819

Lecture #19 of 20+

819

In conclusion, with the Guoy–Chapman–Stern Model we have a semi-quantitative understanding of this interface with some predictive power… 820

…. 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? ~$E_{app}/2$

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

electrode solution

diffuse layer

R

R

M⁺

OHP
IHP

RECALL:

**An ion transfers across the double layer**… *mind = blown, again!*
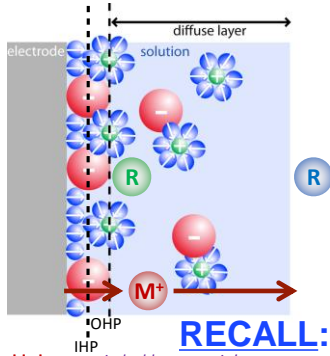
820

In conclusion, with the Guoy–Chapman–Stern Model we have a semi-quantitative understanding of this interface with some predictive power… 821

(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

electrode solution

diffuse layer

OHP
IHP

RECALL:
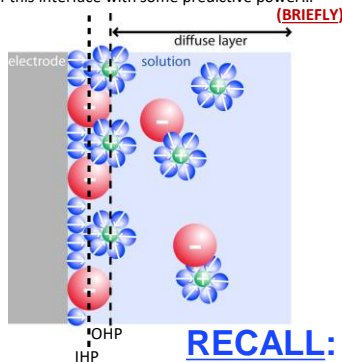
821

822

Interfacial Charge-Transfer Kinetics

Chapter 3

822

823

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

823

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…   824

… 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

824

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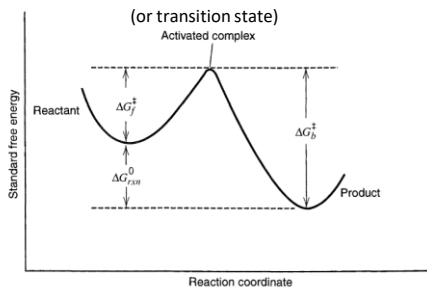
825

... 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):

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

  - **THERMODYNAMICS**: A reaction is spontaneous if the ΔG is negative, and thus ΔE (E_{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. ΔG^0 (ΔE^0, E^0_{cell}))
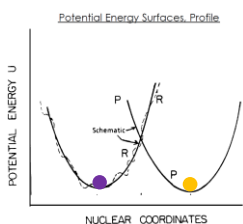 ... Marcus Theory (Nobel Prize in Chemistry in 1992)
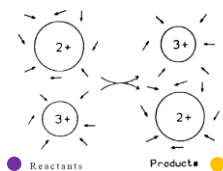
826

... 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
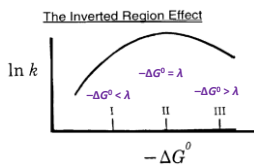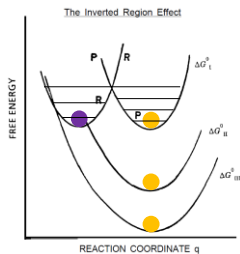
827

3

… Marcus Theory… the idea… 828

- Minor assumptions to go from internal (potential) energy to free energy
  ($\Delta G = \Delta H - T\Delta S$)

  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 $\Delta G^0 = 0$)

- Three regions of electron transfer:
  (I) Normal, (II) Barrierless, (III) Inverted

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

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

828

… Marcus Theory… **Experimental Confirmation!** 829

- Minor assumptions to go from internal (potential) energy to free energy
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Closs & Miller, *Science*, 1988, *240*, 440
http://www.nobelprize.org/nobel_prizes/chemistry/laureates/1992/marcus-lecture.pdf

829

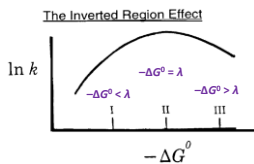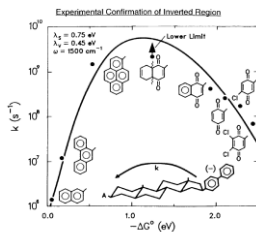… Marcus Theory… **Experimental Confirmation!** 830

