Lesson 3: Electrochemical Reaction Kinetics

Electrochemical Methods and Applications

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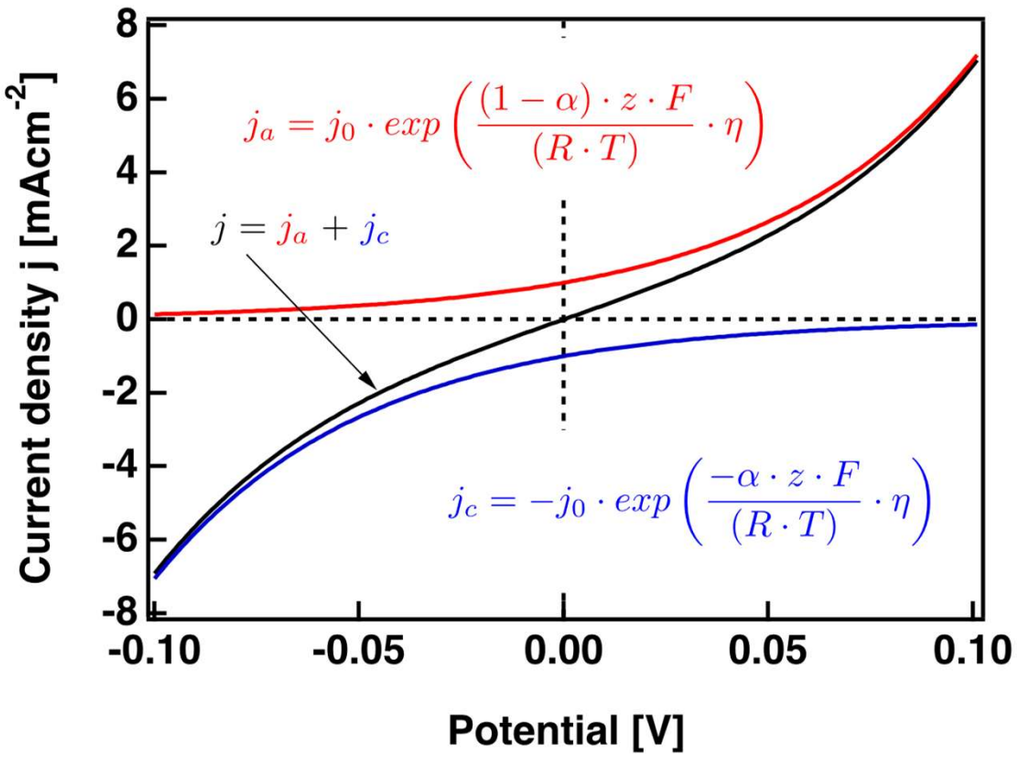
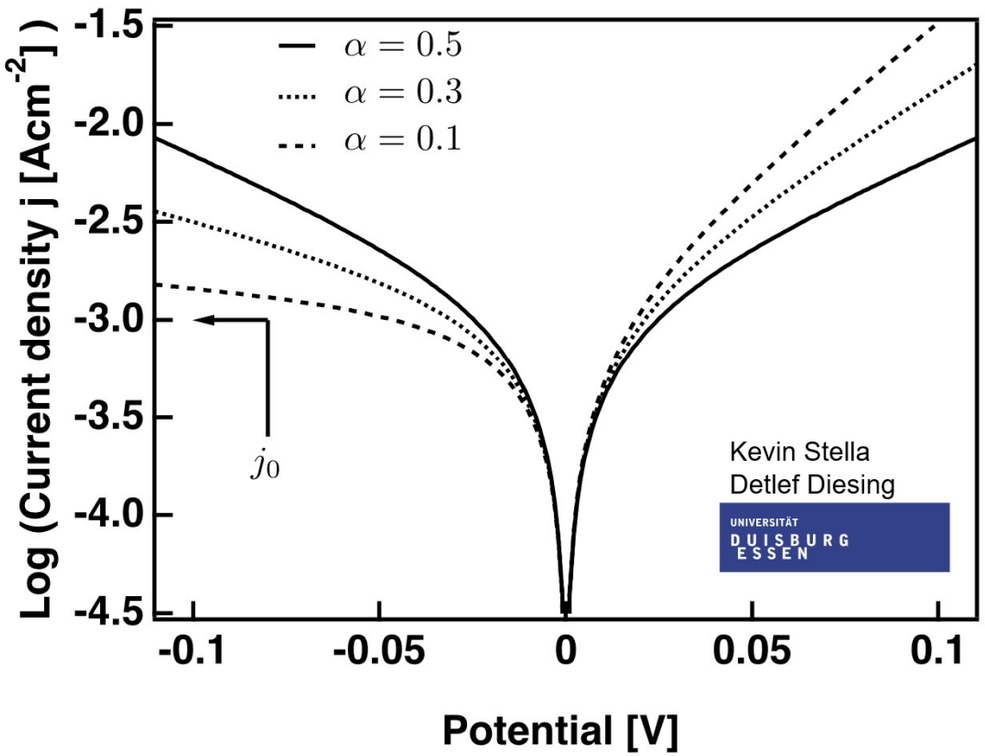
Where we're going today:





