Lecture #15 of 17

Q: What's in this set of lectures?
A: B&F Chapter 3 main concepts:

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

RECALL FROM LAST TIME... Marcus Theory...

- 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...

Cross & Miller, Science, 1988, 240, 440
RECALL FROM LAST TIME...

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

* Linearized Marcus Theory

... Add'em up...
1) "O" is stabilized (i.e. lowered) by $R(E-E_0')$, 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:

\[ R(E-E_0') = (1-\alpha)F(E-E_0') + \alpha F(E-E_0) \]

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 $E$:

\[ \Delta G_a^c = \Delta G_{0a}^c - (1-\alpha)F(E-E_0') \]
\[ \Delta G_c^c = \Delta G_{0c}^c + \alpha F(E-E_0') \]

\(\Delta G_{0c}^c\) is just $\Delta G_c^\circ$ at $E_0' = E_{eq} \)

... so after changing the potential from $E_0'$ to $E$:

\[ \Delta G_a^c = \Delta G_{0a}^c - (1-\alpha)F(E-E_0') \]
\[ \Delta G_c^c = \Delta G_{0c}^c + \alpha F(E-E_0') \]

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

\[ k_f = A_f \exp \left( \frac{-\Delta G_c^c}{RT} \right) \]
\[ k_b = A_b \exp \left( \frac{-\Delta G_a^c}{RT} \right) \]
so after changing the potential from $E^0'$ to $E$:

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

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

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

$$k_f = A_f \exp \left( -\frac{\Delta G^\dagger_c}{RT} \right)$$

$$k_b = A_b \exp \left( -\frac{\Delta G^\dagger_a}{RT} \right)$$

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

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

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

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

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

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

When $E = E^0' = E_{eq}$, $C_O = C_i$ 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!)
When $E = E^{eq}$, $C_0 = C_R$ and $i = 0$ (equilibrium)… plugging into our expression for the current,

\[ i = i_c - i_s = nF[A_k C_O(0, t) - k_b C_P(0, t)] \]

… results in $k_f = k_b = k^0$, the standard heterogeneous electron transfer rate constant…

<table>
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… and like many textbooks, B&F defines a new variable $f = \gamma_{exp}$, which makes the expression a little more compact, but maybe a little harder to interpret…

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and so using \( f \) and \( k^0 \) for the yellow part (\( \Delta G^\ddagger_{0c} = \Delta G^\ddagger_{0a} \) only when \( C_0 = C_R \)), we can write even more compact expressions for \( k_f \) and \( k_b \):

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

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    k_f &= A_f \exp \left( -\frac{\Delta G^\ddagger_{0c}}{RT} \right) \exp \left( -\frac{\alpha F (E - E^0)}{RT} \right) \\
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... and now plug these into our expression for the current:

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

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

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

\[
i = -FEk^0 \left[ C_O(0, t)e^{-\alpha f (E - E^0)} - C_R(0, t)e^{(1 - \alpha) f (E - E^0)} \right]
\]

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

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

\[ i = FAK_0 \left[ \frac{C_O(0, t)e^{-\alpha f(E - E^0)}}{C^*_O} - \frac{C_R(0, t)e^{(1-\alpha)f(E - E^0)}}{C^*_R} \right] \]

replace \((E - E^0)\) with \(\eta = (E - E_{eq})\)...
and \(i_i = FAK_0 C_O^{K^0 - \alpha} C^*_R^{\alpha}\)

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

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

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

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replace \((E - E^0)\) with \(\eta = (E - E_{eq})\)...
and \(i_i = FAK_0 C_O^{K^0 - \alpha} C^*_R^{\alpha}\)

eliminate effects due to mass transfer...
... stir well... 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 Eq. 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 (+, +)...

the Current–Overpotential Equation

What do these equations predict? * Note: These quadrants are flipped... but at least they are (−, −) and (+, +)...

the exponential increase of $i_c$...

the exponential increase of $i_a$

What do these equations predict? * Note: These quadrants are flipped... but at least they are (−, −) and (+, +)...