- 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…
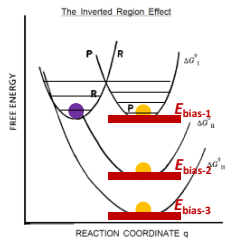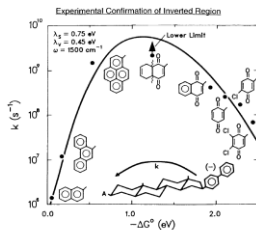
Closs & Miller, *Science*, 1988, *240*, 440
http://www.nobelprize.org/nobel_prizes/chemistry/laureates/1992/marcus-lecture.pdf

830

Electrochemical kinetics: [831]
The Butler–Volmer Reaction (current as a function of potential)

Derivation… start with the generic reaction:

$$O + ne^- \underset{k_f}{\overset{k_b}{\rightleftharpoons}} R^{n-}$$
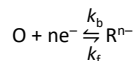
the rate of the forward and backward reactions are:

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

$$v_b = k_b C_R(0, t) = \frac{i_a}{nFA}$$

The units of v are moles cm^{-2} 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

831

---

the overall (microscopically reversible) reaction rate, v_{net}, is thus [832]
given by the difference between the forward and backward rates:

$$v_{net} = v_f - v_b = k_f C_O(0, t) - k_b C_R(0, t) = \frac{-i}{nFA}$$

or, in terms of the current:

$$i = i_c - i_a = -nFA[k_f C_O(0, t) - k_b C_R(0, t)]$$
(don't forget this… we will come back to it later)

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

… 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*, $\Delta G^{\ddagger}$…

832

Again, from transition state theory (TST) (activated complex theory [833]
(ACT)), the *standard Gibb's free energy of activation*, $\Delta G^{\ddagger}$ is defined as
follows…
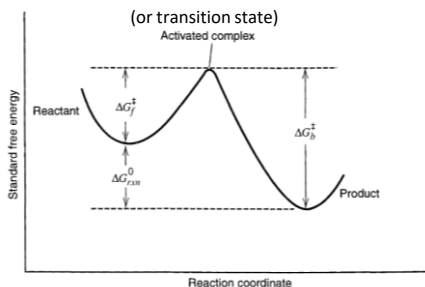
833

… and here is the effect of electrode potential on the <u>product</u> and <u>reactant</u> free energy (Marcus) curves (**not inverted!**)…

834

$E = E_{eq}$

$E < E_{eq}$

$E > E_{eq}$
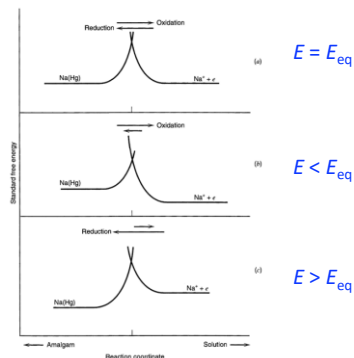
834

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

835

What happens to $\Delta G_c^{\ddagger}$ and $\Delta G_a^{\ddagger}$ when the potential is changed by E?

(assume $E_{eq} = E^{0'}$)

At $E^{0'}$

ZOOM IN

$\Delta G_{0a}^{\ddagger}$

At E

$\Delta G_{0c}^{\ddagger}$

$\Delta G_a^{\ddagger}$

$\Delta G_c^{\ddagger}$

$F(E - E^{0'})$

E

Marcus Theory

$O + e$

R

Standard free energy

Reaction coordinate
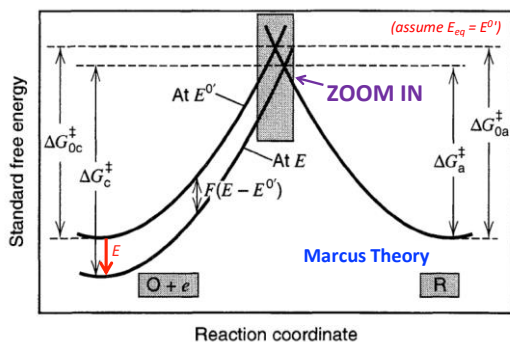
Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 3.3.2

835

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

836

What happens to $\Delta G_c^{\ddagger}$ and $\Delta G_a^{\ddagger}$ when the potential is changed by E?