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Homogeneous Kinetics Review

$$A \leftrightarrow B$$

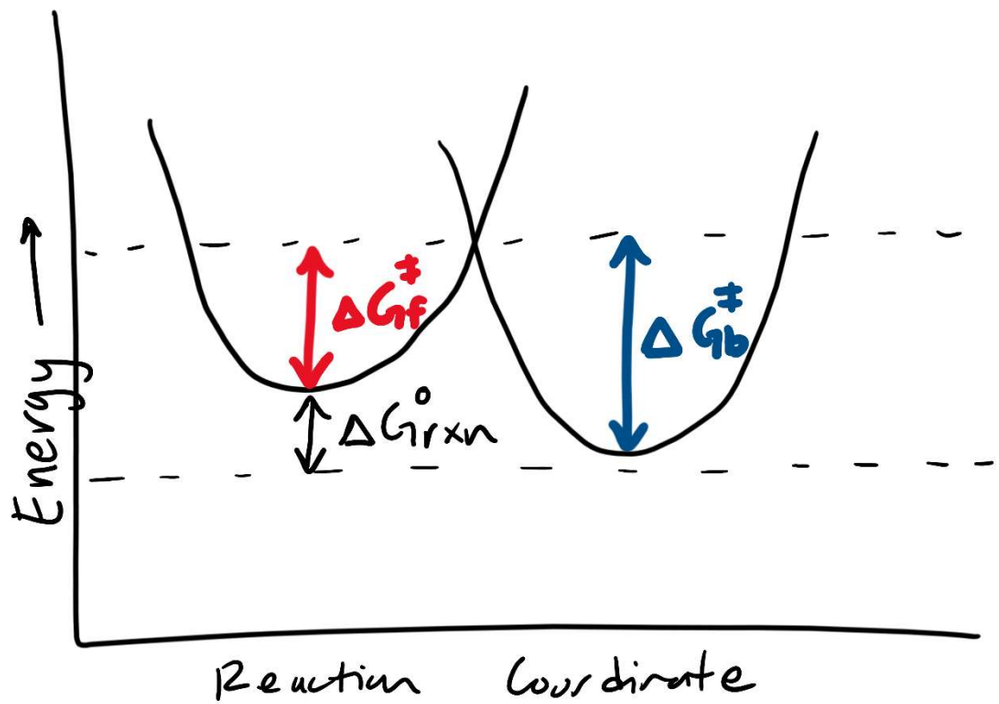
$$r_f = k_f C_A \text{ and } r_b = k_b C_B$$

$$r = k_f C_A - k_b C_B$$

At equilibrium: $\frac{k_f}{k_b} = K = \frac{C_B}{C_A}$

Arrhenius: $k_k = A_k e^{-E_{A,k}/RT}$

Arrhenius: $k_k \approx A'_k e^{-\Delta G_k^{\ddagger}/RT}$



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Heterogenous Electrochemical Kinetics

$$Ox + e^- \leftrightarrow Red$$

$$r = k_f a_{Ox} a_e - k_b a_{Red}$$

Let $a_{e^-} = 1$ and $\gamma_i = 1$

$$r = k_f C_{Ox} - k_b C_{Red}$$

$$k_k = A_k e^{-E_{A,k}/RT}$$

$$E_A = \Delta U^{\ddagger} = \Delta H^{\ddagger} - \cancel{\Delta(PV)}\ 0$$

$$E_A \approx \Delta H^{\ddagger} = \Delta G^{\ddagger} + \mathrm{T}\Delta S^{\ddagger}$$

$$Ae^{-\frac{(\Delta G^{\ddagger} + \mathrm{T}\Delta S^{\ddagger})}{RT}} = Ae^{-\frac{\Delta S^{\ddagger}}{R}} e^{-\frac{\Delta G^{\ddagger}}{RT}} = A^* e^{-\frac{\Delta G^{\ddagger}}{RT}}$$

$$k_k = A_k^* e^{-\frac{\Delta G_k^{\ddagger}}{RT}}$$

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Heterogenous Electrochemical Kinetics

$$Ox + e^- = Red$$

$$k_i = A_i^* e^{-\frac{\Delta G_i^{\ddagger}}{RT}}$$

$$\Delta G_a^{\ddagger} = \Delta G_a^{\ddagger 0} - (1-\alpha)F\left(E - E^{0'}\right)$$

