Lecture #15 of 18
In conclusion, with the GCS Model, we have a semi-quantitative understanding of this interface with some predictive power…

Now what about this behavior…

… plus Faradaic charge-transfer kinetics?!?!?!

… Oh yeah!!! …

… Now we're talking!
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, 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

**Electrode kinetics**, … finally!
Flashback/Warm-up... Previously, we distinguished between two classifications of electrochemical cells:

1. galvanic: $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} > 0.0 \text{ V}$, and the cell spontaneously “discharges”

2. electrolytic: $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} < 0.0 \text{ V}$, and a voltage $E_{\text{cell}}$ must be applied in order for the cell reaction to proceed

Figure 1.3.1  (a) Galvanic and (b) electrolytic cells.
Recall, electrolytic cells require a potential bias to offset $E_{\text{cell}}$ ($E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} < 0.0 \text{ V}$) in order for the cell reaction to proceed.

* Assume that each curve (positive & negative current) was obtained independently by a 3-electrode measurement
Recall, electrolytic cells require a potential bias to offset $E_{\text{cell}}$ ($E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} < 0.0 \text{ V}$) in order for the cell reaction to proceed.

* Assume that each curve (positive & negative current) was obtained independently by a 3-electrode measurement.

What is this curvature due to?

... Kinetics!!!

... Oh yeah!!! ...
... and that for galvanic cells $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} > 0.0 \text{ V}$, and the cell spontaneously “discharges”... But at what rate?

* Again, assume that each curve (positive & negative current) was obtained independently by a 3-electrode measurement

Note: $E_{\text{cathode}} - E_{\text{anode}}$ will be $> 0$ in this case
... and that for galvanic cells \( E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} > 0.0 \text{ V}, \)
and the cell spontaneously “discharges”... But at what rate?

... a, b, or c... and why?

* Again, assume that each curve (positive & negative current) was obtained independently by a 3-electrode measurement

Note: \( E_{\text{cathode}} - E_{\text{anode}} \) will be \( > 0 \) in this case
Devise an electrochemical cell for which the following reaction can be made to occur:

\[ \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- \]

a) What half-cell reactions would be useful to setup this reaction?
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**cathode:** \[ 2\text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{H}_2 + 2\text{OH}^- \] \( E^0 = -0.828 \text{ V vs. SHE} \)

**anode:** \[ \text{H}_2 \rightleftharpoons 2\text{H}^+ + 2\text{e}^- \] \( E^0 = 0.000 \text{ V vs. SHE} \)

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a final example, to start this off: B&F Problems 2.1 (a) and 2.7

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\[ \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- \]

… are there reductions that are more thermodynamically favorable at Pt (i.e. that have a larger, less negative, \( E^0 \))?

- \[ \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2\text{O}_2 \] \[ E^0 = 0.695 \text{ V vs. SHE} \]
- \[ \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O} \] \[ E^0 = 1.229 \text{ V vs. SHE} \]
- \[ \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightleftharpoons 2\text{OH}^- \] \[ E^0 = 0.401 \text{ V vs. SHE} \]

Yes, if \( \text{O}_2 \) is around, so it will be important to exclude \( \text{O}_2 \)!
a final example, to start this off: B&F Problems 2.1 (a) and 2.7

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\[ \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- \]

… what about oxidations? Are there any with a *more negative* $E^0$?

\[ \text{H}_2\text{O? O}_2? \text{N}_2? \quad \ldots \quad \text{Nope!} \]
so the situation is as illustrated here:

\[ 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \]

\[ H_2 \rightarrow 2H^+ + 2e^- \]

\[ O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad E_0 = 0.695 \text{ V vs. SHE} \]
\[ O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad E_0 = 1.229 \text{ V vs. SHE} \]
\[ O_2 + 2H_2O + 4e^- \rightarrow 2OH^- \quad E_0 = 0.401 \text{ V vs. SHE} \]

these will produce a galvanic cell that consumes \( O_2 \)...
so the situation is as illustrated here:

a galvanic cell that exists in the presence of $O_2$

does not produce a galvanic cell

our electrolytic cell

cathodic current

$H_2 \rightarrow 2H^+ + 2e^-$

anodic current

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

... these will produce a galvanic cell that consumes $O_2$
we are not concerned with it in this example, but, as above, an important property of galvanic cells pertaining to Chapter 3 is apparent in this diagram...

