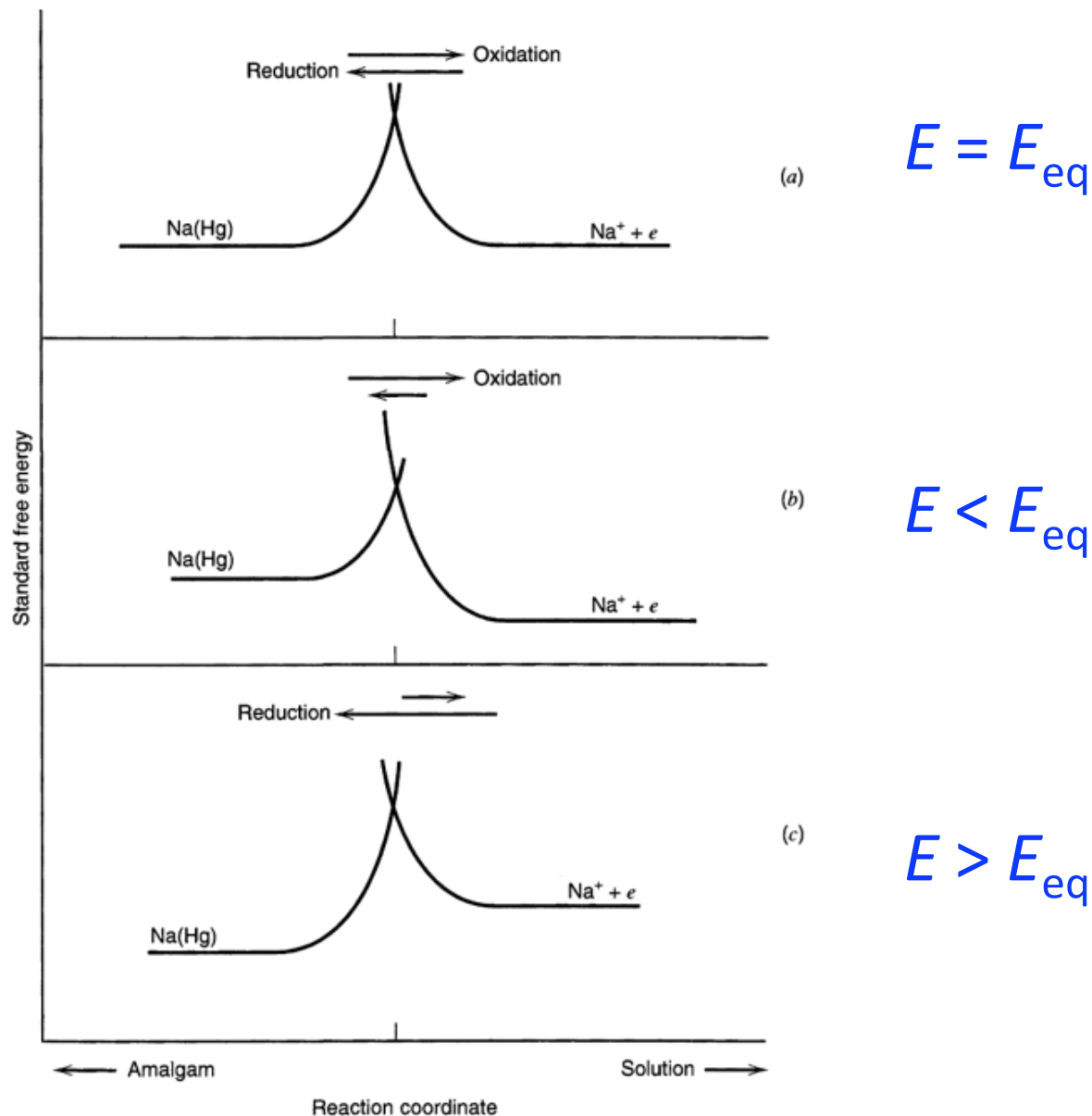
next we need expressions for k_f and k_b in terms of $\eta = (E - E_{\text{eq}})$...

... let's start by writing expressions for k_f and k_b from transition-state theory (TST) using the *standard Gibb's free energy of activation*, ΔG^\ddagger ...

Again, from transition state theory (TST) (activated complex theory (ACT)), the *standard Gibb's free energy of activation*, ΔG^\ddagger is defined as follows...

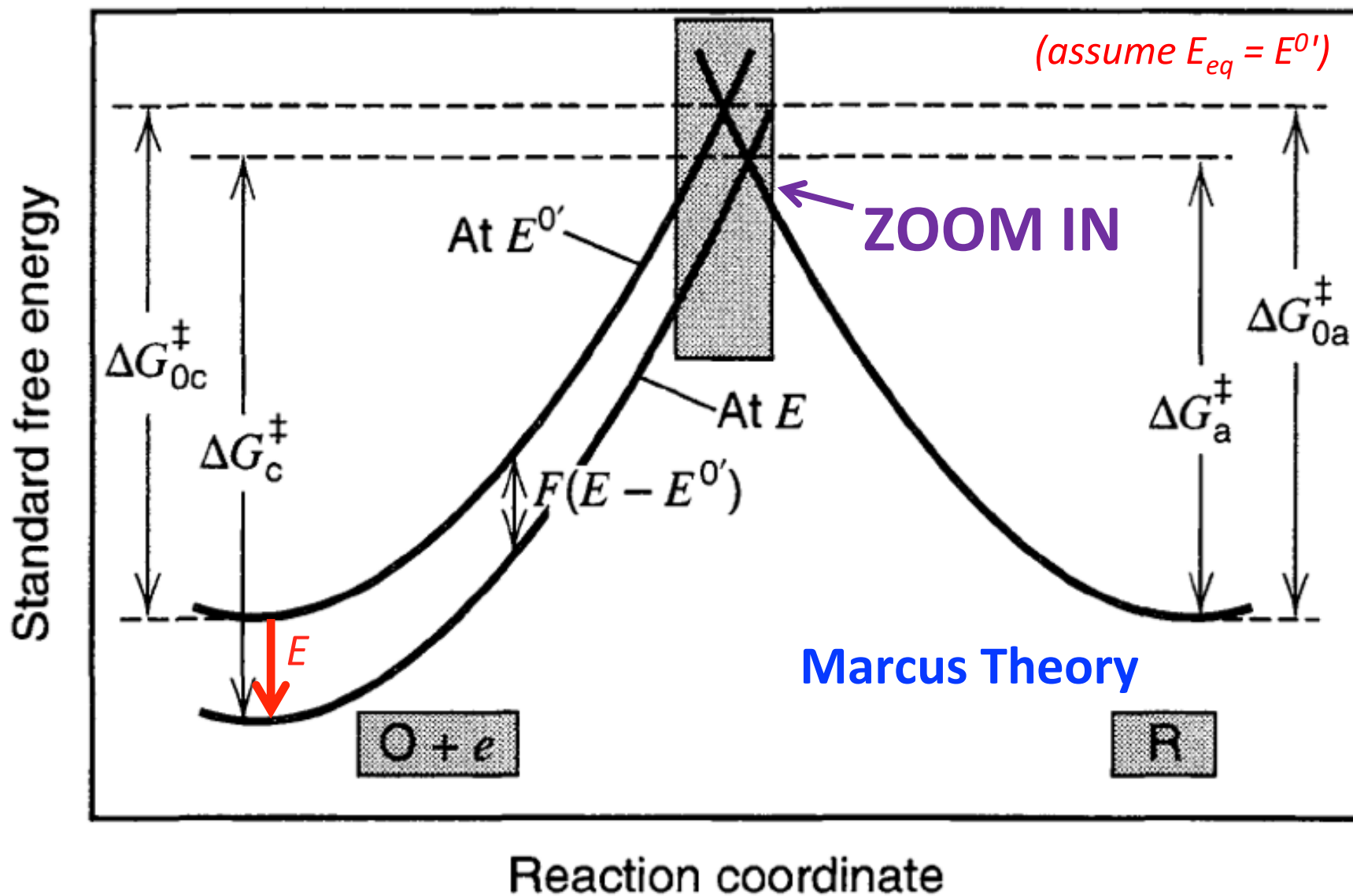


... and here is the effect of electrode potential on the product and reactant free energy (Marcus) curves (**not inverted!**)...



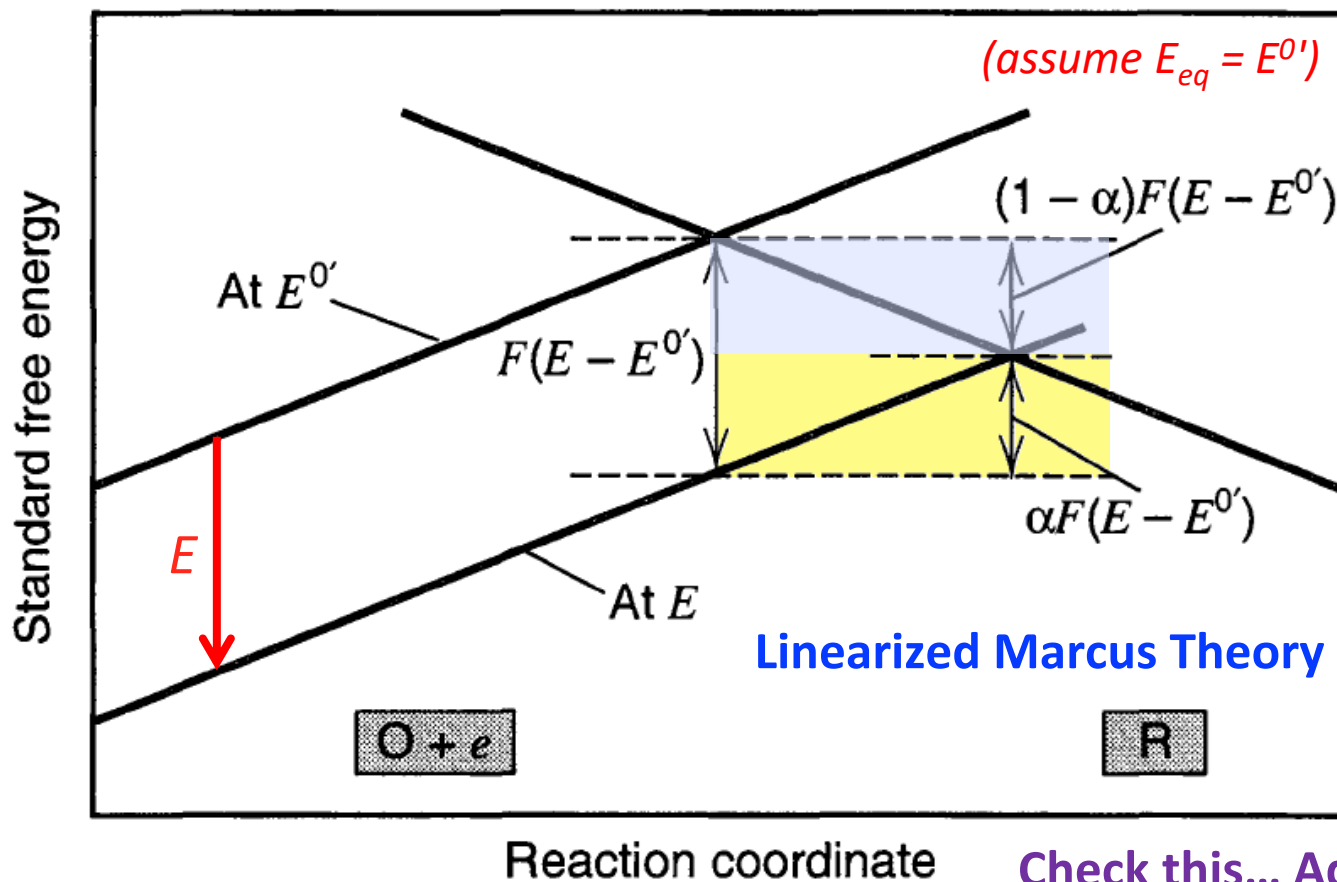
here's a thought experiment that gets us an expression for k_f :

What happens to ΔG_c^\ddagger and ΔG_a^\ddagger when the potential is changed by E ?



here's a thought experiment that gets us an expression for k_f :

What happens to ΔG_c^\ddagger and ΔG_a^\ddagger when the potential is changed by E ?



(1) "O" is stabilized (i.e. lowered) by $F(E - E^{0'})$...

... that is, (3) + (4) = ...

(2) ... and the barrier height decreased by $(1 - \alpha)F(E - E^{0'})$...

... (1) ... Nice!

(3) ... the net change in the *cathodic* barrier is the difference:

$$F(E - E^{0'}) - (1 - \alpha)F(E - E^{0'}) = \alpha F(E - E^{0'})$$

NOTE: It's positive; the *cathodic* barrier became larger (to the right)

(4) ... and the *anodic* barrier just decreased by $(1 - \alpha)F(E - E^{0'})$ (to the left)...

