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? $E_{\text{app}}$

What is the potential difference between one side and near the middle? $\sim E_{\text{app}}/2$

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

An ion transfers across the double layer... mind = blown, again!
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
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, $\mu_i$, 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)), the *standard Gibb’s free energy of activation*, $\Delta G^\ddagger$ is defined as follows... and electron-transfer reactions exhibit unique behavior...
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):

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

**THERMODYNAMICS**: A reaction is spontaneous if the \( \Delta G \) is negative, and thus \( \Delta E (E_{cell}) \) 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. \( \Delta G^0 (\Delta E^0, E^0_{cell}) \)) … Marcus Theory (Nobel Prize in Chemistry in 1992)

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.

---

... 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:
  1. Normal, (II) Barrierless, (III) Inverted

The nuclear reorganization energy, \( \lambda \), 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 \( \Delta G^0 = 0 \))

\[
\ln k = \begin{cases} 
-\Delta G^0 = \lambda \\
-\Delta G^0 < \lambda \\
-\Delta G^0 > \lambda 
\end{cases}
\]

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

... 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

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\]


... 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...


Electrochemical kinetics:

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

Derivation... start with the generic reaction:

\[
O + ne^- \rightleftharpoons R^{n-}
\]

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

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

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 $\eta = (E - E_{\text{eq}})$...

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

![Graph showing the reaction coordinate with standard free energy on the y-axis and reaction coordinate on the x-axis. Key points are labeled: Reactant, Activated complex, Product, $\Delta G_f^\dagger$, $\Delta G_{rxn}^0$, $\Delta G_b^\dagger$.](image)
... and here is the effect of electrode potential on the product and reactant free energy (Marcus) curves (not inverted!)...

\[ E = E_{\text{eq}} \]

\[ E < E_{\text{eq}} \]

\[ E > E_{\text{eq}} \]
here’s a thought experiment that gets us an expression for $k_f$:

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

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

Marcus Theory

Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 3.3.2
Here’s a thought experiment that gets us an expression for $k_f$:

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

(1) “O” is stabilized (i.e. lowered) by $F(E - E^0')$...

(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)...

Check this... Add’em up...

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

... (1) ... Nice!
... so after changing the potential from $E^{0'}$ to $E$:

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

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

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

$\alpha$ 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 $\beta$ is called the *symmetry factor*...

... *$\beta$ is the fundamental factor, not $\alpha$!* ...

... 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, $\beta$, of $E$ vs. $E^{0'}$ is screened by the double layer to modulate $\Delta G^{\ddagger}$

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

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

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

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

$$
k_f = A_f \exp \left( \frac{-\Delta G^\ddagger_c}{RT} \right) \quad k_b = A_b \exp \left( \frac{-\Delta G^\ddagger_a}{RT} \right)
$$

... 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 $E = E_0 = E_{eq}$, $C_O = C_R$ and $i = 0$ (equilibrium)... plugging 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 told you not to forget this equation!)

... 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 $f = \frac{F}{RT}$, which makes the expression a little more compact, but likely more difficult to interpret...

<table>
<thead>
<tr>
<th>potential independent</th>
<th>potential dependent</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_f = A_f \exp\left(\frac{-\Delta G_{0c}^{\ddagger}}{RT}\right)$</td>
<td>$\exp\left(\frac{-\alpha F (E - E_0')}{RT}\right)$</td>
</tr>
<tr>
<td>$k_b = A_b \exp\left(\frac{-\Delta G_{0a}^{\ddagger}}{RT}\right)$</td>
<td>$\exp\left(\frac{(1 - \alpha) F (E - E_0')}{RT}\right)$</td>
</tr>
</tbody>
</table>
... and now plug these into our expression for the current:

\[ i = i_c - i_a = -nF \Delta G^{\pm}_{0c} - k_b C_R(0, t) \]

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

\[
\begin{align*}
k_f &= k^0 \exp \left[ -\alpha f (E - E^{0'}) \right] \\
k_b &= k^0 \exp \left[ (1 - \alpha) f (E - E^{0'}) \right]
\end{align*}
\]

\[
\begin{align*}
k_f &= A_f \exp \left( \frac{-\Delta G^{\pm}_{0c}}{RT} \right) \exp \left( \frac{-\alpha F (E - E^{0'})}{RT} \right) \\
k_b &= A_b \exp \left( \frac{-\Delta G^{\pm}_{0a}}{RT} \right) \exp \left( \frac{(1 - \alpha) F (E - E^{0'})}{RT} \right)
\end{align*}
\]
... 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:

\[ i = c_i - a_i = -nFA[k_f C_O(0, t) - k_b C_R(0, t)] \]

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

replace \((E - E^{0'})\) with \(\eta = (E - E_{eq})\)...

... and \(i_0\) (B&F, pp. 98–99)

\[ i_0 = FAk^0 C^{\ast (1-\alpha)}_O C^{\ast \alpha}_R \]

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

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?

the exponential increase of $i_c$

Figure 3.4.1 Current-overpotential curves for the system $O + e \rightleftharpoons R$ with $\alpha = 0.5$, $T = 298$ K, $i_{t,c} = -i_{t,a} = i_t$ and $i_0/i_t = 0.2$. 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 (+, +)...
... now that I 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
... 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 $O + e \leftrightarrow R$ with $\alpha = 0.5$, $T = 298$ K, and $i_{l,c} = -i_{l,a} = i_l$. Numbers by curves show $i_0/i_l$. 