(assume $E_{eq} = E^{0'}$)

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

At $E^{0'}$

$F(E - E^{0'})$

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

E

At E

Linearized Marcus Theory

$O + e$

R

Standard free energy

Reaction coordinate
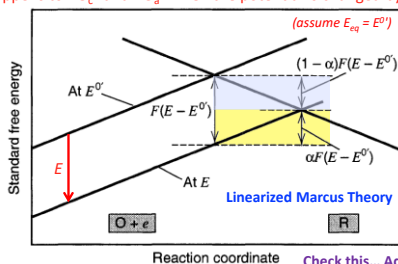
Check this… Add'em up…

… that is, (3) + (4) = …

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

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

(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)*…

836

6

… so after changing the potential from $E^{0\prime}$ to E: 837

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

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

$\Delta G^{\ddagger}_{0c}$ is just $\Delta G^{\ddagger}_{c}$ at $E^{0\prime}$ (= E_{eq})

α is the *transfer coefficient* [0, 1], and is the fraction of $E - E^{0\prime}$ 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!

… while geometry is simple, this really means that electron tunneling occurs at a thermally excited confirmation present at a distance, x',… where only the fraction, β, of E vs. $E^{0\prime}$ is screened by the double layer to modulate $\Delta G^{\ddagger}$
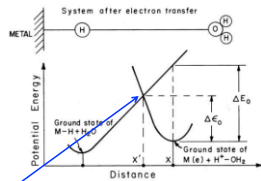
Bockris & Nagy, *J. Chem. Educ.*, 1973, 50, 839

837

… so after changing the potential from $E^{0\prime}$ to E: 838

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

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

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

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

… to obtain these potential-dependent expressions…

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

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

838

When $E = E^{0\prime} = E_{eq}$, $C_O = C_R$ and $i = 0$ (equilibrium)… plugging into our expression for the current, 839

(I told you not to forget this equation!)

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

… results in $k_f = k_b = k^0$, the *standard heterogeneous electron-transfer rate constant*…
… and plugging in below leads to just the potential-independent terms and so when $C_O = C_R$, 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

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

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

839

... 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 ($\Delta G^{\ddagger}_{0c} = \Delta G^{\ddagger}_{0a}$, only when $C_O = C_R$), we can write even more compact expressions for k_f and k_b...

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

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

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

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

840

... 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...

841

... 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

842

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

843

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

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

844

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
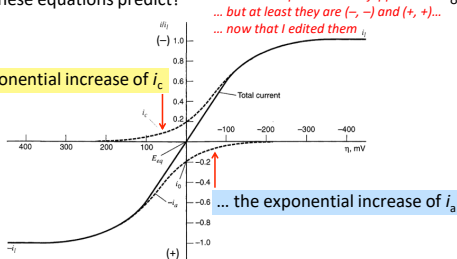
… the exponential increase of i_a

Figure 3.4.1   Current-overpotential curves for the system $O + e \rightleftarrows R$ 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

845

What do these equations predict?

Note: These quadrants are flipped…
… but at least they are (–, –) and (+, +)…
… now they edited them

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

the Current–Overpotential Equation
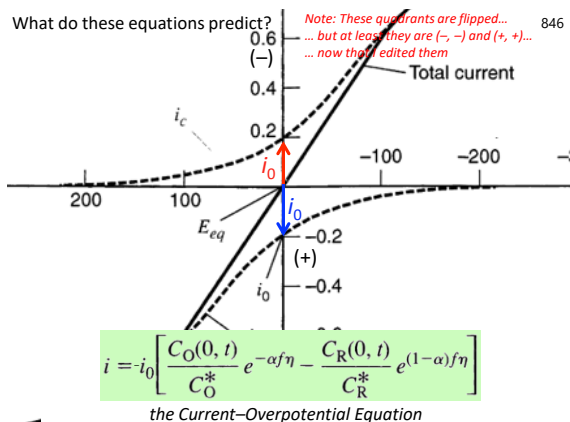
846

… 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*… **(SKIPPED)**

847

This looks familiar…
… mass transfer only
… still some slope to the data

Note: These quadrants are flipped… but at least they are (–, –) and (+, +) now
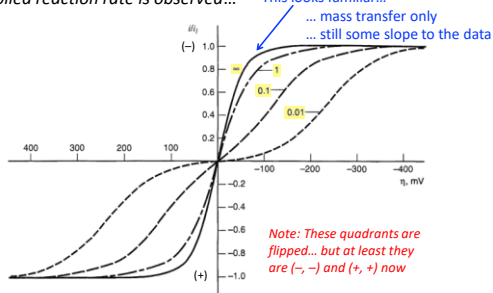
Figure 3.4.6 Relationship between the activation overpotential and net current demand relative to the exchange current. The reaction is O + e ⇌ R with α = 0.5, T = 298 K, and $i_{l,c} = -i_{l,a} = i_l$. Numbers by curves show i_0/i_l.