... so after changing the potential from $E^{0'}$ to E :

$$\Delta G_a^\ddagger = \Delta G_{0a}^\ddagger - (1 - \alpha)F(E - E^{0'})$$

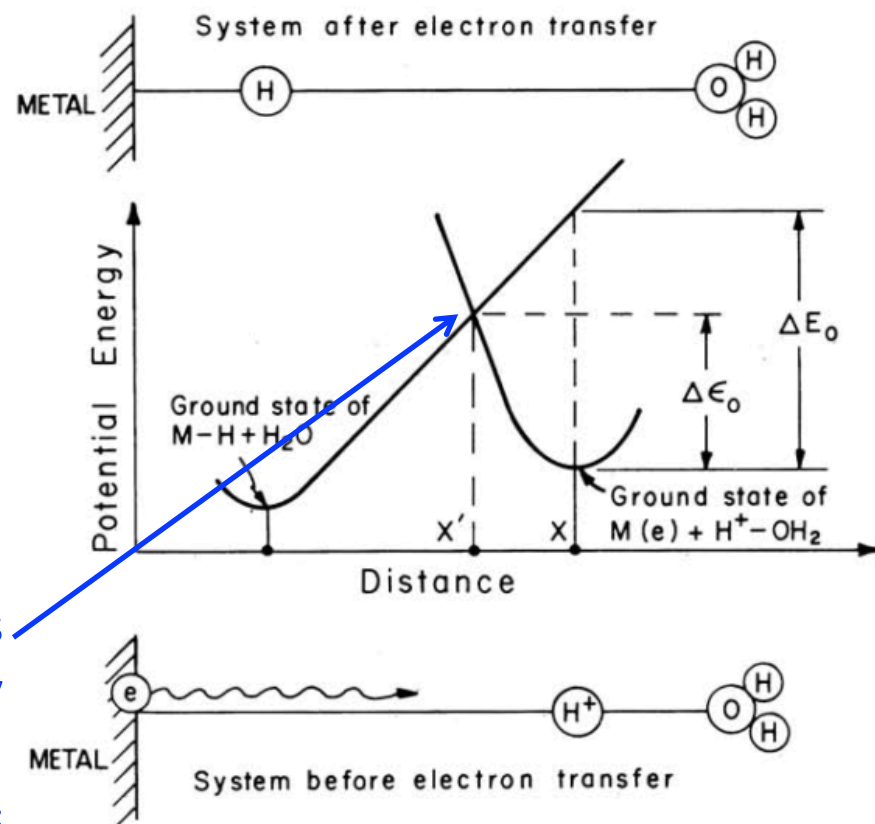
$$\Delta G_c^\ddagger = \Delta G_{0c}^\ddagger + \alpha F(E - E^{0'})$$

ΔG_{0c}^\ddagger is just ΔG_c^\ddagger at $E^{0'} (= E_{eq})$

α is the *transfer coefficient* [0, 1], and is the fraction of $E - E^{0'}$ added to the barrier for the *cathodic* reaction...

... for one-electron-transfer reactions, $\alpha = \beta$, where β is called the *symmetry factor*...

... β is the *fundamental factor*, not α !



... so after changing the potential from $E^{0'}$ to E :

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$$\Delta G_a^\ddagger = \Delta G_{0a}^\ddagger - (1 - \alpha)F(E - E^{0'})$$

$$\Delta G_c^\ddagger = \Delta G_{0c}^\ddagger + \alpha F(E - E^{0'})$$

... substitute these into the Eyring/Arrhenius equations for k_f and k_b ...

$$k_f = A_f \exp\left(\frac{-\Delta G_c^\ddagger}{RT}\right) \quad k_b = A_b \exp\left(\frac{-\Delta G_a^\ddagger}{RT}\right)$$

... to obtain these potential-dependent expressions...

$$k_f = A_f \exp\left(\frac{-\Delta G_{0c}^\ddagger}{RT}\right) \exp\left(\frac{-\alpha F(E - E^{0'})}{RT}\right)$$

$$k_b = A_b \exp\left(\frac{-\Delta G_{0a}^\ddagger}{RT}\right) \exp\left(\frac{(1 - \alpha)F(E - E^{0'})}{RT}\right)$$

When $E = E^{0'} = E_{\text{eq}}$, $C_{\text{O}} = C_{\text{R}}$ and $i = 0$ (equilibrium)... plugging into our expression for the current,

(I told you not to forget this equation!)

$$i = i_{\text{c}} - i_{\text{a}} = -nFA[k_{\text{f}} C_{\text{O}}(0, t) - k_{\text{b}} C_{\text{R}}(0, t)]$$

... results in $k_{\text{f}} = k_{\text{b}} = k^0$, the *standard heterogeneous electron-transfer rate constant*...
 ... and plugging in below leads to just the potential-independent terms and so when $C_{\text{O}} = C_{\text{R}}$, k^0 equals the yellow part...

... and like many textbooks, B&F defines a new variable $f = F/RT$, which makes the expression a little more compact, but likely more difficult to interpret...

potential independent

potential dependent

$$k_{\text{f}} = A_{\text{f}} \exp\left(\frac{-\Delta G_{0c}^{\ddagger}}{RT}\right) \exp\left(\frac{-\alpha F(E - E^{0'})}{RT}\right)$$

$$k_{\text{b}} = A_{\text{b}} \exp\left(\frac{-\Delta G_{0a}^{\ddagger}}{RT}\right) \exp\left(\frac{(1 - \alpha)F(E - E^{0'})}{RT}\right)$$

... and now plug these into our expression for the current:

$$i = i_c - i_a = -nFA[k_f C_O(0, t) - k_b C_R(0, t)]$$

... and so using f , and k^0 for the yellow part ($\Delta G_{0c}^\ddagger = \Delta G_{0a}^\ddagger$, only when $C_O = C_R$), we can write even more compact expressions for k_f and k_b ...

$$k_f = k^0 \exp[-\alpha f (E - E^{0'})]$$

$$k_b = k^0 \exp[(1 - \alpha)f (E - E^{0'})]$$

$$k_f = A_f \exp\left(\frac{-\Delta G_{0c}^\ddagger}{RT}\right) \exp\left(\frac{-\alpha F (E - E^{0'})}{RT}\right)$$

$$k_b = A_b \exp\left(\frac{-\Delta G_{0a}^\ddagger}{RT}\right) \exp\left(\frac{(1 - \alpha)F (E - E^{0'})}{RT}\right)$$

... and now plug these into our expression for the current:

$$i = i_c - i_a = -nFA[k_f C_O(0, t) - k_b C_R(0, t)]$$

$$i = -FAk^0 \left[C_O(0, t)e^{-\alpha f(E - E^{0'})} - C_R(0, t)e^{(1-\alpha)f(E - E^{0'})} \right]$$

... this is our first important result, called the *Current–Potential Characteristic*, and it is the master equation of *Butler–Volmer kinetics* from which all other electron-transfer models are obtained...

... and now plug these into our expression for the current:

$$i = i_c - i_a = -nFA[k_f C_O(0, t) - k_b C_R(0, t)]$$

$$i = -FAk^0 \left[C_O(0, t) e^{-\alpha f(E - E^{0'})} - C_R(0, t) e^{(1-\alpha)f(E - E^{0'})} \right]$$

↓ replace $(E - E^{0'})$ with $\eta = (E - E_{eq})$...
 ... and i_0 (B&F, pp. 98–99) $i_0 = FAk^0 C_O^{*(1-\alpha)} C_R^{*\alpha}$

$$i = -i_0 \left[\frac{C_O(0, t)}{C_O^*} e^{-\alpha f\eta} - \frac{C_R(0, t)}{C_R^*} e^{(1-\alpha)f\eta} \right]$$

the Current–Overpotential Equation,
 which clearly includes effects due to mass transfer

... and now plug these into our expression for the current:

$$i = i_c - i_a = -nFA[k_f C_O(0, t) - k_b C_R(0, t)]$$

$$i = -FAk^0 \left[C_O(0, t) e^{-\alpha f(E - E^{0'})} - C_R(0, t) e^{(1-\alpha)f(E - E^{0'})} \right]$$

↓ replace $(E - E^{0'})$ with $\eta = (E - E_{eq})$...
 ... and i_0 (B&F, pp. 98–99) $i_0 = FAk^0 C_O^{*(1-\alpha)} C_R^{*\alpha}$

$$i = -i_0 \left[\frac{C_O(0, t)}{C_O^*} e^{-\alpha f\eta} - \frac{C_R(0, t)}{C_R^*} e^{(1-\alpha)f\eta} \right]$$

↓ eliminate effects due to mass transfer...
 ... stir well in the bulk... or pass a small
 current... or use
 surface-adsorbed
 species!

Butler–Volmer Equation:
$$i = -i_0 \left[e^{-\alpha f\eta} - e^{(1-\alpha)f\eta} \right]$$

The Butler–Volmer Equation was first derived by Max Volmer in a paper published in 1930

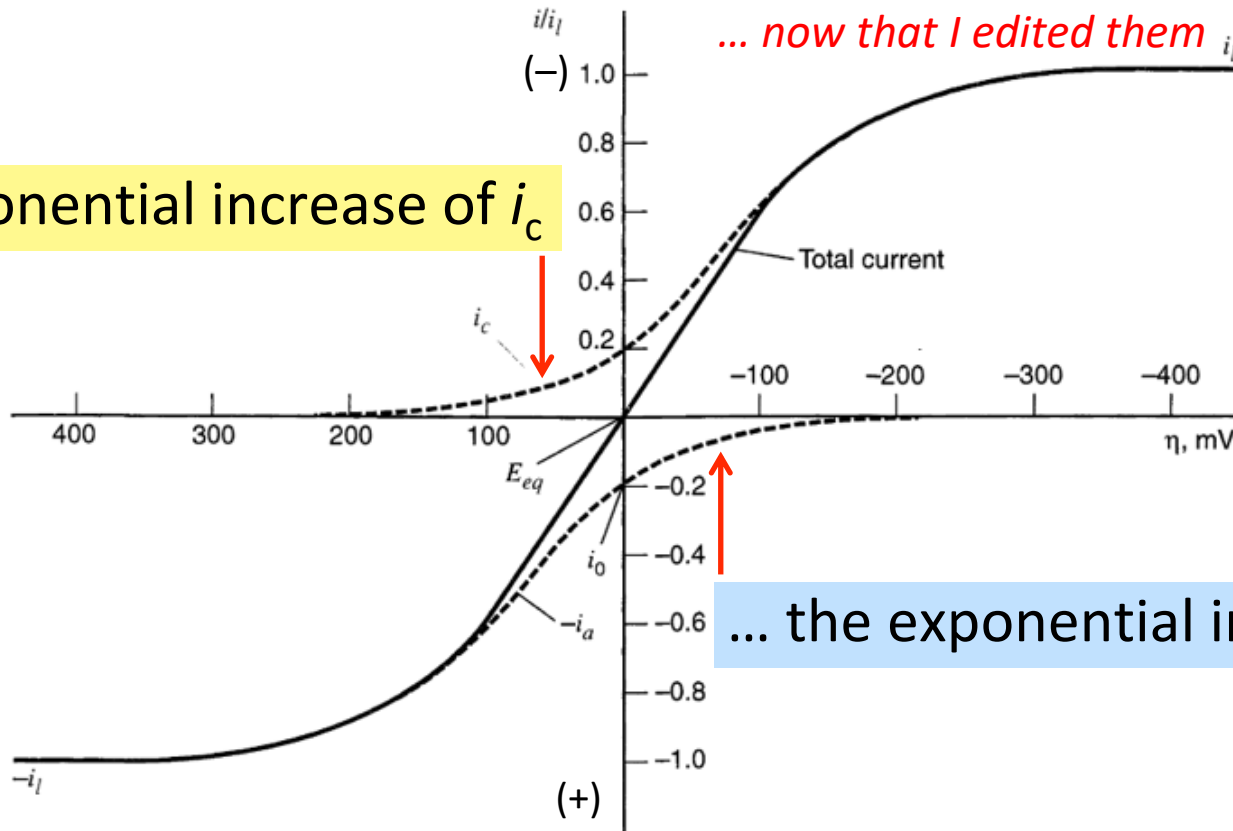


http://en.wikipedia.org/wiki/Max_Volmer

What do these equations predict?