... overpotential effects...

... these will produce a galvanic cell that consumes O₂

... the power output is set by the load (resistance) in the external circuit
a final example, to start this off: B&F Problems 2.1 (a) and 2.7

Devise an electrochemical cell for which the following reaction can be made to occur:

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a) What half-cell reactions would be useful to setup this reaction?

\[
\begin{align*}
\text{cathode:} & \quad 2\text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{H}_2 + 2\text{OH}^- \\
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E^0 &= 0.000 \text{ V vs. SHE}
\end{align*}
\]

Anyway…

b) What does a cell look like that can do these two reactions?

\[
\begin{align*}
\text{cathode:} & \quad \text{Pt/H}_2 (P_{\text{H}_2} = 1 \text{ bar}), \text{KOH (1.00 M)} \\
\text{anode:} & \quad \text{Pt/H}_2 (P_{\text{H}_2} = 1 \text{ bar}), \text{HClO}_4 (1.00 \text{ M})
\end{align*}
\]

c) Is a salt bridge necessary?
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\end{align*}

b) What does a cell look like that can do these two reactions?

\[ \text{Pt/H}_2 \ (P_{\text{H}_2} = 1 \text{ bar}), \ \text{KOH or HClO}_4 \ (1.00 \text{ M}) \]

c) Is a salt bridge necessary?

Yes, or else the initial pH gradient will not be present for very long… … and given use of a salt bridge (or glass frit), what type of potential drop exists in/across the frit? A liquid junction potential!
that’s B&F Problem 2.1 (a), **what about 2.7?**

Obtain the *autoprotolysis constant* (IUPAC) of water, $K_w$, using this cell
… that’s B&F Problem 2.1 (a), **what about 2.7?**

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... at **standard state**, $E_{\text{cell}} = E^{0}_{\text{cathode}} - E^{0}_{\text{anode}} = -0.828$ V, and given...

$$E^{0}_{\text{H}_2\text{O}/\text{H}_2,\text{OH}^-} = \frac{0.05916 \text{ V}}{2} \log \left( \frac{[\text{OH}^-]^2}{1} \right) \quad E^{0}_{\text{H}^+ / \text{H}_2} = \frac{0.05916 \text{ V}}{2} \log \left( \frac{1}{[\text{H}^+]^2} \right)$$

$$2\text{H}_2\text{O} + 2e^- \rightleftharpoons \text{H}_2 + 2\text{OH}^- \quad \text{(cathode)} \quad 2\text{H}^+ + 2e^- \rightleftharpoons \text{H}_2 \quad \text{(anode)}$$
… that’s B&F Problem 2.1 (a), what about 2.7?

Obtain the autoprotolysis constant (IUPAC) of water, $K_w$, using this cell

… at standard state, $E_{\text{cell}} = E_{\text{cathode}}^0 - E_{\text{anode}}^0 = -0.828 \text{ V}$, and given…

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2H$_2$O + 2e$^-$ $\iff$ H$_2$ + 2OH$^-$  
(cathode)  

2H$^+$ + 2e$^-$ $\iff$ H$_2$  
(anode)

$$E_{\text{H}_2\text{O}/\text{H}_2,\text{OH}^-}^0 - E_{\text{H}^+/\text{H}_2}^0 = -0.828 \text{ V} = \frac{0.05916 \text{ V}}{1} \log ([\text{H}^+][\text{OH}^-])$$
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\[-0.828 \text{ V} = (0.05916 \text{ V}) \log(K_w)\]
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$$-0.828 \text{ V} = (0.05916 \text{ V}) \log (K_w)$$

$$-14 = \log (K_w) \quad \Rightarrow \quad K_w = 10^{-14}$$
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, TST (ACT), Marcus Theory)

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- Section 3.5: Multistep ET Mechanisms

(Electrode) kinetics, ... finally!
From transition state theory (TST) (activated complex theory (ACT)), the *standard Gibb’s free energy of activation*, $\Delta G^\dagger$ is defined as... and there is something *really* neat about ET rxns!

(or transition state)

![Diagram showing energy changes in a reaction coordinate](image)
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 electron transfer reactions!