(SKIPPED)
... 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:

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

\( i_0 \) (\( j_0 \)) 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

\textbf{Note: These quadrants are flipped... but at least they are (−, −) and (+, +) now}

\textbf{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/cm\(^2\) (curve is indistinguishable from the current axis), (b) \( j_0 = 10^{-6} \) A/cm\(^2\), (c) \( j_0 = 10^{-9} \) A/cm\(^2\). For all cases the reaction is \( O + e \rightleftharpoons R \) with \( \alpha = 0.5 \) and \( T = 298 \) K.
$j_0$ can vary by up to twenty orders of magnitude! Consider just one reaction: proton reduction ($\text{H}_2$ evolution)...

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

To test materials in this table below Pt, do not use a CE made of Pt, because in acid $\text{PtO}_x$ dissolves!

10$^{10}$!
Sabatier Principle and Volcano plots for, for example, proton reduction (H₂ evolution)...

“Spillover” (synergism)

Simple, multistep electron-transfer mechanisms...

Volmer-Tafel mechanism

Volmer-Heyrovsky mechanism

chemical desorption

electrochemical desorption

... $\alpha$ values depend on the rate-determining step... they do not often add up to 1 for complex, multistep reactions... lots of fun kinetic analyses!
Simple, multistep electron-transfer mechanisms...

...it can get complex... imagine $\text{CO}_2 + 8e^- + 8\text{H}^+ \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$... Wow!
... and where $\alpha$ (or $\beta$) introduces asymmetry into this $J$–$E$ curve.

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

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 $T = 298$ K and $j_0 = 10^{-6}$ A/cm$^2$. 
note that for a one-electron-transfer reaction and $\alpha$ (or $\beta$) $< \frac{1}{2}$, oxidation is preferentially accelerated at any $\eta$ value.
note that for a one-electron-transfer reaction and $\alpha$ (or $\beta$) > $\frac{1}{2}$, reduction is preferentially accelerated at any $\eta$ value (SKIPPED)

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

Note: These quadrants are flipped... but at least they are ($-$, $-$) and ($+$, $+$) now.
... now, more specifically, $\alpha$ (actually $\beta$) is related to the symmetry of the barrier in the vicinity of the crossing point...

\[
\alpha = \frac{\tan \theta}{\tan \phi + \tan \theta}
\]

\(\tan = \frac{\text{opposite}}{\text{adjacent}}\)

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

\[\tan \theta = \frac{\alpha FE}{x}\]
\[\tan \phi = \frac{(1 - \alpha) FE}{x}\]
... if the barrier is symmetrical...

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

---

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

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

Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 3.3.4
... two limiting cases for the Butler–Volmer Equation are important...

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

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

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

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

- B–V: \( \exp(0.58) = 1.78 \)  
  T/M: \( 1 + 0.58 = 1.5 \) (error = -11%)
... two limiting cases for the Butler–Volmer Equation are important...

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

... first, if \( \eta \) 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 \( \alpha \)!
... and it looks ohmic.
... two limiting cases for the Butler–Volmer Equation are important...

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

... if, instead, \( \eta \) is large, then either \( i_c \) or \( i_a \) can be neglected...

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

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

\[ i = -i_0 \exp(-\alpha f \eta) \ldots \quad \ln|i| = \ln(i_0) - \alpha f \eta \]

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

\[ i = +i_0 \exp(-(1 - \alpha)f \eta) \ldots \quad \ln|i| = \ln(i_0) + (1 - \alpha)f \eta \]
Slope -1 = Tafel Slope ("mV per decade")

Figure 3.4.4  Tafel plots for anodic and cathodic branches of the current-overpotential curve for O + e ⇌ R with α = 0.5, T = 298 K, and j0 = 10⁻⁶ A/cm².

Note: The x axis is flipped... sorry
Quick Quiz: Which catalyst is best?
(A) $j_o = 10^{-4} \text{ A cm}^{-2}$ and 120 mV decade$^{-1}$
(B) $j_o = 10^{-7} \text{ A cm}^{-2}$ 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!

**Note:** The x axis is flipped... sorry

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

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**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/cm$^2$.

$^9$Note that for $\alpha = 0.5$, $b = 0.118$ V, a value that is sometimes quoted as a “typical” Tafel slope.
What does real data look like, so that I can indicate the overpotential?

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

\[ O + ne^- \rightleftharpoons R^{n-} \text{ (insoluble)} \]

\[ C_R^* = 0 \]

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

e.g. \( Ag^+ + e^- \rightleftharpoons Ag^0 \)

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

\[ E = E^0' + \frac{RT}{nF} \ln C_O^* + \frac{RT}{nF} \ln \left( \frac{i_l - i}{i_l} \right) \]

\[ E - E_{eq} = \eta_{conc} = \frac{RT}{nF} \ln \left( \frac{i_l - i}{i_l} \right) \]
Recall, and for clarity, that we have already encountered an overpotential... and seen a case where it is important...

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O + \text{ne}^- \rightleftharpoons R^{n-} \text{ (insoluble)}
\]

\[
C_R^* = 0
\]

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

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

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

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

...**Interpretation:** An extra potential, beyond \( E_{\text{eq}} \), is required to drive mass transfer of species to the electrode surface...
What's happening here (not electrocatalysis)?

\[ O + ne^- \rightleftharpoons R^{n-} \text{ (insoluble)} \]
An overpotential that is derived from rate-limiting mass transfer alone is called a *concentration overpotential*, $\eta_{\text{conc}}$...

... 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