the Current–Overpotential Equation
if mass transport effects can be neglected (by rapidly stirring the solution, for example), then the Butler–Volmer Eq. is valid:

\[
i = i_0 e^{-\alpha F \eta / R T}
\]

... a challenge in all types of kinetic analyses is making the mass-transfer-limited current, \(i_0\), high enough so that a kinetically-controlled reaction rate is observed...

\[
i_0 (\eta) \text{ is called the exchange current (density) and is the current that is equal and opposite at an electrode at equilibrium (think microscopic reversibility).}
\]

... it is the most convenient indicator of the kinetic facility of an electrochemical reaction...
\( j_0 \) can vary over twenty orders of magnitude! Consider just one reaction: proton reduction (\( \text{H}_2 \) evolution).

<table>
<thead>
<tr>
<th>Metal</th>
<th>( j_0 ) (A cm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palladium, Pd</td>
<td>( 1.0 \times 10^{-1} )</td>
</tr>
<tr>
<td>Platinum, Pt</td>
<td>( 8.0 \times 10^{-6} )</td>
</tr>
<tr>
<td>Rhodium, Rh</td>
<td>( 2.5 \times 10^{-5} )</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^{-5} )</td>
</tr>
<tr>
<td>Gold, Au</td>
<td>( 4.0 \times 10^{-5} )</td>
</tr>
<tr>
<td>Tungsten, W</td>
<td>( 1.3 \times 10^{-3} )</td>
</tr>
<tr>
<td>Niobium, Nb</td>
<td>( 1.5 \times 10^{-3} )</td>
</tr>
<tr>
<td>Titanium, Ti</td>
<td>( 7.0 \times 10^{-4} )</td>
</tr>
<tr>
<td>Cadmium, Cd</td>
<td>( 1.5 \times 10^{-5} )</td>
</tr>
<tr>
<td>Manganese, Mn</td>
<td>( 1.3 \times 10^{-6} )</td>
</tr>
<tr>
<td>Thallium, TI</td>
<td>( 1.0 \times 10^{-1} )</td>
</tr>
<tr>
<td>Lead, Pb</td>
<td>( 1.0 \times 10^{-1} )</td>
</tr>
<tr>
<td>Mercury, Hg</td>
<td>( 0.5 \times 10^{-1} )</td>
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To test the materials below Pt, don't use a CE made of Pt as in acid PtO\(_x\) dissolves!

Sabatier Principle and Volcano plots for, for example, proton reduction (\( \text{H}_2 \) evolution).

\[ \text{Parsons, Trans. Faraday Soc., 1958, 54, 1053} \]
\[ \text{Trasatti, Electroanal. Chem. Interfac. Electrochem., 1972, 39, 163} \]
Sabatier Principle and Volcano plots for, for example, proton reduction (H₂ evolution)...
Simple, multistep electron-transfer mechanisms...

… Tafel slope depends on rate-determining step… fun kinetics!

… it can get complex… imagine \( \text{CO}_2 + 8e^- + 8H^+ \rightarrow CH_4 + 2H_2O \)
... and where \( \alpha \) introduces asymmetry into this \( J-E \) curve

\[ i = i_0 e^{\frac{-\alpha \eta}{1 - \alpha \eta}} \]

the Butler–Volmer Equation

![Diagram](image)

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

...note that when \( \alpha < \frac{1}{2} \), at any \( \eta \) value, oxidation is preferentially accelerated

![Diagram](image)

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...note that when \( \alpha > \frac{1}{2} \), at any \( \eta \) value, reduction is preferentially accelerated

![Diagram](image)

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... now, more specifically, $\alpha$ is related to the symmetry of the barrier in the vicinity of the crossing point...

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

tan $\theta$ = opposite/adjacent

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

\[
\tan \theta = \frac{\alpha \text{FE}}{x}
\]
\[
\tan \phi = \frac{(1 - \alpha) \text{FE}}{x}
\]

... 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...

\[
\alpha > \frac{1}{2}
\]

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

... two limiting cases for the B-V Eq. are important...

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

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

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

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\]

What’s small?

