Q: What was 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

But wait! You told us that Marcus Theory led to an inverted region… is there evidence for the inverted region via electrochemistry?

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

\[ \Delta G^0 < \lambda \quad \Delta G^0 > \lambda \]

... and you told us that this had a Gaussian shape...

$E_{\text{bias}}$ varies the probability function (0, 1)… resulting in (D)istributions of occupied metal states

$\rho$ has units of cm$^{-2}$ eV$^{-1}$

$\rho$ and has units of cm$^{-3}$ eV$^{-1}$

... one cannot easily detect the inverted region! Thank you, Fermi, Marcus & Gerischer!
... one cannot easily detect the inverted region!

\[ \rho \text{ has units of } \text{cm}^2 \text{eV}^{-1} \]

... and has units of \( \text{cm}^{-3} \text{eV}^{-1} \)

\[ \Phi_{\text{bulk}}(E) = \frac{1}{2} \left( 1 + \exp\left( \frac{E - E_c}{k_B T} \right) \right) \]

... it's that Gaussian term!

... the rate of electron transfer is dictated by the law of mass action 1175

\[ k = \int e^{-\frac{E}{k_B T}} \Phi_{\text{electrode}}(E) \Phi_{\text{bulk}}(E) \text{d}E \]

... the rate of electron transfer is dictated by the law of mass action 1176

\[ k = \int e^{-\frac{E}{k_B T}} \Phi_{\text{electrode}}(E) \Phi_{\text{bulk}}(E) \text{d}E \]

\[ E_{\text{bias}} \text{ varies the probability function } (0, 1) \]

... resulting in (D)istributions of occupied metal states & molecule states

\[ \rho \text{ has units of } \text{cm}^3 \text{eV}^{-1} \]

... and has units of \( \text{cm}^{-3} \text{eV}^{-1} \)

... it's that Gaussian term!
... the rate of electron transfer is dictated by the law of mass action

\[ k_t = \nu \int_{-\infty}^{\infty} \epsilon_{\text{mol}}(E)W_{\text{s}(E, E)}(1 - f(E))\rho(E)dE = 0 \]

\[ k_t = \nu \int_{-\infty}^{\infty} \epsilon_{\text{mol}}(E)W_{\text{s}(E, E)}(1 - f(E))\rho(E)dE \]

\( E_{\text{bias}} \) varies the probability function (0, 1)
... resulting in distributions of occupied metal states & molecule states

... experimental validation of the theory and lack of inverted region

\[ \kappa_{01}(x) = \kappa_{01} \exp(-\beta x) \]  

(3.6.39)

Sikes, Smalley, Dudek, Cook, Newton, Chidsey & Feldberg, Science, 2001, 291, 1519
Chidsey, Science, 1991, 251, 919

... experimental validation of the theory and lack of inverted region

\( \lambda = 0.85 \text{ eV} \)

Chidsey, Science, 1991, 251, 919
... experimental validation of the theory and lack of inverted region

... and there was no inverted region because at large driving forces there was always a state in the metal that overlapped the most probable $D_0$

Chidsey, Science, 1991, 251, 919

... experimental validation of the theory and lack of inverted region

... and there was no inverted region because at large driving forces there was always a state in the metal that overlapped the most probable $D_0$

Chidsey, Science, 1991, 251, 919

... experimental validation of the theory and lack of inverted region

... and there was no inverted region because at large driving forces there was always a state in the metal that overlapped the most probable $D_0$

Chidsey, Science, 1991, 251, 919
Well, that was disappointing… when is there an inverted region? … at semiconductors! … but how?

![Diagram]


Well, that was disappointing… when is there an inverted region? … at semiconductors! … but how?

![Diagram]


Well, that was disappointing… when is there an inverted region? … at semiconductors! … but how?

… Vary the molecule, not the bias! … but $\lambda$ must be “the same” for each!

![Diagram]

Well, that was disappointing… when is there an inverted region? … at semiconductors!

\[ \lambda = 0.67 \text{ eV} \]

... cm² s⁻¹... a second order rate constant (... x concentration²)

... but more work is still needed in order to really validate this!