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

$$k_f = A_f^* e^{-\Delta G_c^{\ddagger 0}/RT} e^{-\alpha F(E-E^{0'})/RT}$$

$$k_b = A_b^* e^{-\Delta G_a^{\ddagger 0}/RT} e^{(1-\alpha)F(E-E^{0'})/RT}$$

$$\text{Let } f = \frac{F}{RT}$$

$$\text{If } \eta = 0, k_f = k_b$$

$$\therefore A_f^* e^{-\Delta G_c^{\ddagger 0}/RT} = A_b^* e^{-\Delta G_a^{\ddagger 0}/RT} = k^0$$

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

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

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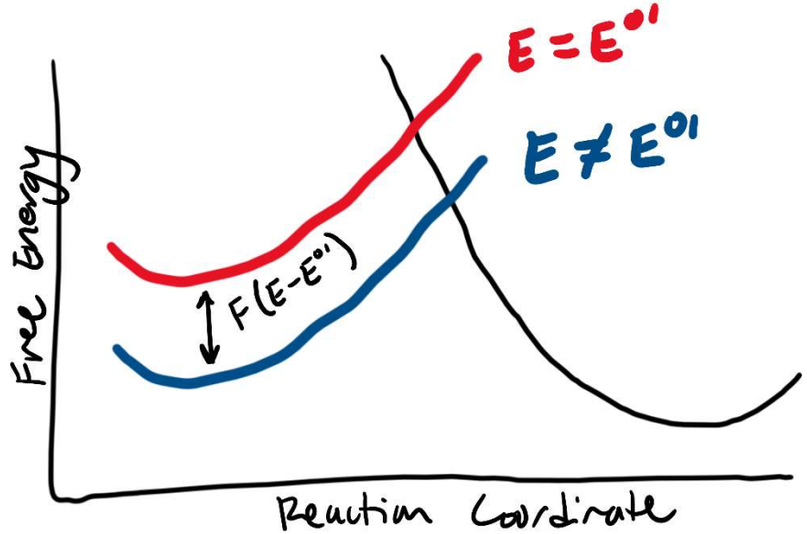
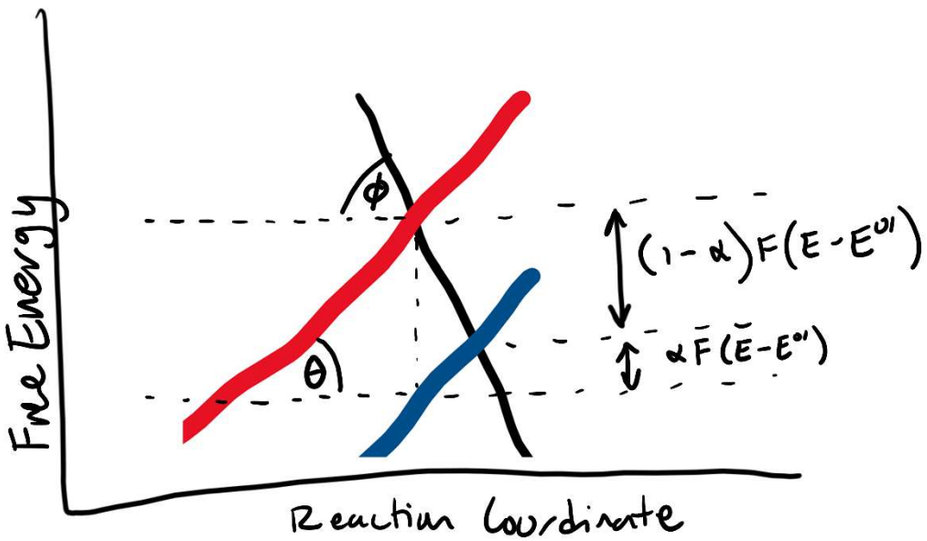
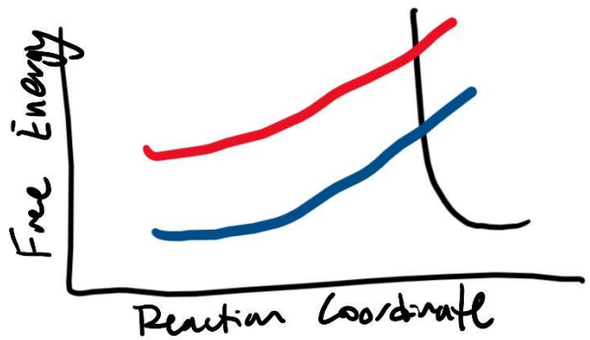
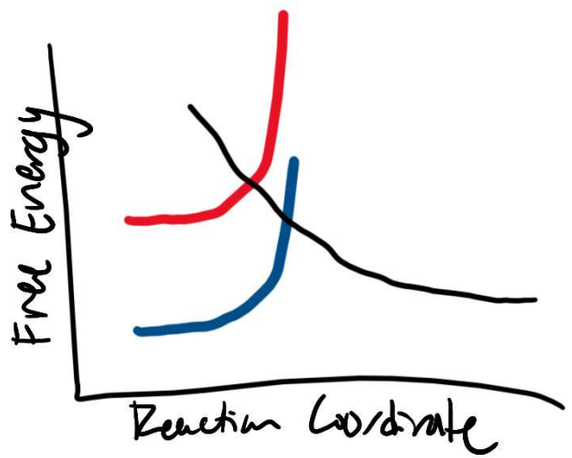
Aside on Transfer Coefficients (α)