Note: These quadrants are flipped...
... but at least they are (-, -) and (+, +)...
... now that I edited them

the exponential increase of i_c



... the exponential increase of i_a

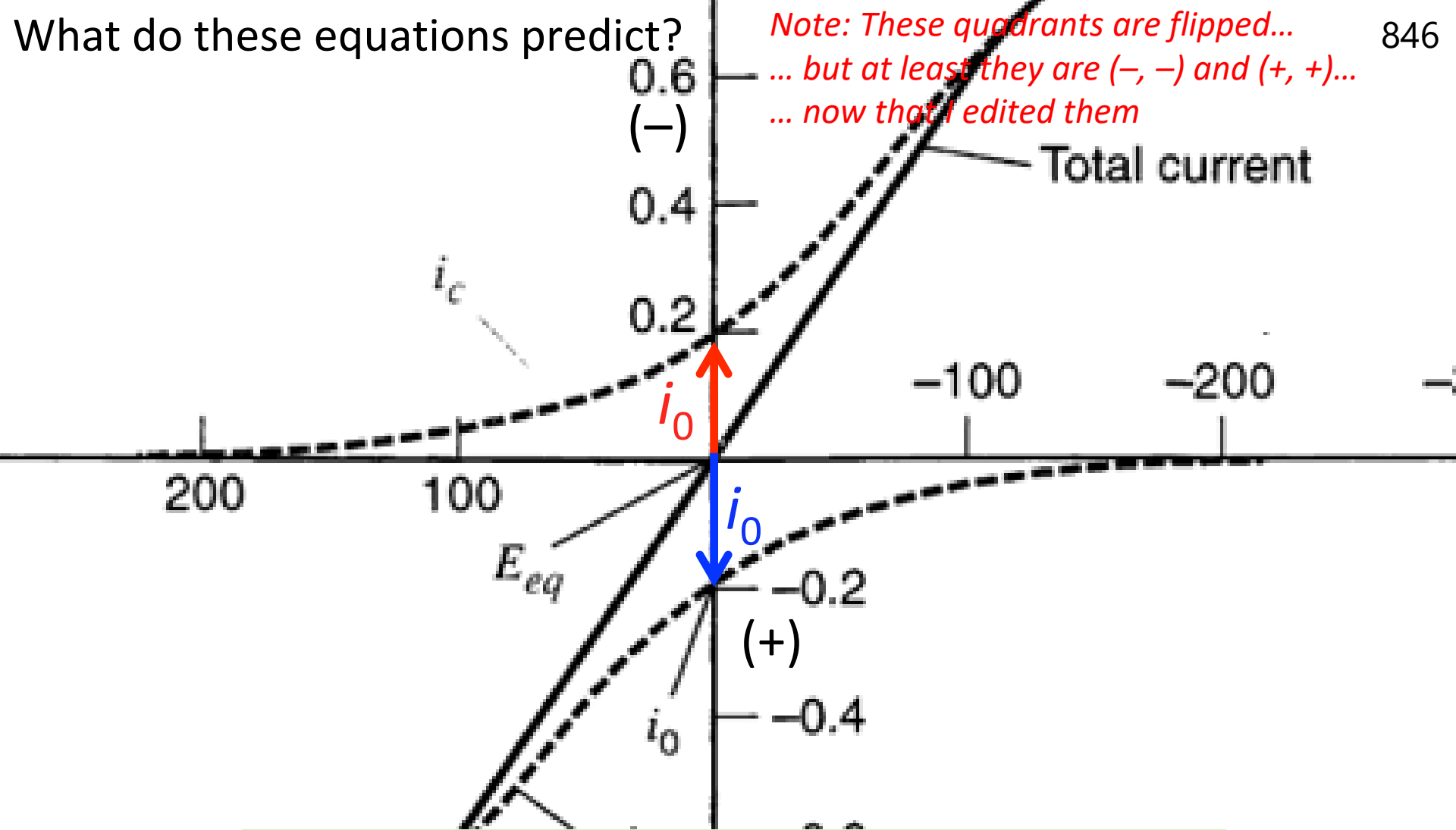
Figure 3.4.1 Current-overpotential curves for the system $O + e \rightleftharpoons R$ with $\alpha = 0.5$, $T = 298$ K, $i_{l,c} = -i_{l,a} = i_l$ and $i_0/i_l = 0.2$. The dashed lines show the component currents i_c and i_a .

$$i = -i_0 \left[\frac{C_O(0, t)}{C_O^*} e^{-\alpha f \eta} - \frac{C_R(0, t)}{C_R^*} e^{(1-\alpha) f \eta} \right]$$

the Current-Overpotential Equation

What do these equations predict?

Note: These quadrants are flipped...
... but at least they are (-, -) and (+, +)...
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$$i = -i_0 \left[\frac{C_O(0, t)}{C_O^*} e^{-\alpha f \eta} - \frac{C_R(0, t)}{C_R^*} e^{(1-\alpha) f \eta} \right]$$

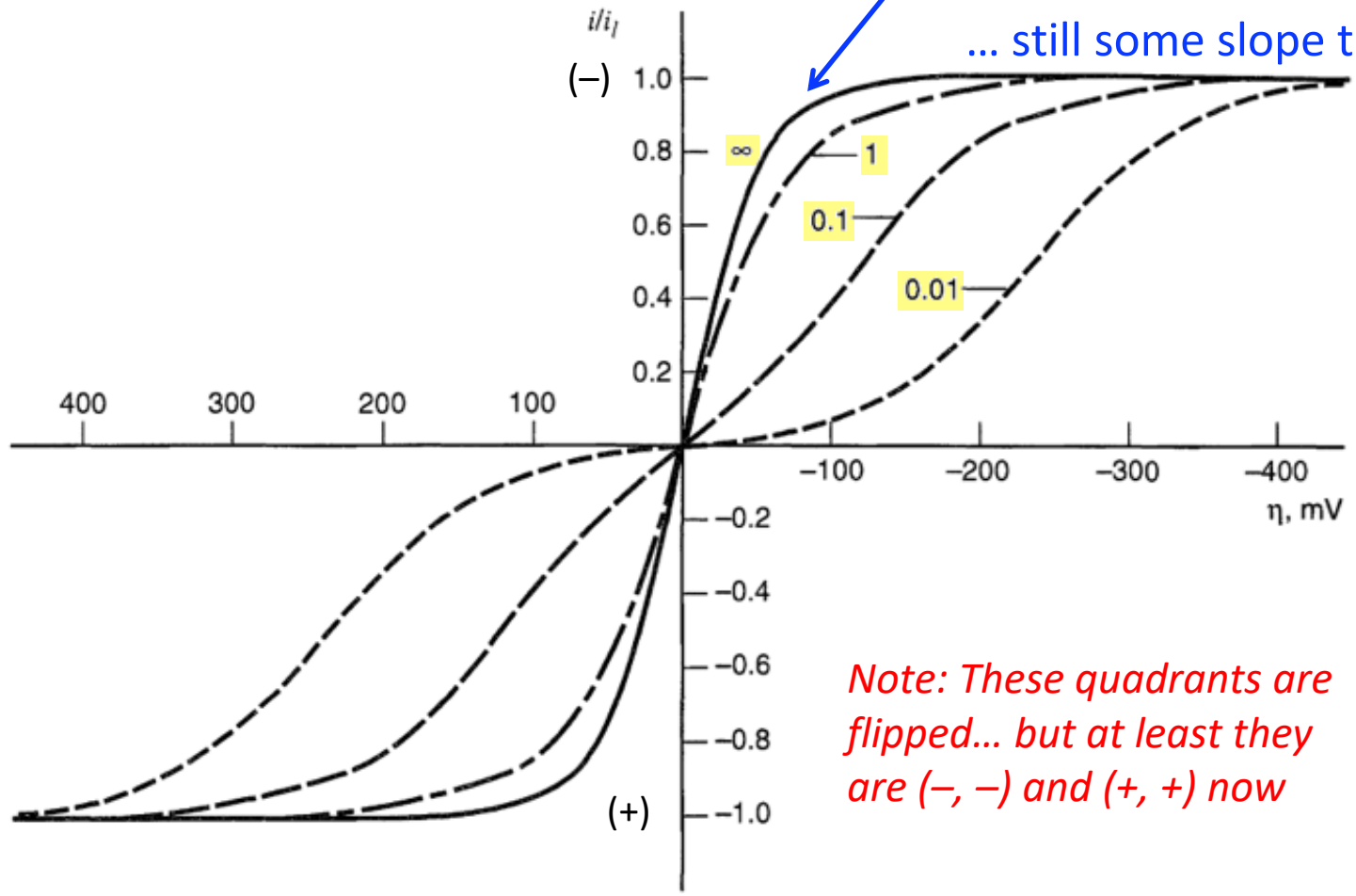
the Current-Overpotential Equation

(SKIPPED)

... a challenge in all types of kinetic analyses is making the mass-transfer-limited current, i_l , large enough so that a *kinetically-controlled reaction rate is observed*...

This looks familiar...

... mass transfer only
... still some slope to the data



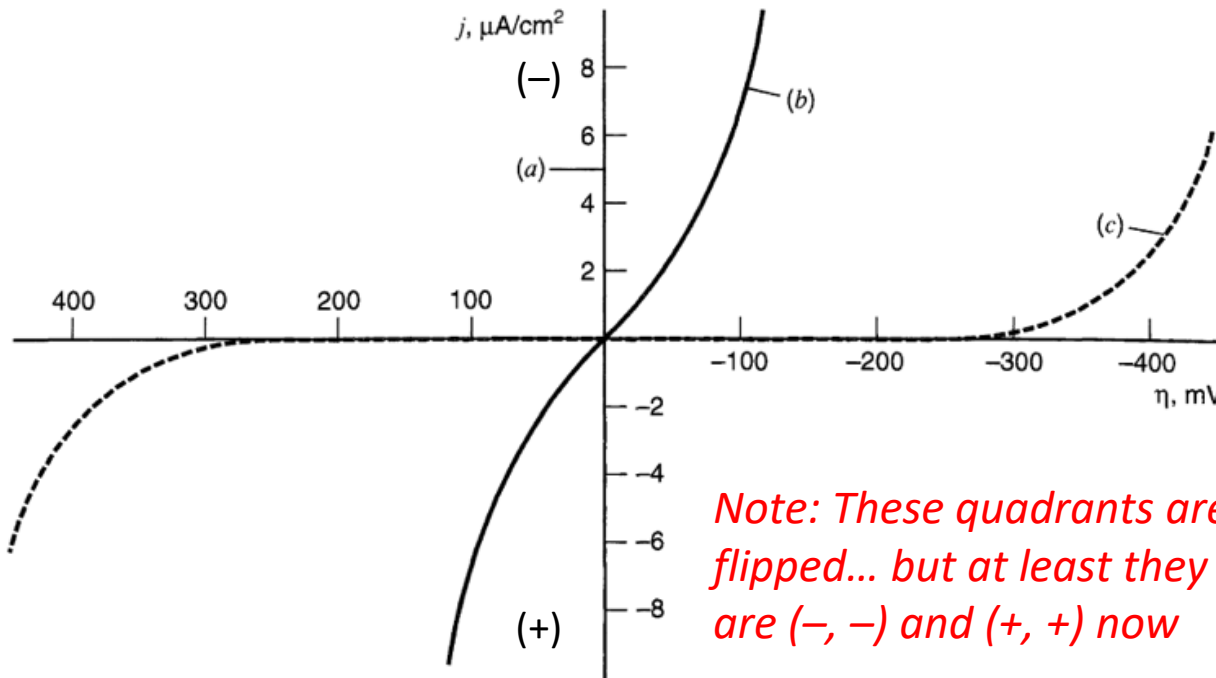
Note: These quadrants are flipped... but at least they are (-, -) and (+, +) now

Figure 3.4.6 Relationship between the activation overpotential and net current demand relative to the exchange current. The reaction is $O + e \rightleftharpoons R$ with $\alpha = 0.5$, $T = 298$ K, and $i_{l,c} = -i_{l,a} = i_l$. Numbers by curves show i_0/i_l .

... if effects due to mass transfer can be neglected (by rapidly stirring ⁸⁴⁸ the bulk solution **or using a UME**, as examples), then the Butler-Volmer Equation is valid:

$$i = -i_0 \left[e^{-\alpha f \eta} - e^{(1-\alpha) f \eta} \right]$$

*i*₀ (*j*₀) is called the exchange current (density) and is the current that is *equal and opposite* at an electrode at equilibrium (think microscopic reversibility)...



Note: These quadrants are flipped... but at least they are (-, -) and (+, +) now

... it is the most convenient indicator of the kinetic facility of an electrochemical reaction

Figure 3.4.2 Effect of exchange current density on the activation overpotential required to deliver net current densities. (a) $j_0 = 10^{-3} \text{ A}/\text{cm}^2$ (curve is indistinguishable from the current axis), (b) $j_0 = 10^{-6} \text{ A}/\text{cm}^2$, (c) $j_0 = 10^{-9} \text{ A}/\text{cm}^2$. For all cases the reaction is $\text{O} + e \rightleftharpoons \text{R}$ with $\alpha = 0.5$ and $T = 298 \text{ K}$.

(SKIPPED)

j_0 can vary by up to twenty orders of magnitude! Consider just one reaction: proton reduction (H_2 evolution)...