847

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

848

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

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)…

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

Note: These quadrants are flipped… but at least they are (–, –) and (+, +) now
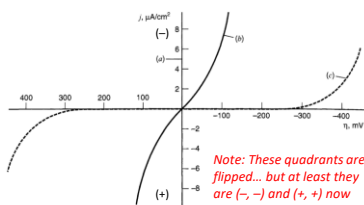
Figure 3.4.2 Effect of exchange current density on the activation overpotential required to deliver net current densities. (a) $j_0 = 10^{-3}$ A/cm² (curve is indistinguishable from the current axis), (b) $j_0 = 10^{-6}$ A/cm², (c) $j_0 = 10^{-9}$ A/cm². For all cases the reaction is O + e ⇌ R with α = 0.5 and T = 298 K.

848

j_0 can vary by up to twenty orders of magnitude! Consider just one reaction: proton reduction (H_2 evolution)… **(SKIPPED)** 849

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

http://www.scielo.br/img/revistas/qn/v28n6/26839t1.gif

849

Sabatier Principle and *Volcano plots* for, for example, proton reduction (H_2 evolution)… **(SKIPPED)** 850

"Spillover" (synergism)
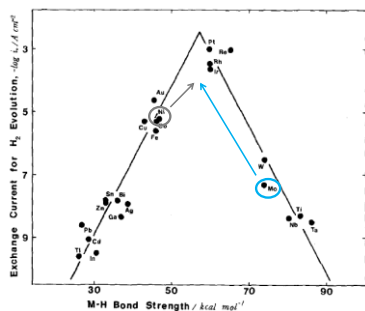
Parsons, *Trans. Faraday Soc.*, 1958, *54*, 1053
Trasatti, *Electroanal. Chem. Interfac. Electrochem.*, 1972, *39*, 163

850

Simple, multistep electron-transfer mechanisms… **(SKIPPED)** 851

Volmer-**Tafel** mechanism   Volmer-**Heyrovsky** mechanism
chemical desorption   electrochemical desorption

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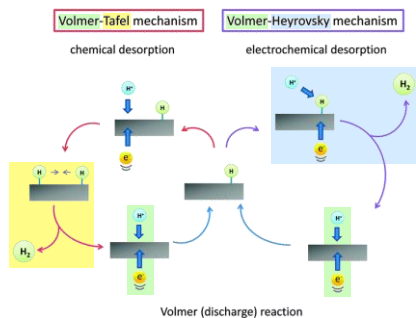
… α values depend on the rate-determining step… they do not often add up to 1 for complex, multistep reactions… lots of fun kinetic analyses!

851

Simple, multistep electron-transfer mechanisms… **(SKIPPED)** 852

Volmer-**Tafel** mechanism | Volmer-Heyrovsky mechanism

chemical desorption | electrochemical desorption

Volmer (discharge) reaction
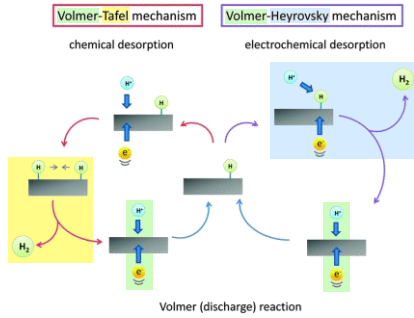
… it can get complex… **imagine $CO_2 + 8e^- + 8H^+ \rightarrow CH_4 + 2H_2O$… Wow!**

852

… and where α (or β) introduces asymmetry into this *J–E* curve 853
(SKIPPED)

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

the Butler–Volmer Equation
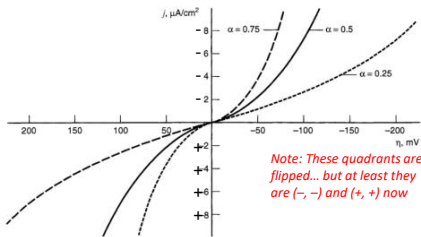
j, µA/cm²

$\alpha = 0.75$ $\alpha = 0.5$

$\alpha = 0.25$

η, mV

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 O + e ⇌ R with T = 298 K and $j_0 = 10^{-6}$ A/cm².