Hamann, Gstine, Brunschwig & Lewis, JACS, 2005, 127, 7815 and JACS, 2005, 127, 13949
Let’s summarize the steady-state behavior from the entire course…

… by looking at data on stirred (non-hysteretic) $I$–$E$ ($J$–$E$) curves…

… and at each location, let’s think about what resistance (not impedance, as no AC contribution) is limiting the observed behavior…

\[ \text{Incorrect circuit representation of an electrochemical cell} \]
\[ \text{(but good enough at this stage for illustration purposes)} \]

Let’s summarize the steady-state behavior from the entire course…

… by looking at data on stirred (non-hysteretic) $I$–$E$ ($J$–$E$) curves…

… and at each location, let’s think about what resistance (not impedance, as no AC contribution) is limiting the observed behavior…

… so, we want to know what dictates $R = \frac{\partial I}{\partial E}$ at each $E$…

**Fe$^{3+}$ and $H^+$ electrocatalysis**

\[ H^+ \text{ electrocatalysis} \]

RECALL… Let’s compare **total capacitance** ($C$) and **differential capacitance** ($C_d$) as follows:

\[
C_d = \left( \frac{\partial \sigma M}{\partial E} \right)
\]

\[
\frac{q}{E} = C
\]

**Figure 13.24**: Schematic plot of charge density vs. potential illustrating the definitions of integral and differential capacitances.

\[ E_z = \text{pzc} \]
Let’s summarize the steady-state behavior from the entire course…

… by looking at data on stirred (non-hysteretic) $I$-$E$ $(J$-$E)$ curves…

… and at each location, let’s think about what resistance (not impedance, as no AC contribution) is limiting the observed behavior…

… so, we want to know what dictates $R = \left( \frac{dt}{dE} \right)^{-1}$ at each $E$…

… but this will be hard because we have several convoluting factors…

Correct circuit representation of an electrochemical cell

… what are the limiting behaviors of each major resistance and can we even begin to piece out which component is responsible? …

Let’s try some examples… EXAMPLE #1
Let's try some examples... EXAMPLE #1

- Electro-catalysis
- Mass transport
- Solution
- Ohmic drop

Let's try some examples... EXAMPLE #2

- Electro-catalysis
- Mass transport
- Solution
- Ohmic drop
Let's try some examples... EXAMPLE #4

Let's try some examples... EXAMPLE #5

Let's try some examples... EXAMPLE #5... You get the idea... ... and what does $E_J$ or $E_{Donn}$ do to these plots? Shifts them left/right!
Let’s try some examples… EXAMPLE #5… You get the idea…

… and what does $E_j$ or $E_{D_{s}}$ do to these plots? Shifts them left/right!

… while a little difficult to look at initially…
… ultimately, this may be clearer, because for each $I$
… you add the series $E$ values…
… in fact many fuel cell $J-E$ curves are plotted this way.

Q: What’s in this set of lectures?
A: B&F Chapters 9, 10, and 6 main concepts:

- Sections 9.1 – 9.4: Rotating (Ring-)Disk Electrochemistry
- Sections 10.1 – 10.4: Electrochemical Impedance Spectroscopy
- Sections 6.1 – 6.6, 11.7, 14.3: Linear Sweep Voltammetry (LSV), Cyclic Voltammetry (CV), Thin-Layer Electrochemistry

… to really learn about your experimental systems…
… move beyond steady-state conditions!

RDE is also a steady-state technique (slide 1 of 3)…

… at high rotation rates, $C(0,t) = C^*$
… then the current is limited by electron-transfer at the electrode ($i_{e}$)
RDE is also a steady-state technique (slide 2 of 3)…

\[
\frac{1}{i} = \frac{1}{nF} \frac{1}{k_0} + \frac{1}{nF} \frac{1}{\alpha} \left( \frac{1}{k_0} - \frac{1}{\alpha} \right) \left( \frac{1}{R_T} - \frac{1}{R} \right)
\]

… by doing this as a function of potential, one can determine \(k_0\) and \(\alpha\)… kinetic parameters without dealing with trying to stir “perfectly”… as required for Butler–Volmer kinetics

... at high rotation rates, \(C(0, t) = C^*\)
... then the current is limited by electron-transfer at the electrode (i_e)

... and RRDE is very useful, too! (slide 3 of 3)...

How do we learn anything from complex systems?

Steady-state reactions and processes can be amazingly complex (e.g. see everything we have covered thus far in the course)... ideally, we need to piece out each mechanistic component from interrelated processes... we do this by performing studies over various time regimes... thus, we need to change the temporal response of our measurements!