Table 1. Exchange current densities of the hydrogen evolution/anodic oxidation reaction at different electrode materials in aqueous 1 N H_2SO_4 solution at ambient temperature

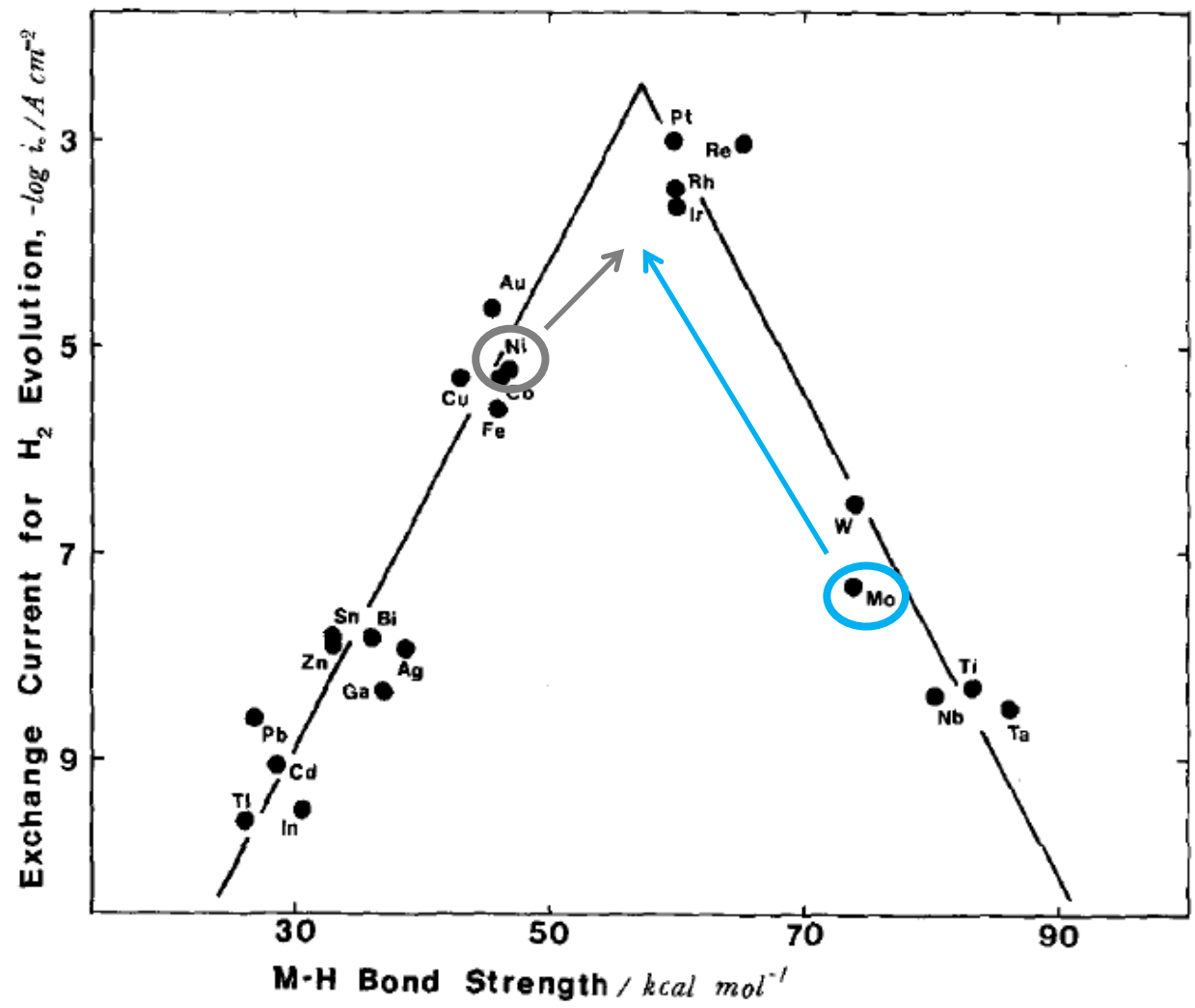
Metal	$i_0/A\text{ cm}^{-2}$
Palladium, Pd	1.0×10^{-3}
Platinum, Pt	8.0×10^{-4}
Rhodium, Rh	2.5×10^{-4}
Iridium, Ir	2.0×10^{-4}
Nickel, Ni	7.0×10^{-6}
Gold, Au	4.0×10^{-6}
Tungsten, W	1.3×10^{-6}
Niobium, Nb	1.5×10^{-7}
Titanium, Ti	7.0×10^{-8}
Cadmium, Cd	1.5×10^{-11}
Manganese, Mn	1.3×10^{-11}
Thallium, Tl	1.0×10^{-11}
Lead, Pb	1.0×10^{-12}
Mercury, Hg	0.5×10^{-13}

$10^{10}!$

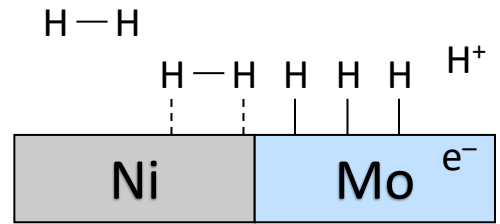
To test materials in this table below Pt, do not use a CE made of Pt, because in acid PtO_x dissolves!

Sabatier Principle and Volcano plots for, for example, proton reduction (H₂ evolution)...

(SKIPPED)

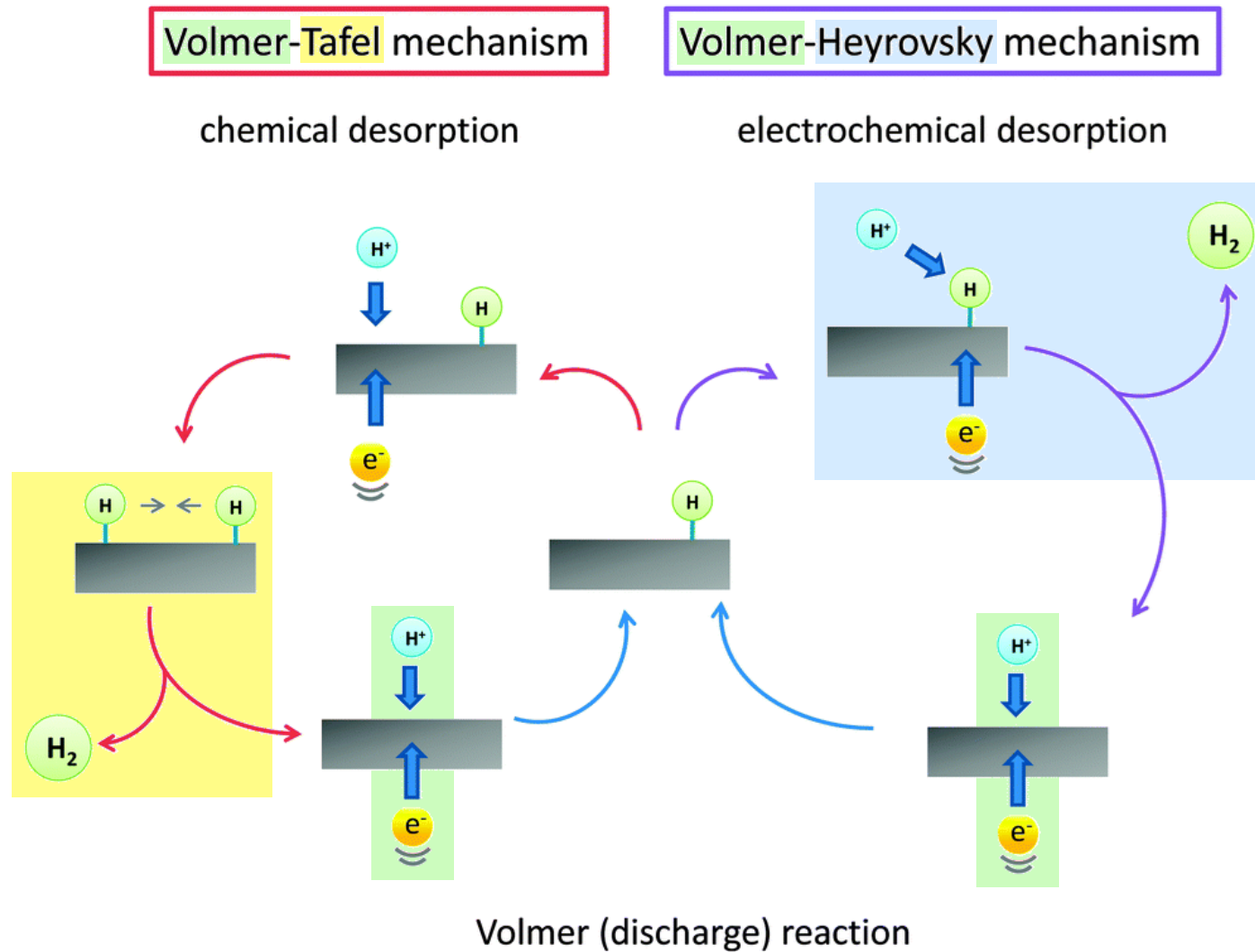


“Spillover”
(synergism)

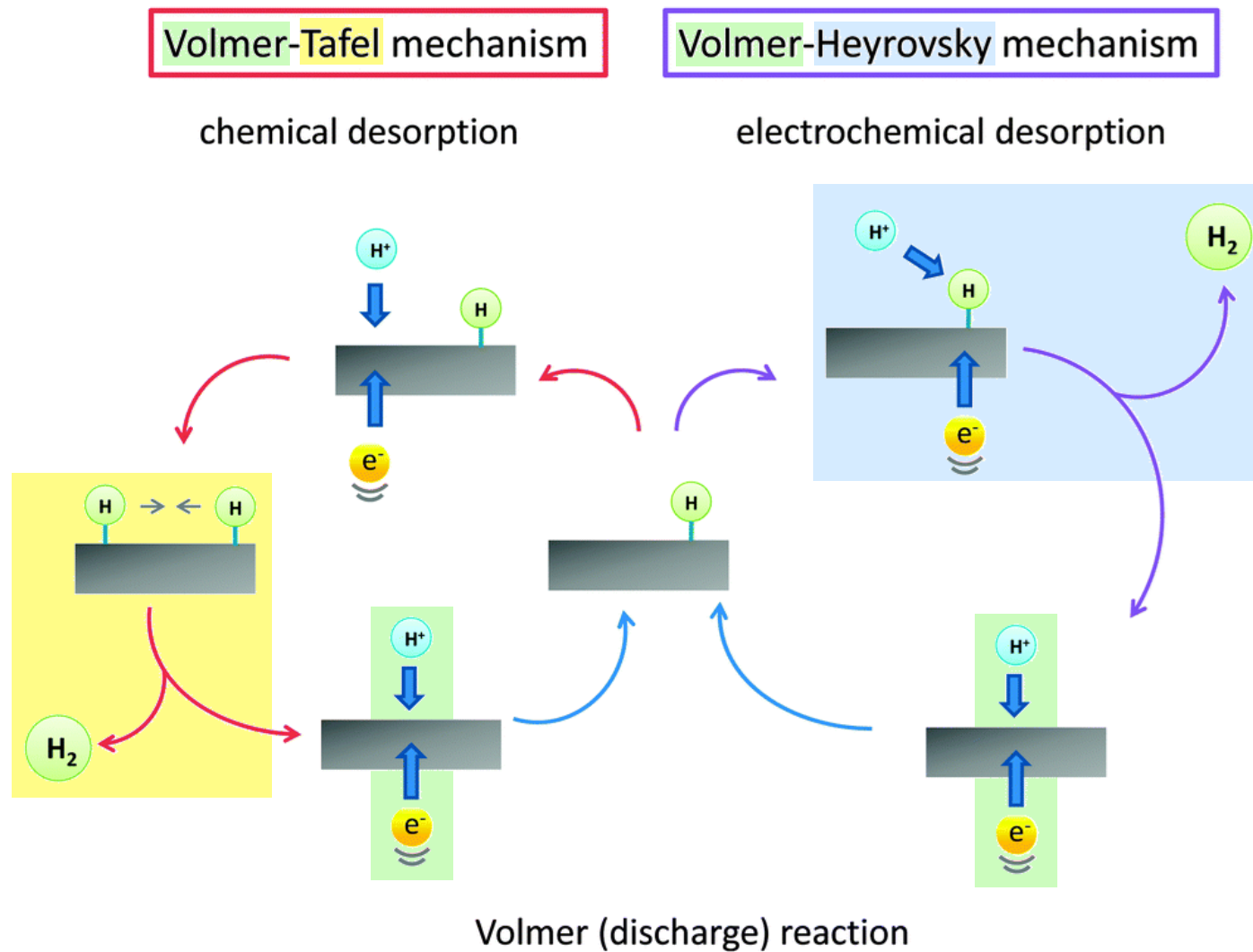


Parsons, *Trans. Faraday Soc.*, 1958, 54, 1053

Trasatti, *Electroanal. Chem. Interfac. Electrochem.*, 1972, 39, 163



... α values depend on the rate-determining step... they do not often add up to 1 for complex, multistep reactions... lots of fun kinetic analyses!