$\alpha < 1/2$



$\alpha > 1/2$

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Heterogenous Electrochemical Kinetics

$$\mathrm{r} = \frac{i}{nFA}$$

$$r = k_f C_{Ox} - k_b C_{Red} = \frac{i}{FA}$$

$$i = FA\left(k_f C_{Ox,x=0} - k_b C_{Red,x=0}\right)$$

$$\boldsymbol{i = FAk^0\left(C_{Red,x=0}e^{(1-\alpha)f\left(E-E^{0'}\right)} - C_{Ox,x=0}e^{-\alpha f\left(E-E^{0'}\right)}\right)}$$

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Questions

What assumptions are made in the derivation of

$$i = FAk^0 \left(C_{Red,x=0} e^{(1-\alpha) f\left(E-E^{0'}\right)} - C_{Ox,x=0} e^{-\alpha f\left(E-E^{0'}\right)} \right)$$

What is the meaning of α?

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Questions

What assumptions are made in the derivation of

$$i = FAk^0\left(C_{Red,x=0}e^{(1-\alpha)f\left(E-E^{0'}\right)} - C_{Ox,x=0}e^{-\alpha f\left(E-E^{0'}\right)}\right)$$

$n = \nu_{e^-} = 1$, $a_e = 1$, $\gamma_{ox} = \gamma_{red} = 1$, $E_a \approx \Delta H^{\ddagger}$

What is the meaning of α?

Transfer coefficient - measure of how E_A for forward + reverse reactions change as E deviates from $E^{0'}$.

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Useful Kinetic Relations

Exchange Current, Current Overpotential, Butler-Volmer, Linear Characterization, Tafel Behavior

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Exchange Current at Equilibrium

$$i = FAk^0\left(C_{Red,x=0}e^{(1-\alpha)f\left(E-E^{0'}\right)} - C_{Ox,x=0}e^{-\alpha\ \left(E-E^{0'}\right)}\right)$$

$$i = 0, E = E_{eq}, C_{Ox,x=0} = C_{Ox}^{*}, \text{and } C_{Red,x=0} = C_{Red}^{*}$$

$$\frac{C_{Ox}^{*}}{C_{Red}^{*}} = e^{(1-\alpha)f\left(E_{eq}-E^{0'}\right)+\alpha f\left(E_{eq}-E^{0'}\right)} = e^{f(E_{eq}-E^{0'})}$$

$$E_{eq} = E^{0'} + \frac{RT}{F}\ln\left(\frac{C_{Ox}^{*}}{C_{Red}^{*}}\right)$$

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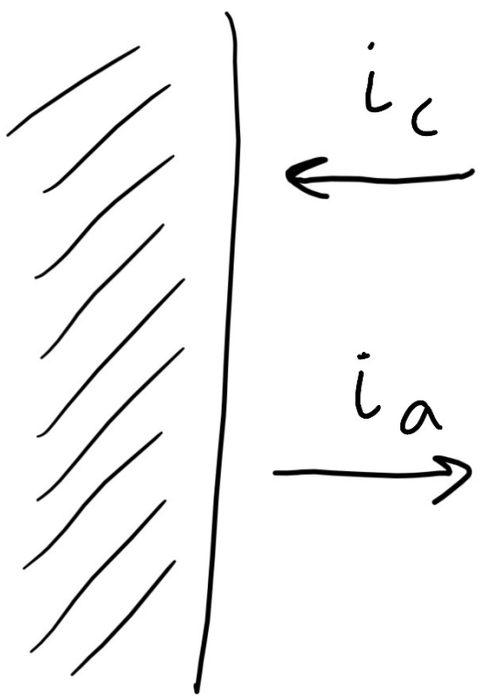
Exchange Current at Equilibrium