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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):

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

- **THERMODYNAMICS**: A reaction is favorable if the $\Delta G$ is negative, and thus $\Delta E (E_{\text{cell}})$ is positive

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

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\]

- **THERMODYNAMICS**: A reaction is favorable 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. $\Delta G^0 (\Delta E^0, E_{cell}^0)$)

... 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.

[Image of Potential Energy Surfaces, Profile and 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

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

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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 product energy potential energy well... but at the nuclear arrangement of the reactant and for $\Delta G^0 = 0$

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$$
\ln k = -\Delta G^0 = \lambda
$$

$$
-\Delta G^0 < \lambda
$$

$$
-\Delta G^0 > \lambda
$$

$$
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)
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… Marcus Theory… **Confirmation**!

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\[
\lambda_s = 0.75 \text{ eV} \\
\lambda_v = 0.45 \text{ eV}^{-1} \\
\omega = 1500 \text{ cm}^{-1}
\]

### Experimental Confirmation of Inverted Region

![Graph showing experimental confirmation of inverted region](image)

### The Inverted Region Effect

\[ \ln k \]

\[ -\Delta G^0 = \lambda \]

- \( -\Delta G^0 < \lambda \)
- \( -\Delta G^0 > \lambda \)

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


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[Experimental Confirmation of Inverted Region](http://www.nobelprize.org/nobel_prizes/chemistry/laureates/1992/marcus-lecture.pdf)
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**Electrode kinetics, ... finally!**
Phenomenological electrochemical kinetics:

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

Derivation... start with the generic reaction:

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

the rate of the forward and backward reactions are:

\[
v_f = k_f \text{C}_\text{O}(0, t) = \frac{-i_c}{nFA}
\]
\[
v_b = k_b \text{C}_\text{R}(0, t) = \frac{i_a}{nFA}
\]

The units of \( v \) are moles cm\(^{-2}\) s\(^{-1}\), and that means \( k_b \), and \( k_f \), have units of...
Phenomenological electrochemical kinetics:

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

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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 reaction rate, \( v_{\text{net}} \), will therefore be 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:

\[
i = i_c - i_a = -nFA[k_f C_O(0, t) - k_b C_R(0, t)]
\]
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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 me… we’ll be back to this 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, $\Delta G^\dagger$…
Again, from transition state theory (TST) (activated complex theory (ACT)), the standard Gibb's free energy of activation, $\Delta G^\ddagger$ is defined as...

(or transition state)
... and here is the effect of electrode potential on the product and reactant free energy (Marcus) curves (Not inverted!)...

\[ E = E_{eq} \]

\[ E < E_{eq} \]

\[ E > E_{eq} \]
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 $E$?

* Marcus Theory

* assume $E_{eq} = E^0'$
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 $E$?

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What happens to $\Delta G_{c}^\ddagger$ and $\Delta G_{a}^\ddagger$ when the potential is changed by $E$?

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

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

* Linearized Marcus Theory

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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 \( E \)?

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 \textit{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 \textit{cathodic} barrier became larger.

* Linearized Marcus Theory

* assume \( E_{eq} = E^0' \)
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 \( E \)?

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.

4) … and the anodic barrier just decreased by \( (1 - \alpha)F(E - E^0') \)…
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 $E$?

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* Assume $E_{eq} = E^0'$

* Linearized Marcus Theory

... Add’em up… that is, 3) + 4) = …
here's a thought experiment that gets us an expression for $k_f$:

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* Linearized Marcus Theory

* assume $E_{eq} = E_0'$

… Add’em up…

that is, 3) + 4) = …

… 1) … Nice!
\[ \Delta G^\ddagger_a = \Delta G^\ddagger_{0a} - (1 - \alpha)F(E - E^{0'}) \]

\[ \Delta G^\ddagger_c = \Delta G^\ddagger_{0c} + \alpha F(E - E^{0'}) \]

\( \alpha \), the *transfer coefficient* \([0, 1]\), is the fraction of \( E - E^{0'} \) applied to the *cathodic* reaction

\( \Delta G^\ddagger_{0c} \) is just \( \Delta G^\ddagger_c \) at \( E^0 \) \((= E_{eq})\)
so after changing the potential from $E^0'$ to $E$:

\[
\Delta G_{a}^{\pm} = \Delta G_{0a}^{\pm} - (1 - \alpha)F(E - E^0')
\]

\[
\Delta G_{c}^{\pm} = \Delta G_{0c}^{\pm} + \alpha F(E - E^0')
\]