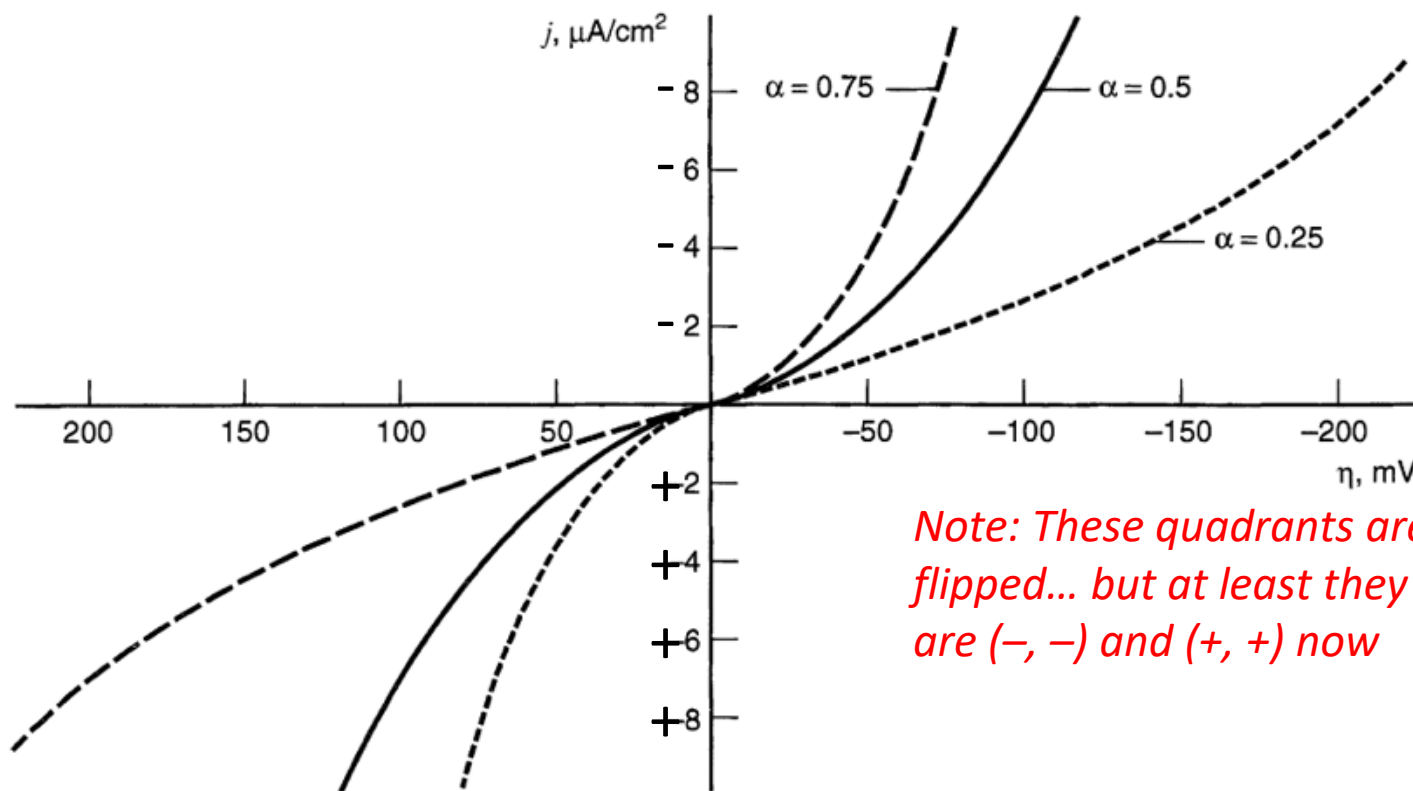
... it can get complex... imagine $\text{CO}_2 + 8\text{e}^- + 8\text{H}^+ \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$... Wow!

... and where α (or β) introduces asymmetry into this J - E curve

(SKIPPED)

$$i = -i_0 \left[e^{-\alpha f \eta} - e^{(1-\alpha) f \eta} \right]$$

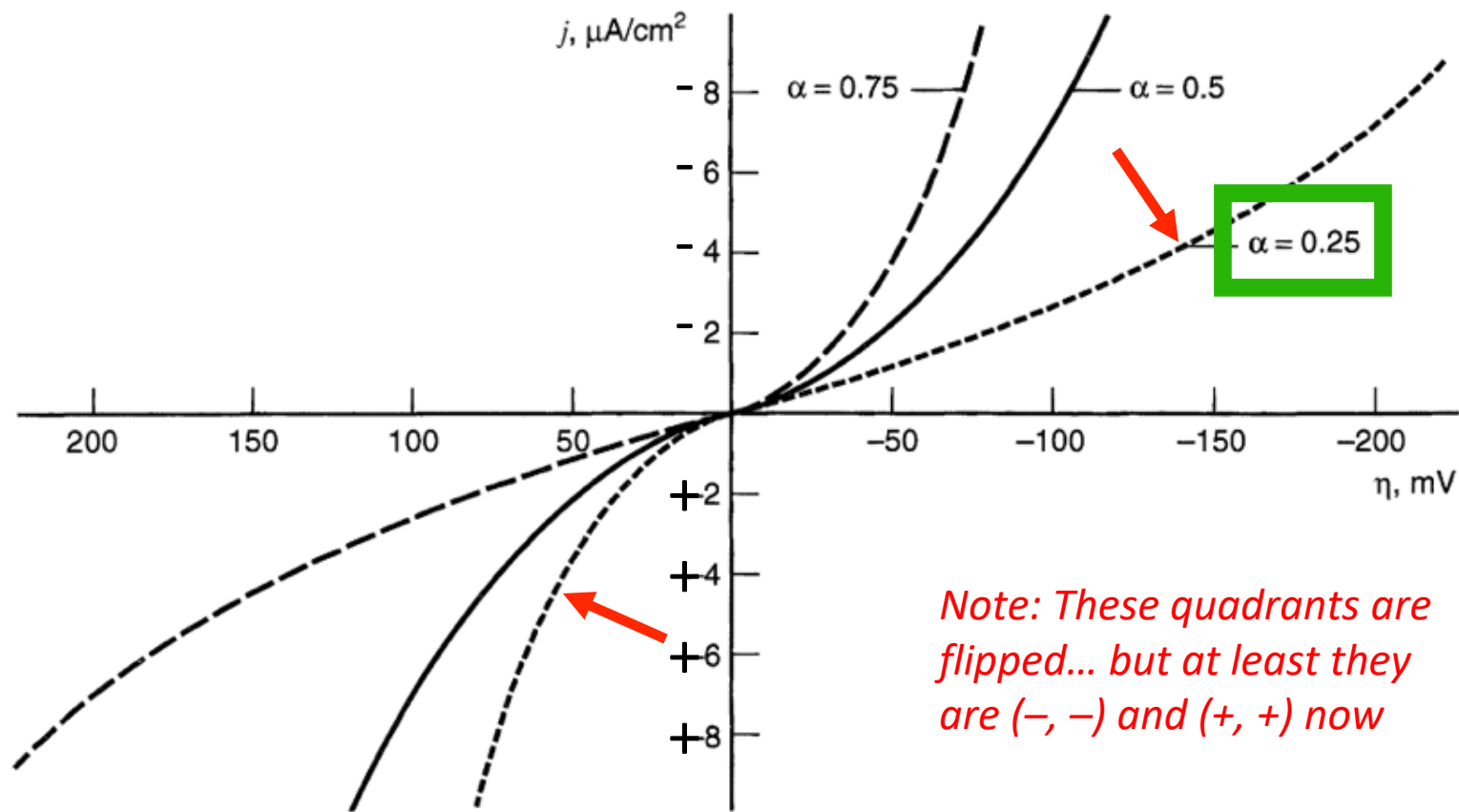
the Butler-Volmer Equation



Note: These quadrants are flipped... but at least they are (-, -) and (+, +) now

Figure 3.4.3 Effect of the transfer coefficient on the symmetry of the current-overpotential curves for $\text{O} + e \rightleftharpoons \text{R}$ with $T = 298 \text{ K}$ and $j_0 = 10^{-6} \text{ A}/\text{cm}^2$.

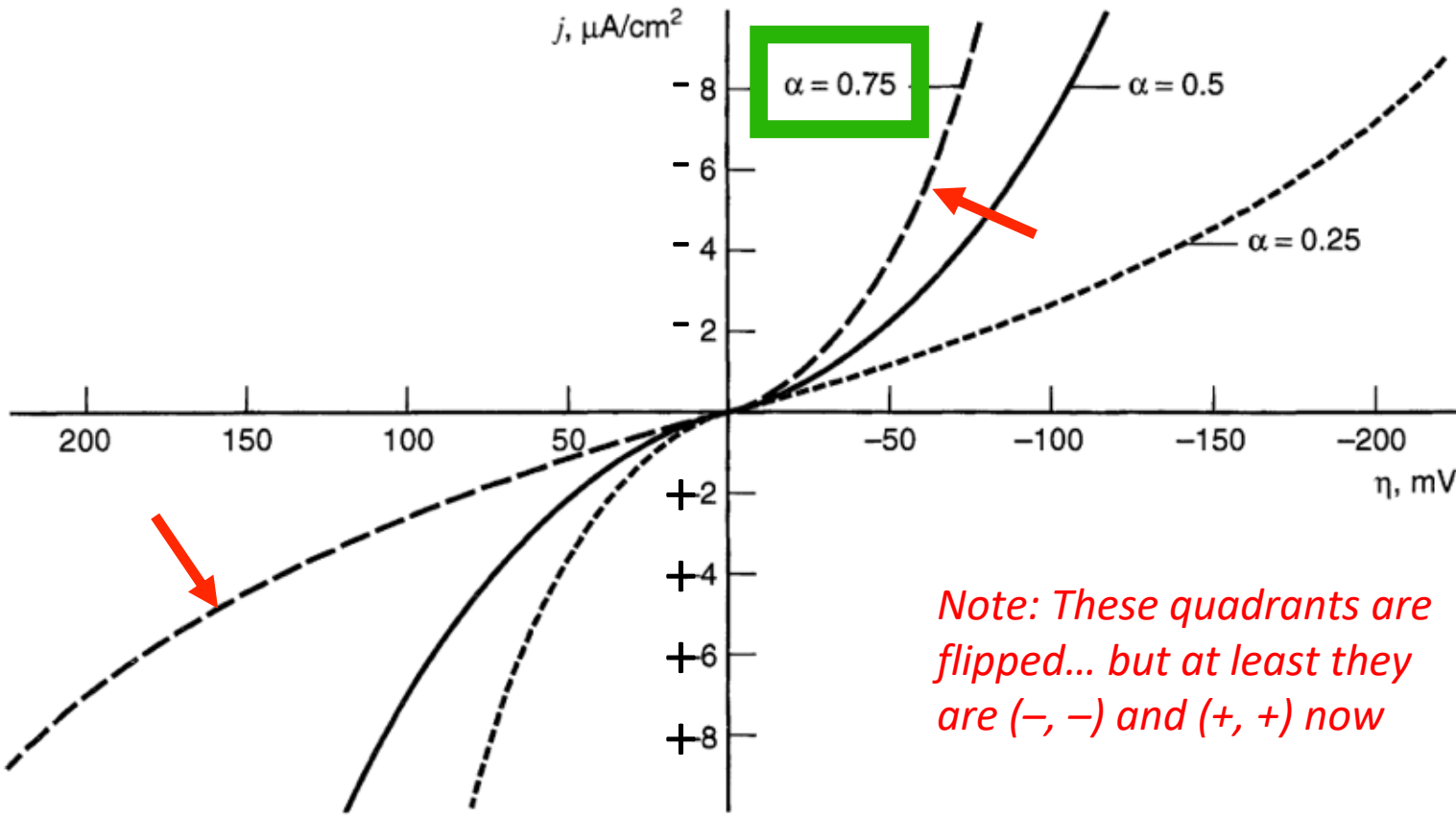
note that for a one-electron-transfer reaction and α (or β) $< 1/2$,
 oxidation is preferentially accelerated at any η value **(SKIPPED)**



Note: These quadrants are flipped... but at least they are (-, -) and (+, +) now

Figure 3.4.3 Effect of the transfer coefficient on the symmetry of the current-overpotential curves for $\text{O} + e \rightleftharpoons \text{R}$ with $T = 298 \text{ K}$ and $j_0 = 10^{-6} \text{ A}/\text{cm}^2$.