853

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note that for a one-electron-transfer reaction and α (or β) $< \frac{1}{2}$, 854
oxidation is preferentially accelerated at any η value **(SKIPPED)**

j, µA/cm²

$\alpha = 0.75$ $\alpha = 0.5$

$\alpha = 0.25$

η, mV

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 O + e ⇌ R with T = 298 K and $j_0 = 10^{-6}$ A/cm².

854

note that for a one-electron-transfer reaction and α (or β) > $\frac{1}{2}$, **(SKIPPED)** 855
reduction is preferentially accelerated at any η value

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

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

855

… now, more specifically, α (actually β) is related to the symmetry of the barrier *in the vicinity of the crossing point*… **(SKIPPED)** 856

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

tan = $^{opposite}/_{adjacent}$

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

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

Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 3.3.3

856

… if the barrier is symmetrical… **(SKIPPED)** 857

$\alpha = \frac{1}{2}$

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

Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 3.3.4

857

13

... if the R side is steeper than the O side...   *(SKIPPED)* 858

$\alpha < \frac{1}{2}$

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.*
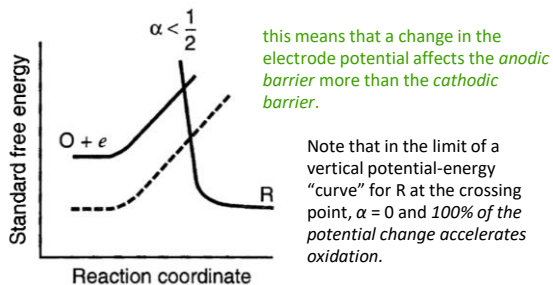
Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 3.3.4

858

... if the R side is more shallow than the O side...   *(SKIPPED)* 859

$\alpha > \frac{1}{2}$

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.*
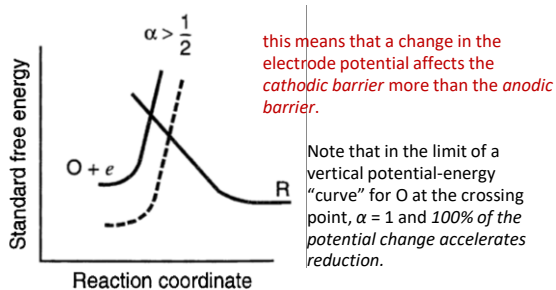
Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 3.3.4

859

... 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?

B–V: exp(0) = 1   T/M: 1 + 0 = 1   (error = 0%)
B–V: exp(1) = 2.7   T/M: 1 + 1 = 2   (error = -26%)

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

B–V: exp(0.58) = 1.78   T/M: 1 + 0.58 = 1.5   (error = -11%)

860

14

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

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

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Note: no α!
... and it looks ohmic

861

... 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)

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

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

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

862

... "η is large" means > 60 mV or so...   863
... both β and i_0 can be obtained from a *J–E* curve in one direction...

Slope = $\frac{(1-\alpha)F}{2.3\,RT}$ Slope = $\frac{-\alpha F}{2.3\,RT}$

log i_0

Slope^{-1} = Tafel Slope ("mV per decade")

Note: The x axis is flipped... sorry

Figure 3.4.4 Tafel plots for anodic and cathodic branches of the current-overpotential curve for O + e ⇌ R with $\alpha = 0.5$, $T = 298$ K, and $j_0 = 10^{-6}$ A/cm^2.

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

863

… "η is large" means > 60 mV or so… **(SKIPPED)** 864
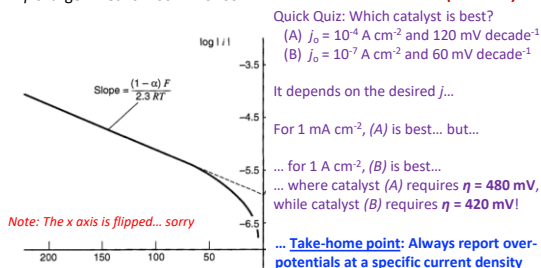
Quick Quiz: Which catalyst is best?
(A) $j_o = 10^{-4}$ A cm^{-2} and 120 mV decade^{-1}
(B) $j_o = 10^{-7}$ A cm^{-2} and 60 mV decade^{-1}

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 η = **480 mV**,
while catalyst *(B)* requires η = **420 mV**!