• R(R)DE: stirring removes mass-transport limits, which is nice... rotating the electrode does the same thing... so precisely change the rotation rate... we can also surround the disk/button by a second ring electrode to observe products of redox reactions

• EIS: sweep/scan potentials over very small range... as CVs... but then change the region (DC)... and also change the sweep/scan rate (AC)

• CV: change the scan rate... mechanisms by Saveant's “Foot of the Wave” analysis (e.g. ECE, etc.)... modeling using BASi DigiSim, EC Lab, etc.

• UME: sweep/scan forward and backward very quickly

Costentin, Nocera & Brodsky, PNAS, 2017, 114, 11303
a few words about electrochemical impedance spectroscopy (EIS)

capacitor only:

![Image of capacitor symbol]

(capacitor &
resistor in series:

![Image of capacitor and resistor in series]

What is the “resistance”?  

$$R = \frac{E(t)}{I(t)}$$

we need a compact way to represent this impedance...

$$Z = R + iX$$

...thank you, Descartes, for coining the term imaginary number for $X$ because it is completely logical... Not!  
...complex numbers just allow people to carry two numbers around... and add their squares later... that's it!

http://en.wikipedia.org/wiki/Electrical_impedance
a complex plane representation of the total electrical impedance... It’s called a Nyquist plot.

\[ Z = R + iX \]

\[ Z_{\text{im}} = \frac{1}{\omega C} \]

the capacitive component of the impedance (reactance)

the resistive component of the impedance

the total impedance

let’s look at Nyquist plots for a few simple circuits:

\[ X = Z_{\text{im}} = \frac{1}{\omega C} = \frac{1}{(0.01)(10^{-5} \text{ F})} = 10^7 \Omega = 10 \text{ M\Omega} \]
first, a series RC circuit... like with double-layer charging

\[ X = Z_{im} = \frac{1}{\omega C} = \frac{1}{(0.01)(10^{-5} \text{ F})} = 10^7 \Omega = 10 \text{ M}\Omega \]

... for a capacitor, as frequency increases (max ~1 MHz), \( Z_{im} \) decreases...

... until you intersect the x-axis, which is the uncompensated resistance in the cell...

... which you already knew!

\[ X = Z_{im} = \omega C = 1 \times 10^{-5} \text{ F} = 10^7 \Omega = 10^7 \text{ M}\Omega \]

\[ C = 10 \mu\text{F} = 10^{-5} \text{ F} \]

... what about a parallel RC circuit?

\[ 100 \Omega \mu\text{F} \]

\[ \text{at low frequency, } Z_{im} << Z_R (= R), \text{ and the circuit behaves like there is no capacitor, and just a resistor} \]

\[ \text{Figure 10.1.11 Nyquist plot for a parallel RC circuit with } R = 100 \Omega \text{ and } C = 1 \mu\text{F}. \]

... a semi-circle... does this make sense?
at high frequency, $Z_{im} = 0$, and the circuit behaves like there is no capacitor and no resistor... so here, $R_u = 0$

in between these limits, the circuit has both capacitive and resistive behavior

... both show “the same” things, but the phase angle is clearer in Bode plots
… to an electrical engineer, an electrochemical cell looks like this:

![Electrochemical Cell Diagram]

$Z_f$ is the Faradaic impedance

… called the Randles equivalent circuit

Here is the Nyquist plot for the “full” Randles equivalent circuit:

![Nyquist Plot]

… phase angle is theoretically 45° for a Warburg impedance, $Z_W$

… for data analysis, fit frequency-dependent $Z$ data to the model

… a simple way to measure $R_e$… but you already knew that!

… that was a brief primer on EIS…

… where S is for spectroscopy?

For example, from Wiki, one type of “IS” is dielectric spectroscopy which monitors the screening (permittivity) of systems as a function of the frequency of light (which is an EM wave and is related to wavelength by the speed (of light))… our data was based on EM AC signals as a function of frequency too… Also, “impedance is the opposition to the flow of alternating current (AC) in a complex system” and so EIS is appropriate… but a little confusing, for sure!

… other quite good resources… Gamry: https://www.gamry.com/application-notes/EIS/

Bio-Logic: https://www.bio-logic.net/applications/eis/