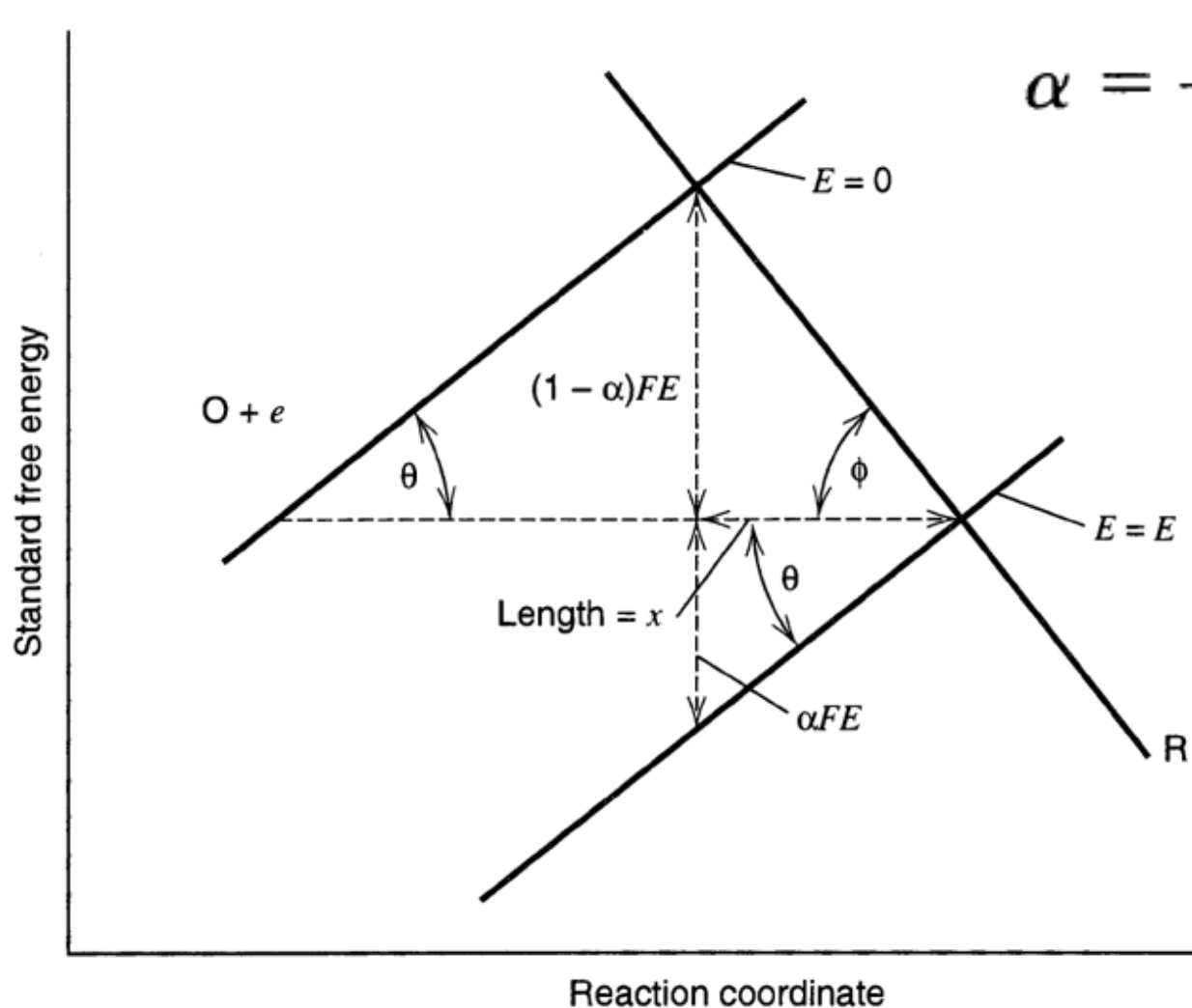
note that for a one-electron-transfer reaction and α (or β) $> 1/2$, reduction is preferentially accelerated at any η value **(SKIPPED)**



Note: These quadrants are flipped... but at least they are (-, -) and (+, +) now

Figure 3.4.3 Effect of the transfer coefficient on the symmetry of the current-overpotential curves for $\text{O} + e \rightleftharpoons \text{R}$ with $T = 298 \text{ K}$ and $j_0 = 10^{-6} \text{ A}/\text{cm}^2$.

... now, more specifically, α (actually β) is related to the symmetry of the barrier *in the vicinity of the crossing point...* **(SKIPPED)**



$$\alpha = \frac{\tan \theta}{\tan \phi + \tan \theta}$$

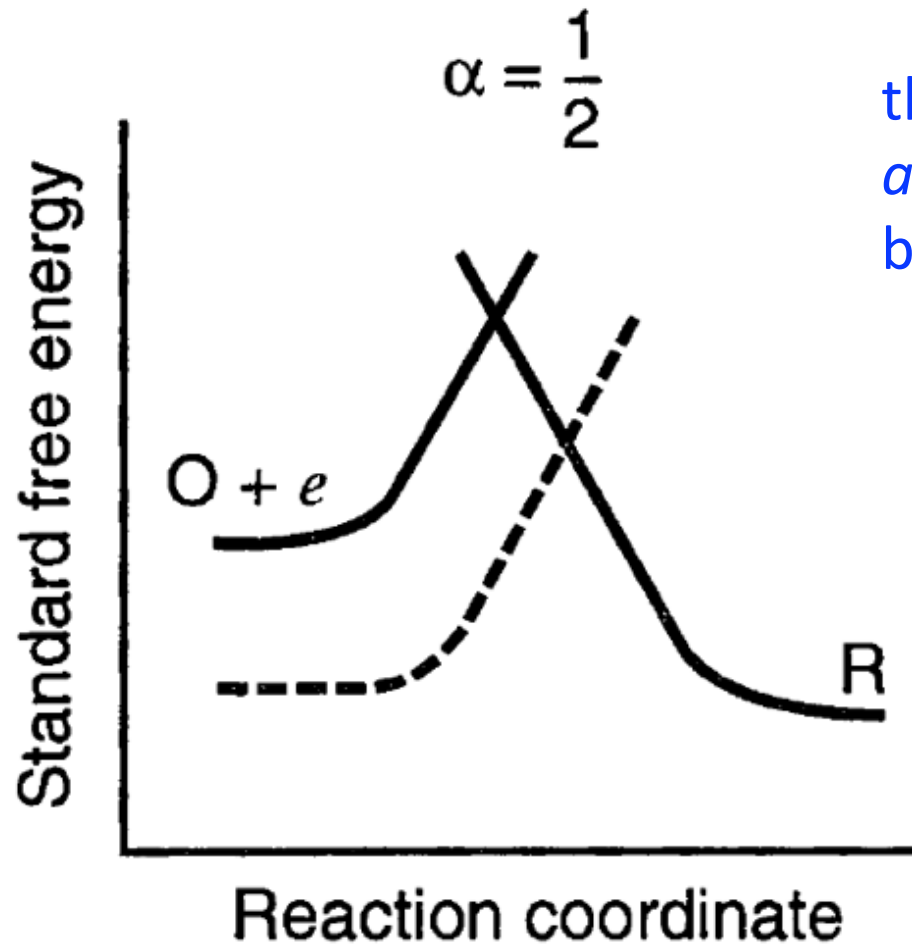
$\tan = \text{opposite} / \text{adjacent}$

derive this by applying "TOA" to the two triangles on the right...

$$\tan \theta = \alpha FE / x$$

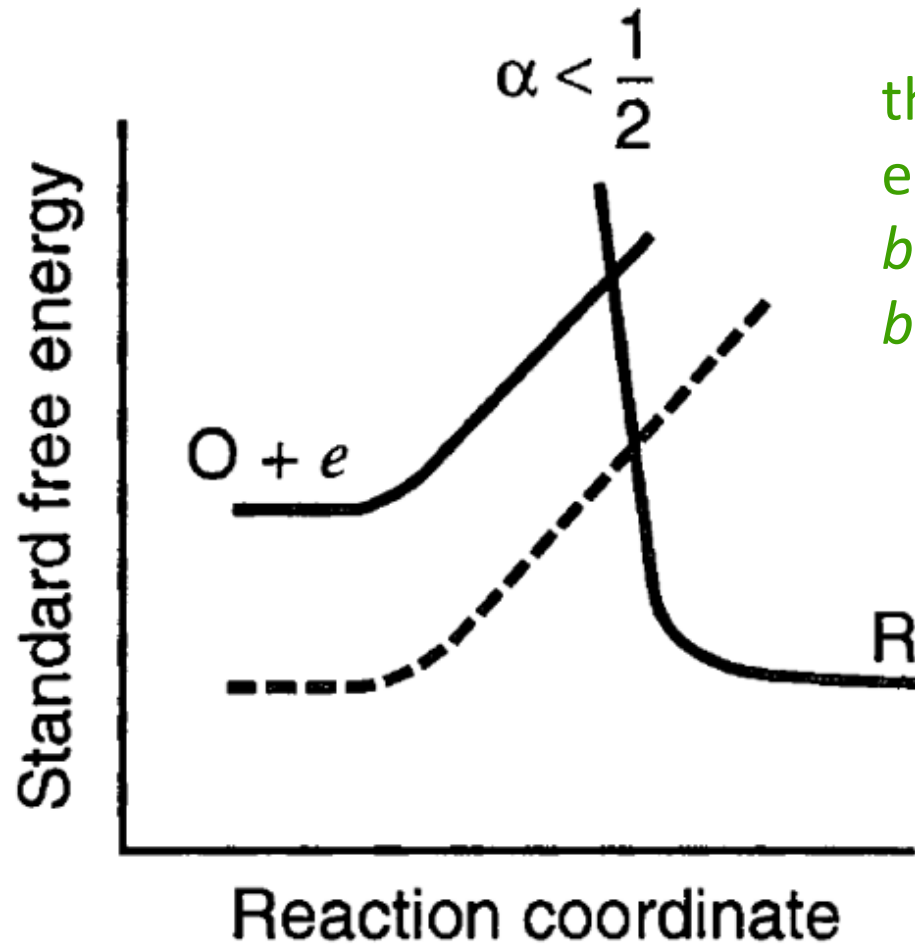
$$\tan \phi = (1 - \alpha) FE / x$$

... if the barrier is symmetrical...



this means that the *cathodic and anodic barriers are affected equally* by the change in potential.

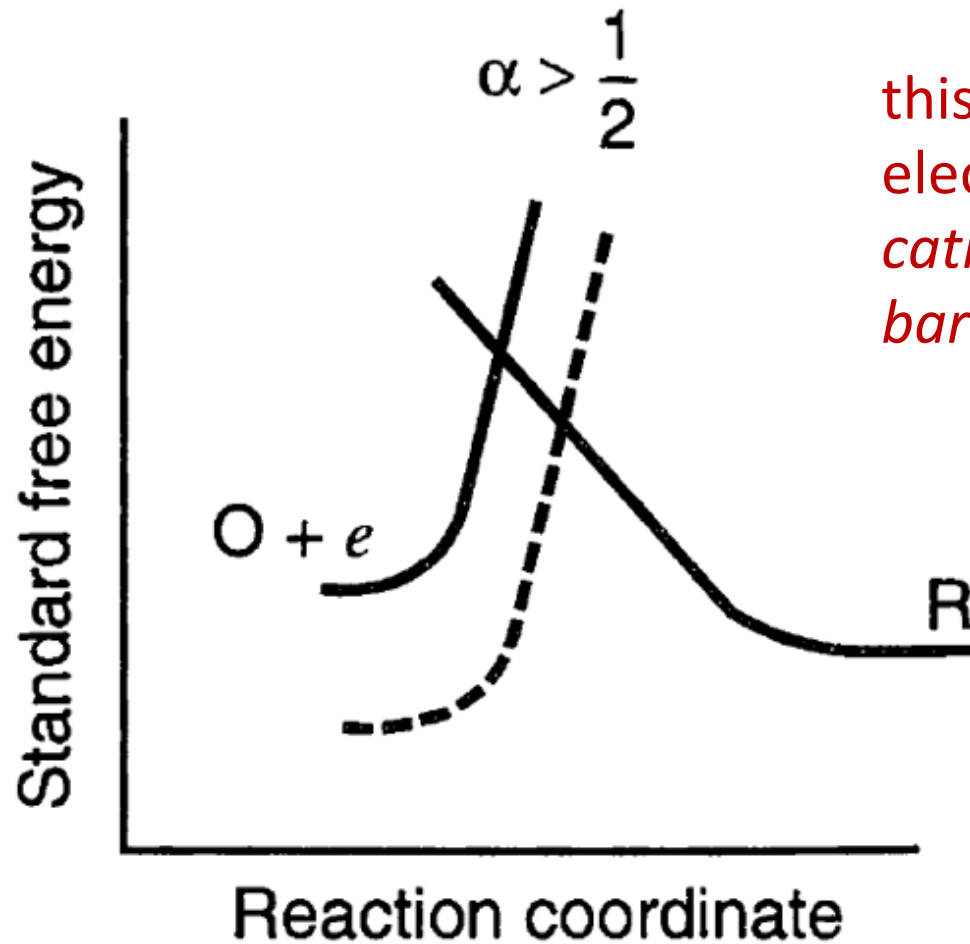
... if the R side is steeper than the O side...



this means that a change in the electrode potential affects the *anodic barrier* more than the *cathodic barrier*.

Note that in the limit of a vertical potential-energy “curve” for R at the crossing point, $\alpha = 0$ and *100% of the potential change accelerates oxidation*.

... if the R side is more shallow than the O side...



this means that a change in the electrode potential affects the *cathodic barrier* more than the *anodic barrier*.

Note that in the limit of a vertical potential-energy “curve” for O at the crossing point, $\alpha = 1$ and *100% of the potential change accelerates reduction*.