- \( \exp(0) = 1 \)  \( 1 + 0 = 1 \) (error = 0\%)
- \( \exp(1) = 2.7 \)  \( 1 + 1 = 2 \) (error = -26\%)

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

\( \exp(0.58) = 1.78 \)  \( 1 + 0.58 = 1.58 \) (error = -11\%)
… two limiting cases for the B-V Eq. are important…

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

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

\[ i = -i_0 \left[ 1 + (-\alpha f\eta) - (1 + (1 - \alpha)f\eta) \right] = +i_0f\eta \]

Note: no \( \alpha! \)
… and ohmic

… two limiting cases for the B-V Eq. are important…

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

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

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

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

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

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

\[ i = +i_0 \exp(-(1 - \alpha)f\eta) \ldots \quad \ln|i| = \ln(i_0) + (1 - \alpha)f\eta \]

both \( \alpha \) and \( i_0 \) (and thus \( k_0 \)) can be obtained from a \( J-E \) curve in one direction…

![Graph showing Tafel plots for anodic and cathodic branches of the current-overpotential relationship](image)

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

Tafel Slope \(^1\) = Tafel Slope (\(^*\)mV per decade\(^*\))

\[^1\text{Note that for } \alpha = 0.5, b = 0.138 \text{ V, a value that is sometimes quoted as a "typical" Tafel slope.}\]

Figure 3.4: Tafel plots for anodic and cathodic branches of the current-overpotential relationship for \( \theta = e \) or \( \theta = R \) with \( \alpha = 0.5, F = 298 \text{ K, and } i_0 = 10^{-5} \text{ Acm}^2. \)
... note: "\( \eta \) is large" means > 120 mV or so

\[ \text{Slope}^1 = \text{Tafel Slope} \quad (\text{"mV per decade"}) \]

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Figure 3.4.4 Tafel plots for anodic and cathodic branches of the current-overpotential curve for \( O = \text{e} R \) with \( n = 0.5, F = 298 \text{ K}, \text{and } j_0 = 10^{-9} \text{ A/cm}^2 \).

*Note that for \( n = 0.5, \theta = 0.138 \text{ V}, a \text{ value that is sometimes quoted as a "typical" Tafel slope.}"

---

Which catalyst is best?
(A) \( j_0 = 10^{-6} \text{ A/cm}^2 \) and 120 mV decade\(^{-1}\)
(B) \( j_0 = 10^{-7} \text{ A/cm}^2 \) and 60 mV decade\(^{-1}\)

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It depends on the desired \( j_\)...

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... note: "η is large" means > 120 mV or so

Which catalyst is best?
(A) \( j_0 = 10^{-4} \, \text{A cm}^{-2} \) and 120 mV decade^{-1}
(B) \( j_0 = 10^{-7} \, \text{A cm}^{-2} \) and 60 mV decade^{-1}

It depends on the desired \( j \)...

For 1 mA cm\(^2\), (A) is best... but...

Figure 3A.4 Table plots for anodic and cathodic branches of the current-overpotential curve for \( O = e + R \) with \( u = 0.5 \), \( T = 298 \, \text{K} \), and \( j_0 = 10^{-9} \, \text{A/cm}^2 \).

*Note: The x axis is flipped; sorry.

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

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

*Note: The x axis is flipped; sorry.

... for 1 A cm\(^2\), (B) is best...

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• **Laboratory #7 Wrap-Up will be presented now**
  • Discuss the activity and its purpose
  • Provide some example results
  • Provide feedback on the activity
  • Recommend other related activities
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OH⁻/H₂O electrocatalysis

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

Water oxidation

... wait, where is \( E^{\circ} (O_2/H_2O) \)?

... \( 1.23 \text{ V vs. SHE} \) ... but how can we tell where that occurs given this SCE scale and no mention of the pH value?
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

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

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

$O + ne^- \rightleftharpoons R^(n-)$ (insoluble)

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

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...

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

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

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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...

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

\[ C_{O^*} = 0 \]

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

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

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)
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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 overpotential... and seen a case where it is important...

\[ \eta_{conc} \rightarrow \text{(Complete concentration polarization)} \]

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

What's happening here (not electrocatalysis)?

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

It's also called a concentration polarization.

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

... we are almost finished this topic...