At equilibrium: $|i_c| = |i_a| = i_0 = FAk^0 C_{Ox}^* e^{-\alpha f\left(E_{eq} - E^{0\prime}\right)}$

Recall: $\frac{C_{Ox}^*}{C_{Red}^*} = e^{f(E_{eq} - E^{0\prime})} \therefore \left(\frac{C_{Ox}^*}{C_{Red}^*}\right)^{-\alpha} = e^{-\alpha f(E_{eq} - E^{0\prime})}$



$$\boldsymbol{i_0 = FAk^0 C_{Ox}^{*\,(1-\alpha)} C_{Red}^{*\,\alpha}}$$

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Current Overpotential Equation

$$i = FAk^0\left(C_{Red,x=0}e^{(1-\alpha)f\left(E-E^{0\prime}\right)} - C_{Ox,x=0}e^{-\alpha\ \left(E-E^{0\prime}\right)}\right)$$

$$i_0 = FAk^0{C_{Ox}^*}^{(1-\alpha)}{C_{Red}^*}^{\alpha}$$

$$\frac{i}{i_0} = \frac{C_{Red,x=0}}{{C_{Ox}^*}^{(1-\alpha)}{C_{Red}^*}^{\alpha}}e^{(1-\alpha)f\left(E-E^{0\prime}\right)} - \frac{C_{Ox,x=0}}{{C_{Ox}^*}^{(1-\alpha)}{C_{Red}^*}^{\alpha}}e^{-\alpha f\left(E-E^{0\prime}\right)}$$

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Current Overpotential Equation

$$\frac{i}{i_0} = \left(\frac{C_{Red,x=0}}{C^*_{Red}}\right) e^{(1-\alpha)f\left(E-E^{0\prime}\right)} \left(\frac{C^*_{Ox}}{C^*_{Red}}\right)^{-(1-\alpha)} - \left(\frac{C_{Ox,x=0}}{C^*_{Ox}}\right) e^{-\alpha f\left(E-E^{0\prime}\right)} \left(\frac{C^*_{Ox}}{C^*_{Red}}\right)^{\alpha}$$

Recall: $\left(\frac{C^*_{Ox}}{C^*_{Red}}\right)^{\alpha} = \mathrm{e}^{\alpha f\left(E_{eq}-E^{0\prime}\right)}$ and $\left(\frac{C^*_{Ox}}{C^*_{Red}}\right)^{-(1-\alpha)} = \mathrm{e}^{-(1-\alpha)f\left(E_{eq}-E^{0\prime}\right)}$

$$\frac{i}{i_0} = \left(\frac{C_{Red,x=0}}{C^*_{Red}}\right) e^{(1-\alpha)f\left(E-E^{0\prime}-E_{eq}+E^{0\prime}\right)} - \left(\frac{C_{Ox,x=0}}{C^*_{Ox}}\right) e^{-\alpha f\left(E-E^{0\prime}-E_{eq}+E^{0\prime}\right)}$$

$$\boldsymbol{\frac{i}{i_0} = \left(\frac{C_{Red,x=0}}{C^*_{Red}}\right) e^{(1-\alpha)f\eta} - \left(\frac{C_{Ox,x=0}}{C^*_{Ox}}\right) e^{-\alpha f\eta}}$$

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Butler-Volmer Equation

If solution is well mixed or currents are low so that:

$$C_i^* = C_{i,x=0}$$

$$\frac{i}{i_0} = \left(\frac{C_{Red,x=0}}{C_{Red}^*}\right) e^{(1-\alpha)f\eta} - \left(\frac{C_{Ox,x=0}}{C_{Ox}^*}\right) e^{-\alpha f\eta}$$

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

*Good approximation when $i < \frac{i_l}{10}$

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Linear Approximation at small η

If η is small, so will i because $i \propto e^{\eta}$

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

$$\lim_{x \to 0} e^x = 1 + x$$

$$i = i_0(\cancel{1} + f\eta - \cancel{\alpha f\eta} - \cancel{1} + \cancel{\alpha f\eta})$$

$$\boldsymbol{i = i_0 f\eta}$$

$$\boldsymbol{\frac{\eta}{i} = R_{ct} = \frac{RT}{Fi_0}}$$

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Log Approximation at large η

If η is large, either the forward or backward reaction will dominate (i.e., irreversible kinetics).

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

$$\ln\left(\frac{-i}{i_0}\right) = -\alpha f\eta$$

$$\eta(i) = \frac{1}{\alpha f}\ln\left(\frac{i_0}{-i}\right)$$

$$\boldsymbol{\eta(i) = \frac{RT}{\alpha F}\ln(i_0) - \frac{RT}{\alpha F}\ln(-i)}$$

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Questions

Try writing the Butler-Volmer equation from memory.