... two limiting cases for the Butler–Volmer Equation are important... 860

(SKIPPED)

$$i = -i_0 \left[e^{-\alpha f \eta} - e^{(1-\alpha) f \eta} \right]$$

... first, if η is small, then $\exp(x)$ can be approximated by a Taylor/Maclaurin series expansion as $1 + x$...

$$i = -i_0 [1 + (-\alpha f \eta) - (1 + (1 - \alpha) f \eta)] = +i_0 f \eta$$

What's small for one term?

$$\text{B-V: } \exp(0) = 1$$

$$\text{T/M: } 1 + 0 = 1$$

(error = 0%)

$$\text{B-V: } \exp(1) = 2.7$$

$$\text{T/M: } 1 + 1 = 2$$

(error = -26%)

so small means $\eta < 30$ mV ($\alpha f \eta = (0.5)(1 / 26 \text{ mV})(30 \text{ mV}) = 0.58$)

$$\text{B-V: } \exp(0.58) = 1.78$$

$$\text{T/M: } 1 + 0.58 = 1.5$$

(error = -11%)

... two limiting cases for the Butler–Volmer Equation are important... 861

(SKIPPED)

$$i = -i_0 \left[e^{-\alpha f \eta} - e^{(1-\alpha) f \eta} \right]$$

... first, if η is small, then $\exp(x)$ can be approximated by a Taylor/Maclaurin series expansion as $1 + x$...

$$i = -i_0 [1 + (-\alpha f \eta) - (1 + (1 - \alpha) f \eta)] = +i_0 f \eta$$

Note: no α !
... and it looks
ohmic

... two limiting cases for the Butler–Volmer Equation are important... 862

(SKIPPED)

$$i = -i_0 \left[e^{-\alpha f \eta} - e^{(1-\alpha) f \eta} \right]$$

... if, instead, η is large, then either i_c or i_a can be neglected...

... and we obtain the famous *Tafel Equation* which has two versions:

for $\eta \ll 0$: (current negative, or reducing/cathodic)

$$i = -i_0 \exp(-\alpha f \eta) \dots$$

$$\ln|i| = \ln(i_0) - \alpha f \eta$$

for $\eta \gg 0$: (current positive, or oxidizing/anodic)

$$i = +i_0 \exp(-(1-\alpha) f \eta) \dots$$

$$\ln|i| = \ln(i_0) + (1-\alpha) f \eta$$

... “ η is large” means > 60 mV or so...

... both β and i_0 can be obtained from a $J-E$ curve in one direction...

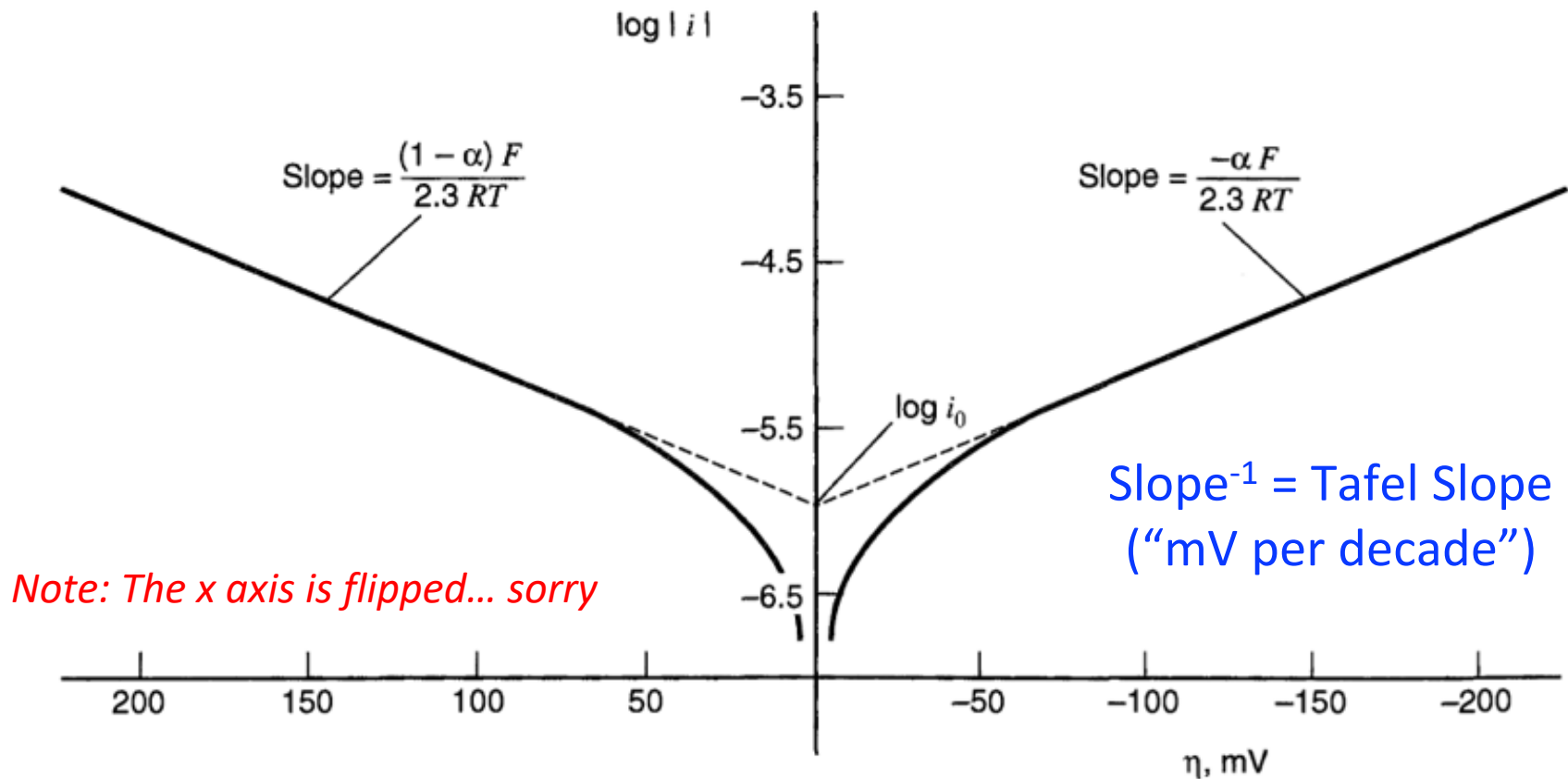


Figure 3.4.4 Tafel plots for anodic and cathodic branches of the current-overpotential curve for $O + e \rightleftharpoons R$ with $\alpha = 0.5$, $T = 298$ K, and $j_0 = 10^{-6}$ A/cm².

⁹Note that for $\alpha = 0.5$, $b = 0.118$ V, a value that is sometimes quoted as a “typical” Tafel slope.

... “ η is large” means > 60 mV or so...

Quick Quiz: Which catalyst is best?

- (A) $j_0 = 10^{-4}$ A cm⁻² and 120 mV decade⁻¹
- (B) $j_0 = 10^{-7}$ A cm⁻² and 60 mV decade⁻¹

It depends on the desired $j...$

For 1 mA cm⁻², (A) is best... but...

... for 1 A cm⁻², (B) is best...

... where catalyst (A) requires $\eta = 480$ mV, while catalyst (B) requires $\eta = 420$ mV!

... Take-home point: Always report overpotentials at a specific current density

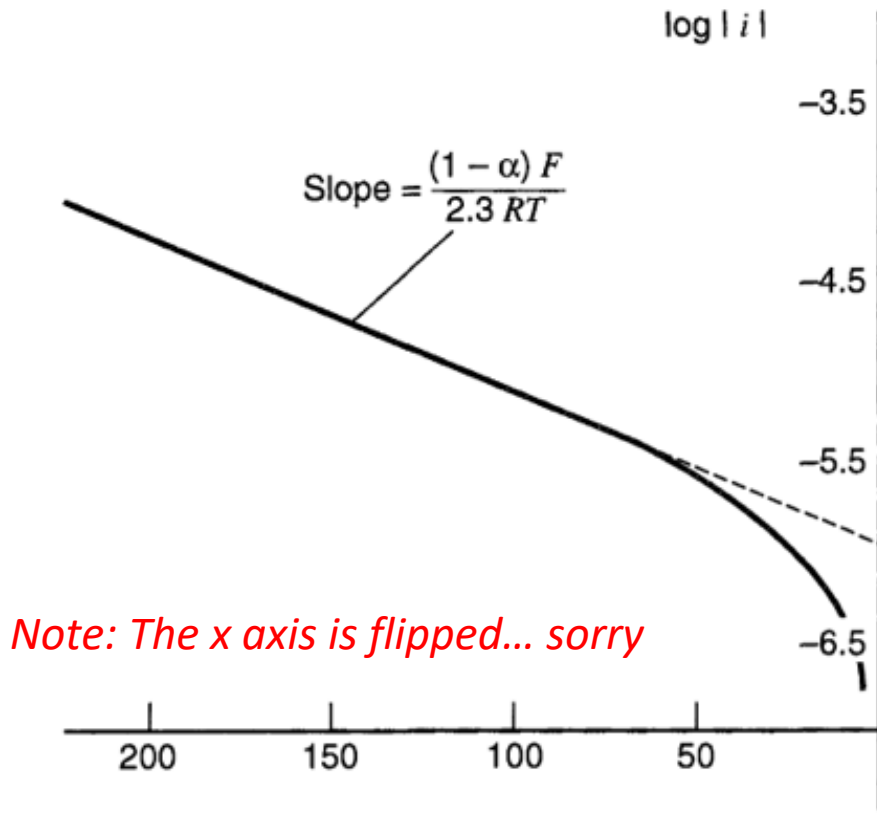
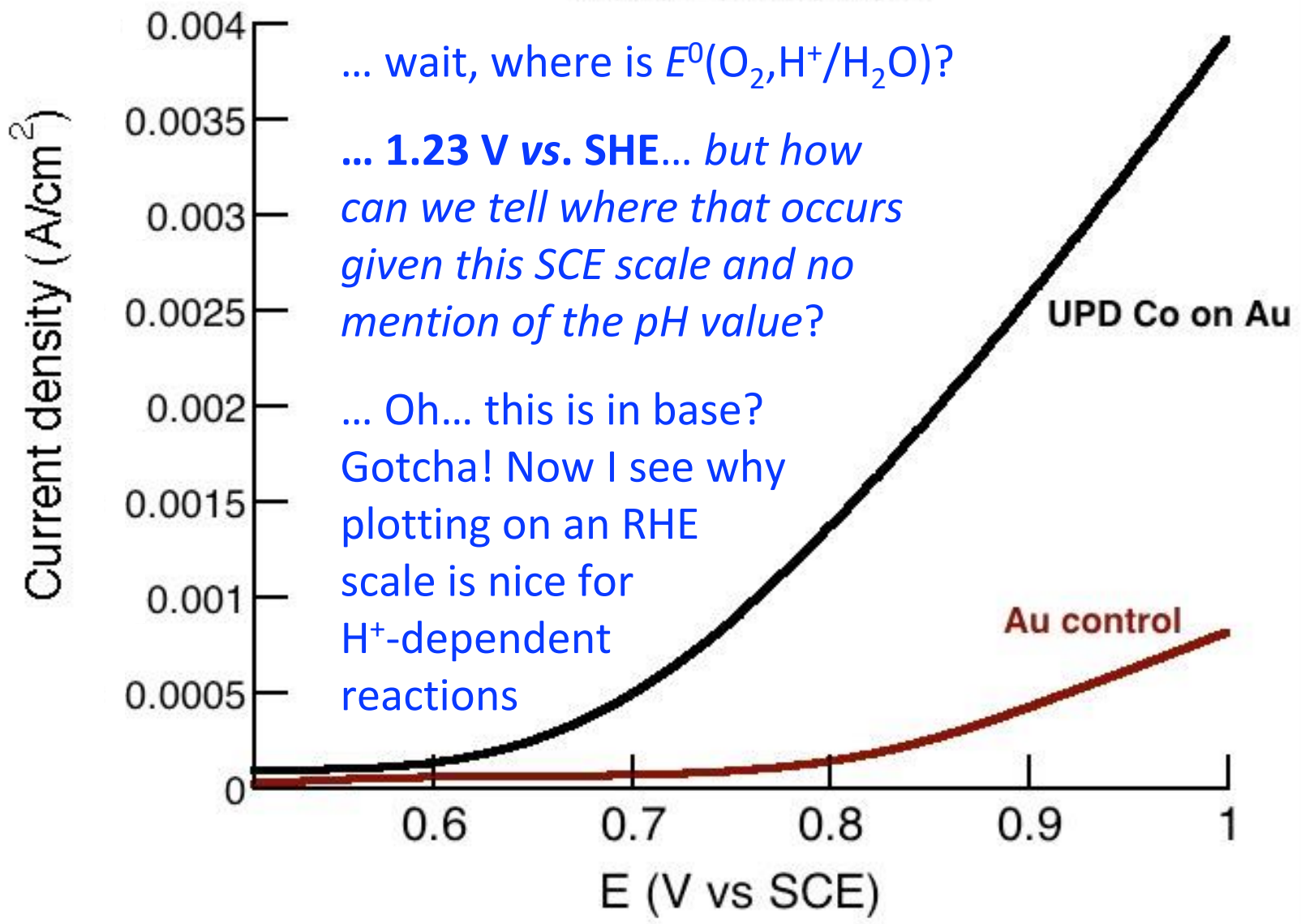


Figure 3.4.4 Tafel plots for anodic and cathodic branches of the current-overpotential curve for $O + e \rightleftharpoons R$ with $\alpha = 0.5$, $T = 298$ K, and $j_0 = 10^{-6}$ A/cm².