… **Take-home point**: Always report over-potentials at a specific current density

log $|i|$

-3.5

Slope = $\dfrac{(1-\alpha)F}{2.3\,RT}$

-4.5

-5.5

-6.5

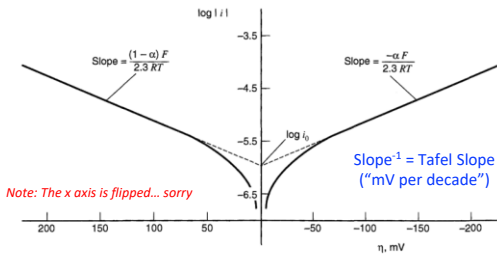*Note: The x axis is flipped… sorry*

200   150   100   50

Figure 3.4.4   Tafel plots for anodic and cathodic branches of the current-overpotential curve for $O + e \rightleftarrows R$ with $\alpha = 0.5$, $T = 298$ K, and $j_0 = 10^{-6}$ A/cm^2.

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

864

What does real data look like, so that I can indicate the overpotential?   865
(SKIPPED)

Water oxidation

… wait, where is $E^0(O_2,H^+/H_2O)$?

… 1.23 V *vs*. SHE… *but how can we tell where that occurs given this SCE scale and no mention of the pH value*?

… Oh… this is in base? Gotcha! Now I see why plotting on an RHE scale is nice for H$^+$-dependent reactions

UPD Co on Au

Au control

Current density (A/cm^2)

E (V vs SCE)
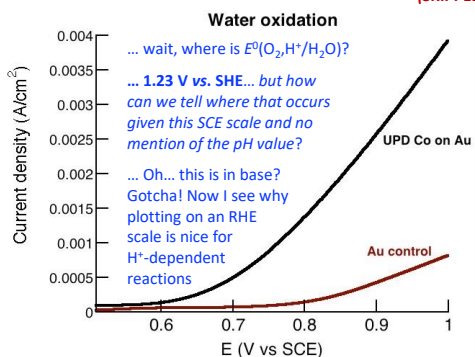
865

… wait, the Tafel Slope (in units of mV/decade) changes?   866
(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

ln [I]

Overpotential (V)

866

Recall, and for clarity, that we have already encountered an *(SKIPPED)* [867]
<u>overpotential</u>... and seen a case where it is important...

$$O + ne^- \leftrightharpoons R^{n-} \text{ (insoluble)}$$

$$C_R{}^* = 0$$

$C_O{}^* = \text{the bulk concentration of O}$

e.g. $Ag^+ + e^- \leftrightharpoons Ag^0$

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

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

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

867

Recall, and for clarity, that we have already encountered an *(SKIPPED)* [868]
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$C_O{}^* = \text{the bulk concentration of O}$

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

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

868

Recall, and for clarity, that we have already encountered an *(SKIPPED)* [869]
<u>overpotential</u>... 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...

869

17

What's happening here (<u>not electrocatalysis</u>)?   **(SKIPPED)** 870

$$O + ne^- \leftrightharpoons R^{n-} \text{ (insoluble)}$$

870

871
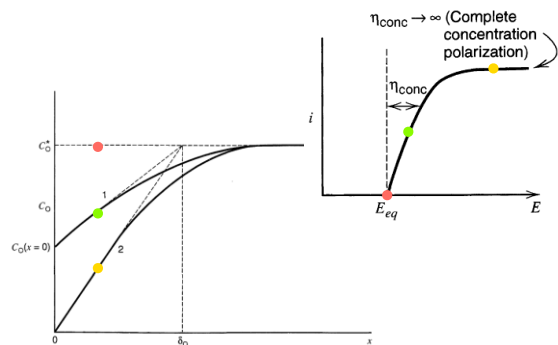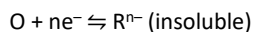
(SKIPPED)

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

871

872

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

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