… substitute these into the Arrhenius equations for $k_f$ and $k_b$…

\[
k_f = A_f \exp \left( \frac{-\Delta G_{c}^{\pm}}{RT} \right)
\]

\[
k_b = A_b \exp \left( \frac{-\Delta G_{a}^{\pm}}{RT} \right)
\]
\[ k_f = A_f \exp \left( \frac{-\Delta G_c^\dagger}{RT} \right) \]

\[ k_b = A_b \exp \left( \frac{-\Delta G_a^\dagger}{RT} \right) \]

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

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

\[ k_b = A_b \exp \left( \frac{-\Delta G_{0a}^\dagger}{RT} \right) \exp \left( \frac{(1 - \alpha) F (E - E^{0'})}{RT} \right) \]
\[ k_f = A_f \exp \left( \frac{-\Delta G_{0c}^\ddagger}{RT} \right) \exp \left( \frac{-\alpha F (E - E^{0'})}{RT} \right) \]

\[ k_b = A_b \exp \left( \frac{-\Delta G_{0a}^\ddagger}{RT} \right) \exp \left( \frac{(1 - \alpha) F (E - E^{0'})}{RT} \right) \]
When $E = E^0$ = $E_{\text{eq}}$, $C_O = C_R$ and $i = 0$ (equilibrium), and 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 me!)

\[
\begin{align*}
k_f &= A_f \exp \left( \frac{-\Delta G_{0c}^\dagger}{RT} \right) \exp \left( \frac{-\alpha F (E - E^{0'})}{RT} \right) \\
k_b &= A_b \exp \left( \frac{-\Delta G_{0a}^\dagger}{RT} \right) \exp \left( \frac{(1 - \alpha) F (E - E^{0'})}{RT} \right)
\end{align*}
\]
When $E = E^{0'} = E_{eq}$, $C_O = C_R$ and $i = 0$ (equilibrium), and plugging into our expression for the current,

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

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

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

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

... 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 $k^0$ equals the yellow part...

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

$$k_b = A_b \exp\left(\frac{-\Delta G_{0a}^\dagger}{RT}\right) \exp\left(\frac{(1 - \alpha) F (E - E^0')}{RT}\right)$$
When \( E = E^{0'} = E_{eq} \), \( C_O = C_R \) and \( i = 0 \) (equilibrium), and plugging into our expression for the current,

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

... 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 \( k^0 \) 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 maybe a little harder to interpret...

<table>
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<td>( k_f = A_f \exp \left( -\frac{\Delta G^{\ddagger}_{0c}}{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^{\ddagger}_{0a}}{RT} \right) )</td>
<td>( \exp \left( \frac{(1 - \alpha) F (E - E^{0'})}{RT} \right) )</td>
</tr>
</tbody>
</table>
... and so using $f$ and $k^0$ for the yellow part ($\Delta G^\ddagger_{0c} = \Delta G^\ddagger_{0a}$), we get even more compact expressions for $k_f$ and $k_b$...

\[
k_f = A_f \exp \left( \frac{-\Delta G^\ddagger_{0c}}{RT} \right) \exp\left( -\alpha f (E - E^0') \right)
\]

\[
k_b = A_b \exp \left( \frac{-\Delta G^\ddagger_{0a}}{RT} \right) \exp\left( (1 - \alpha) f (E - E^0') \right)
\]

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

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

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

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

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

\[ i = -FAk^0 \left[ C_O(0, t)e^{-\alpha f(E - E_0')} - C_R(0, t)e^{(1-\alpha)f(E - E_0')} \right] \]

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 mass transfer effects
Butler–Volmer Equation:

\[ i = -i_0 \left[ \frac{e^{-\alpha f \eta}}{C^*_O} - \frac{e^{(1-\alpha)f\eta}}{C^*_R} \right] \]

... 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)

\[ i_0 = FAk^0 C^*_O C^*_R \]

eliminate effects due to mass transfer...

... stir well... or pass a small current...

or use surface-adsorbed species!
B–V Eq. 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

Figure 3.4.1 Current–overpotential curves for the system O + e ⇄ R with α = 0.5, T = 298 K, \( i_{t,c} = -i_{t,a} = i_i \) and \( i_0/i_i = 0.2 \). 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