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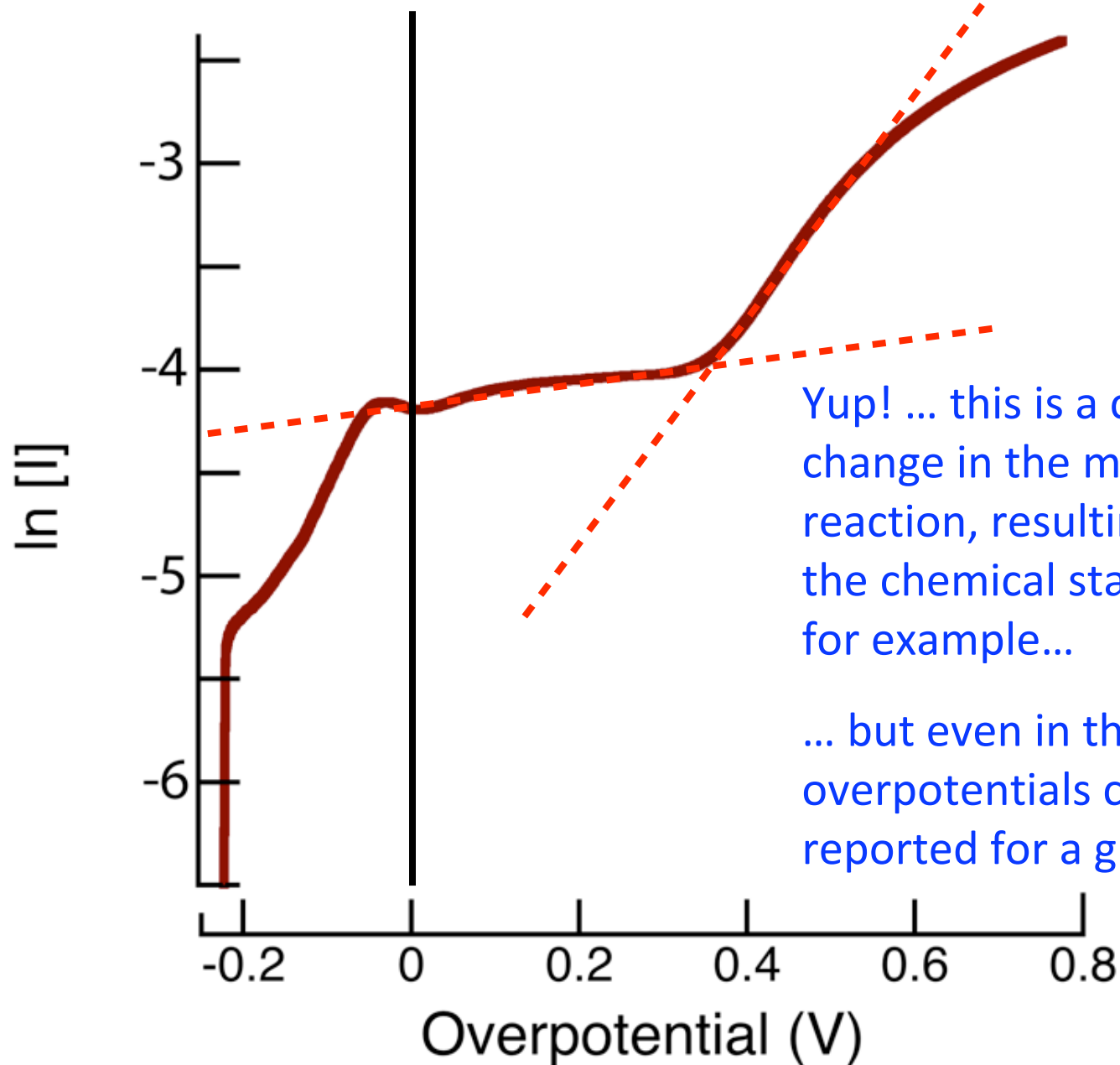
What does real data look like, so that I can indicate the overpotential?
(SKIPPED)

Water oxidation



... wait, the Tafel Slope (in units of mV/decade) changes?

(SKIPPED)

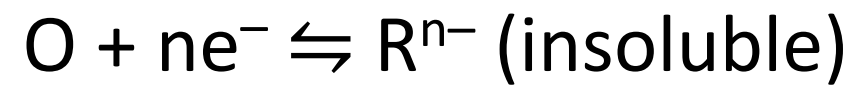


Yup! ... this is a consequence of a change in the mechanism of the reaction, resulting from a change in the chemical state of the catalyst, for example...

... but even in this case, overpotentials can and should be reported for a given current density

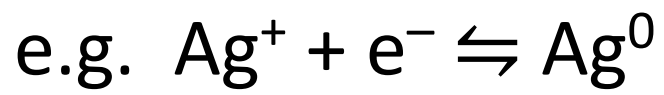
(SKIPPED)

Recall, and for clarity, that we have already encountered an overpotential... and seen a case where it is important...



$$C_R^* = 0$$

C_O^* = the bulk concentration of O



Repeating a derivation akin to one we did in Chapter 1...

$$E = \underbrace{E^{0'} + \frac{RT}{nF} \ln C_O^*}_{E_{eq}} + \frac{RT}{nF} \ln \left(\frac{i_l - i}{i_l} \right)$$

$$E - E_{eq} = \eta_{conc} = \frac{RT}{nF} \ln \left(\frac{i_l - i}{i_l} \right)$$

(SKIPPED)

Recall, and for clarity, that we have already encountered an overpotential... and seen a case where it is important...



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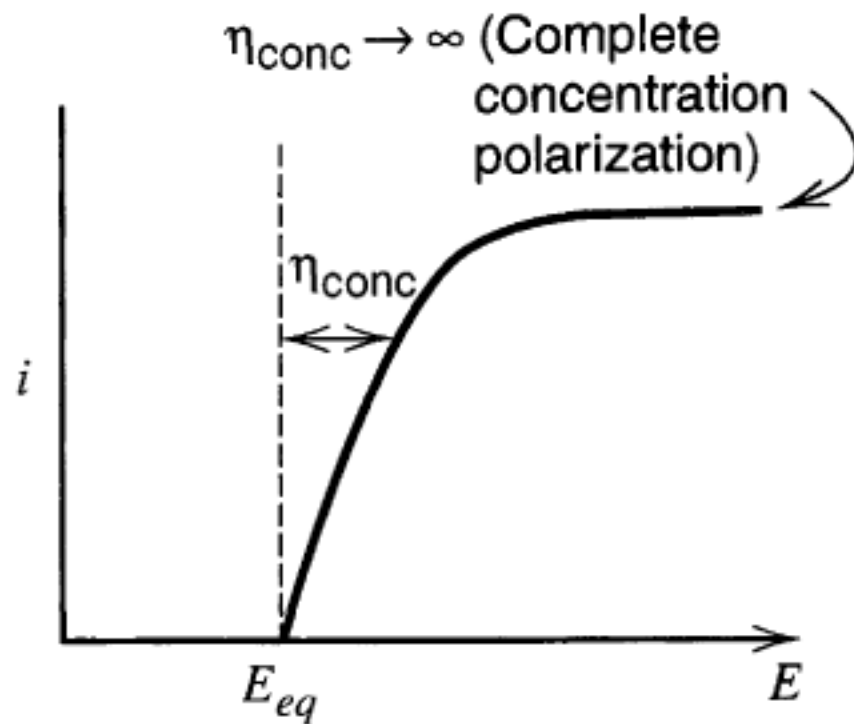
... **Interpretation**: An extra potential, beyond E_{eq} , is required to drive mass transfer of species to the electrode surface...

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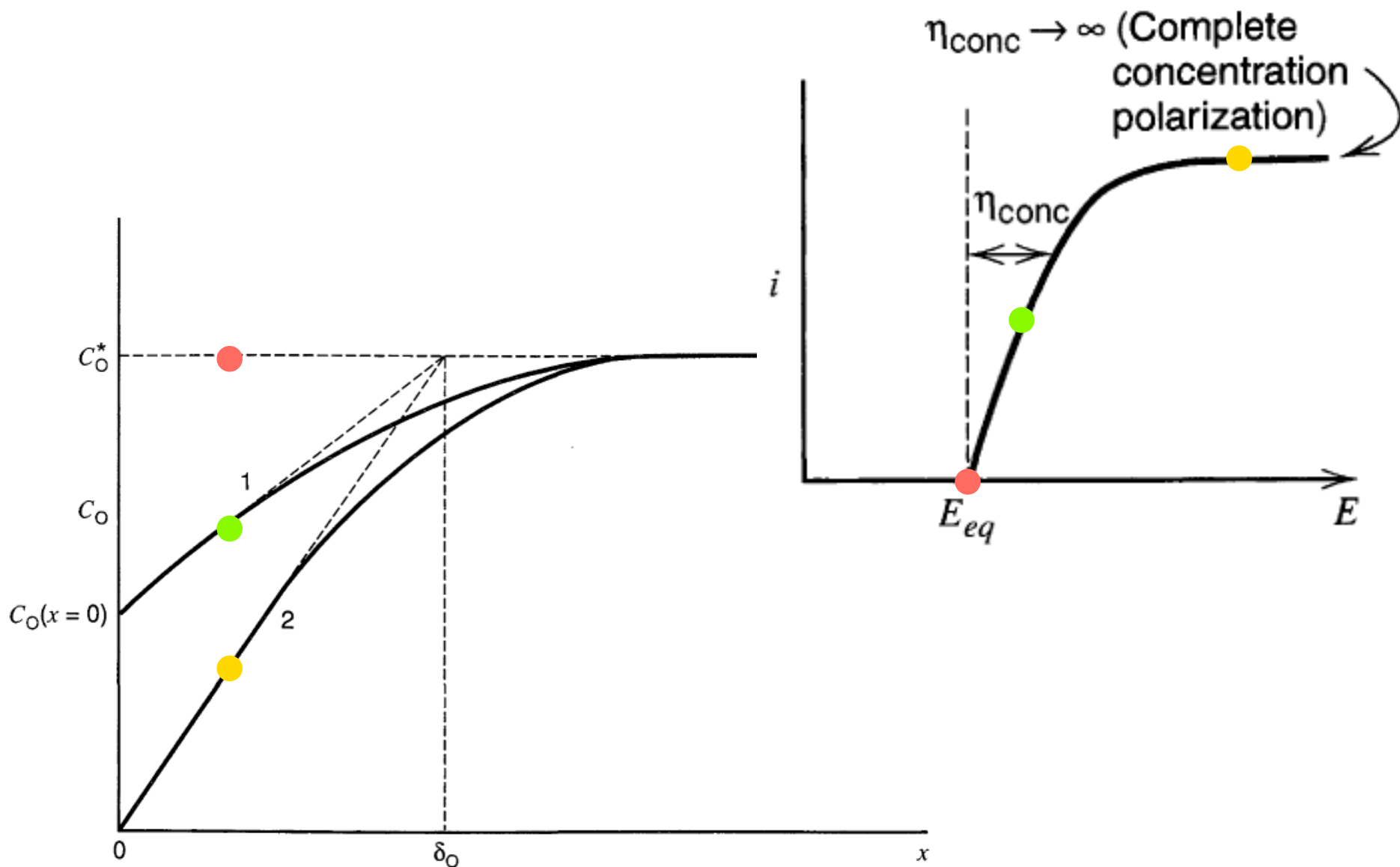
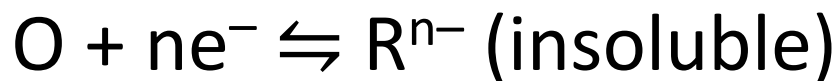
$$E - E_{eq} = \eta_{conc} = \frac{RT}{nF} \ln \left(\frac{i_l - i}{i_l} \right)$$

Recall, and for clarity, that we have already encountered an **(SKIPPED)** overpotential... and seen a case where it is important...



$$\eta_{conc} = \frac{RT}{nF} \ln \left(\frac{i_l - i}{i_l} \right)$$

... **Interpretation**: An extra potential, beyond E_{eq} , is required to drive mass transfer of species to the electrode surface...

(SKIPPED)What's happening here (not electrocatalysis)?

(SKIPPED)

An overpotential that is derived from rate-limiting mass transfer alone is called a *concentration overpotential*, η_{conc} ...

... it is also called a *concentration polarization*.

Kinetic overpotential is often just called *overpotential*, but can also be called *activation overpotential*...

... okay, that summarizes this topic nicely... there is lots more to learn that your book lays out in great detail related to complex reactions and mechanisms, but this suffices for our course

Q: What *was* in this set of lectures?

A: B&F Chapter 3 main concepts:

- Sections 3.1 & 3.6: Homogeneous Electron-Transfer (ET) (Arrhenius, Eyring, Transition-State Theory (Activated Complex Theory), Marcus Theory)
- Sections 3.2, 3.3, 3.4 & 3.6: Heterogeneous ET (Butler–Volmer Equation, Tafel Equation, Volcano Plot, Gerischer Theory, Quantum Mechanical Tunneling)
- Section 3.5: Multistep ET Mechanisms