What conditions are required for the Butler-Volmer equation to hold?

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Questions

Try writing the Butler-Volmer equation from memory.

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

What conditions are required for the Butler-Volmer equation to hold?

$n = \nu_{e^-} = 1$

$\Delta H^{\ddagger} \approx E_a \rightarrow \Delta(PV) = 0$

$a_{e^-} = 1$

$C_{i,x=0} = C_i^*$

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Statistics and Curve Fitting

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Parameter Fitting Methods

Common Method

$$\eta(i) = \frac{RT}{\alpha F}\ln(i_0) - \frac{RT}{\alpha F}\ln(-i)$$

Linearize by plotting η vs $\ln(-i)$ and fit a straight line to the extremes on the curve

$$slope = m = -\frac{RT}{\alpha F}$$

$$intercept = b = \frac{RT}{\alpha F}\ln(i_0)$$

$$\alpha = -\frac{RT}{mF} \text{ and } i_0 = e^{\frac{b\alpha F}{RT}} = e^{\left(\frac{bF}{RT}\right)\left(-\frac{RT}{mF}\right)} = \mathrm{e}^{-\frac{b}{m}}$$

Suggested Methods

1. Use the full, non-linearized expression, fit with SSE minimization:

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

2. Fit the simplified, but non-linearized forms to the extremes of the curve with SSE minimization:

$$i = -i_0 e^{-\alpha f\eta}$$

or

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

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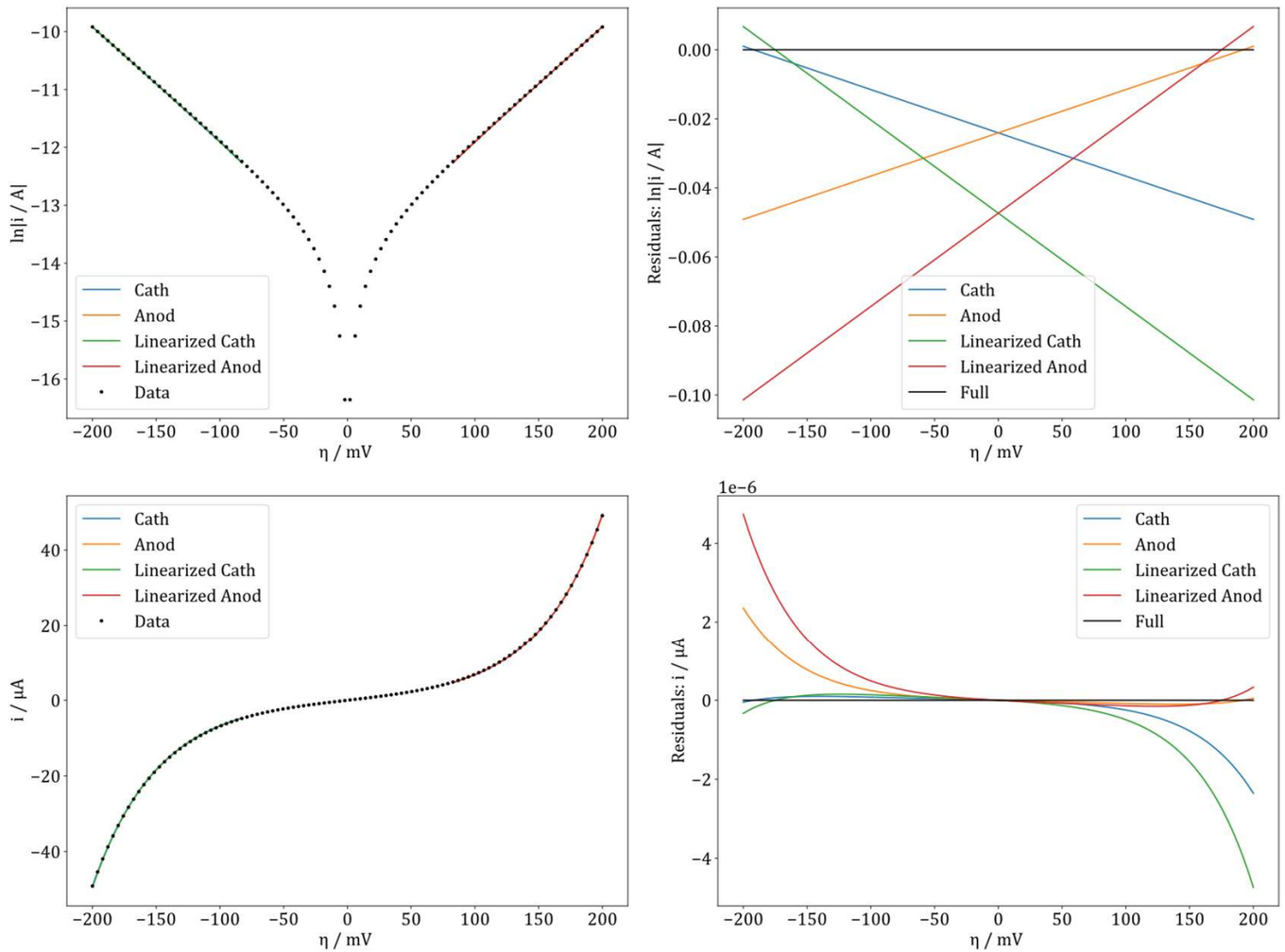
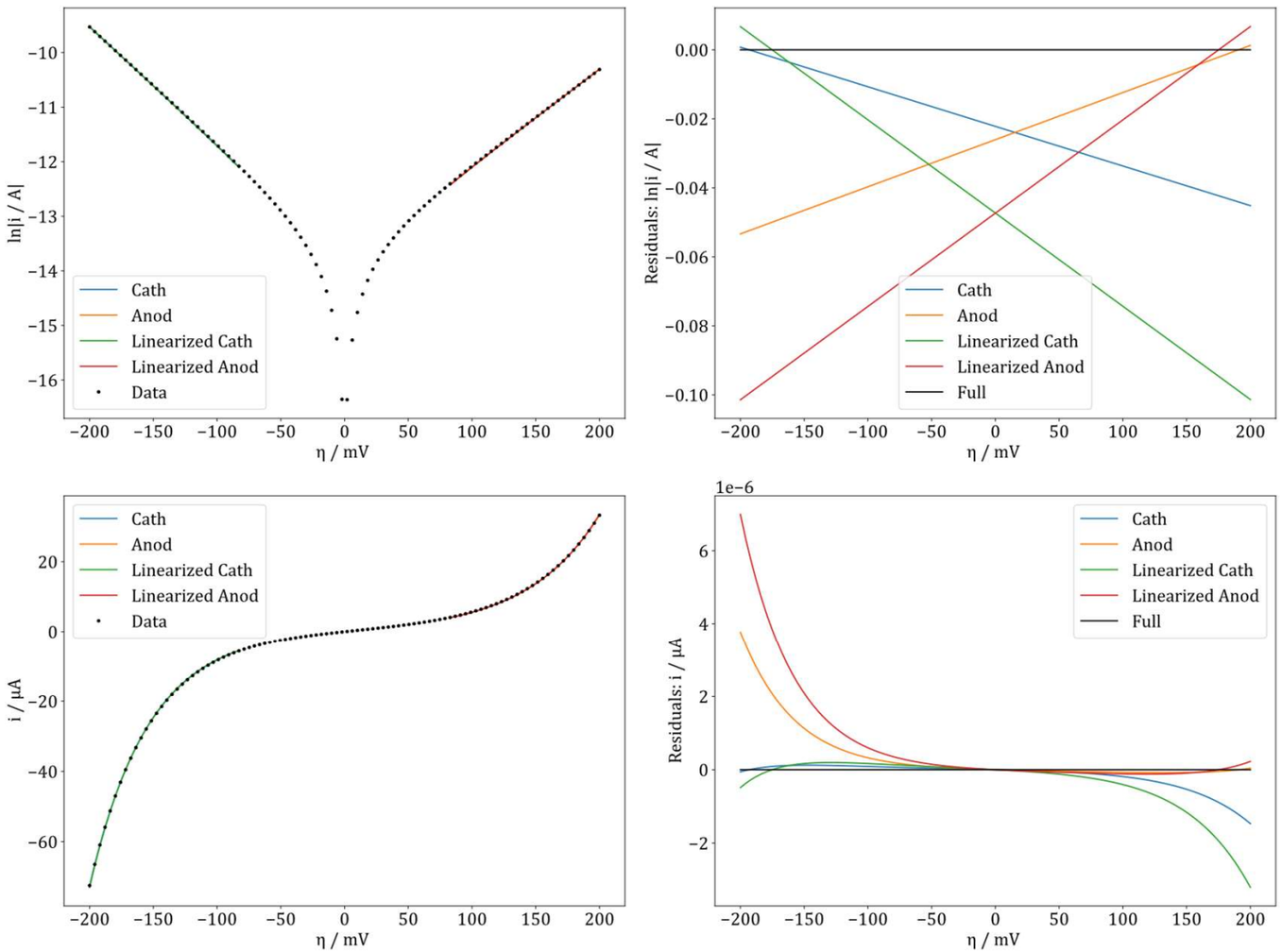
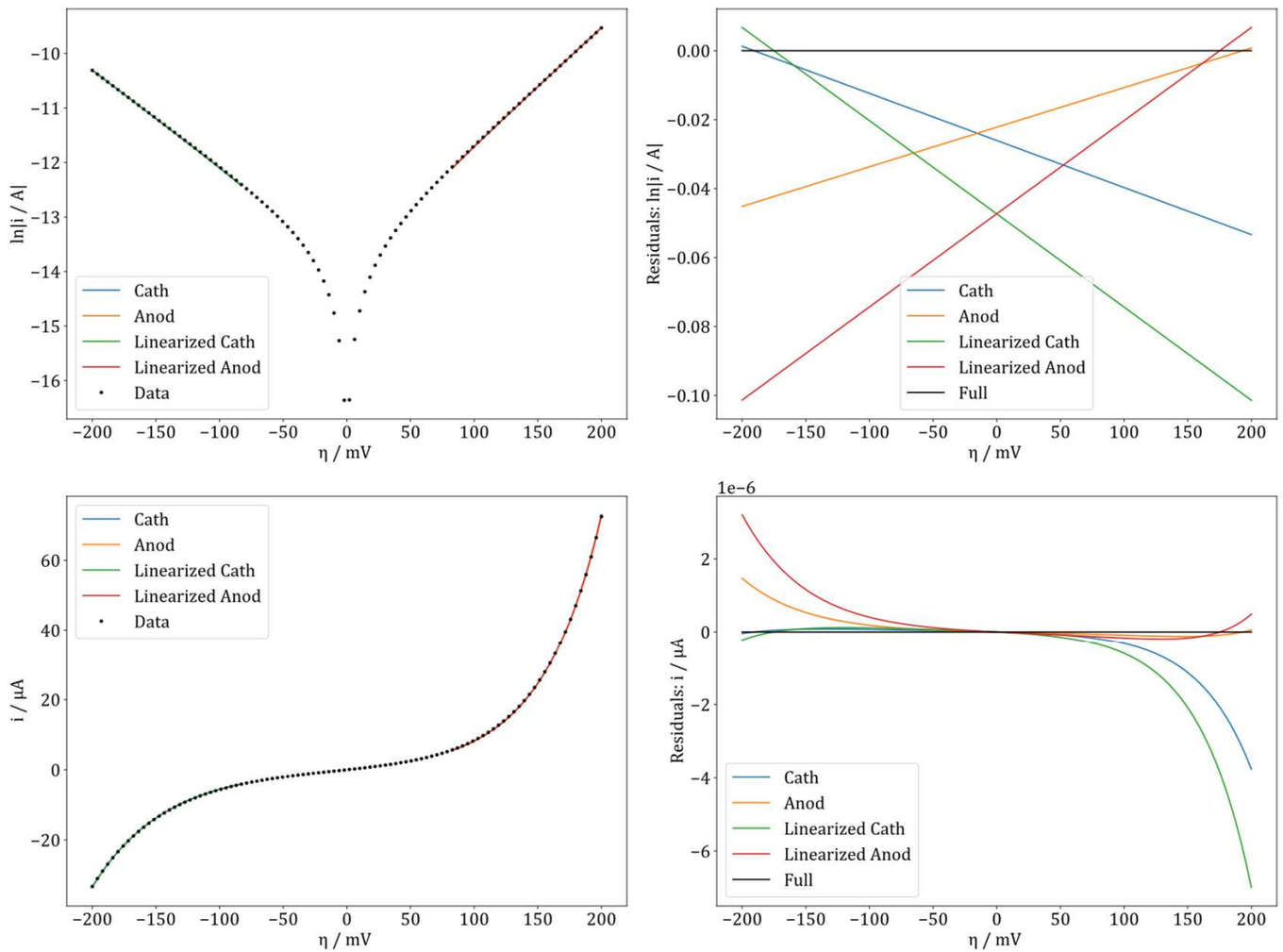
Example: $\alpha = 0.5, i_0 = 1\ \mu A$



Example: $\alpha = 0.55, i_0 = 1\ \mu A$



Example: $\alpha = 0.45, i_0 = 1\ \mu A$



Burying Linearization

- Linearization was very handy prior to broad access to digital computing.
- Process of linearization changes the variance, and not uniformly. Homogeneous variances are fundamental to statistical analysis.
- Parameters fit through linearization are always more likely to be incorrect.

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Questions

Will you ever linearize your data to fit parameters again?

What if it’s not in an electrochemical context?

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Questions

Will you ever linearize your data to fit parameters again?

Never

What if it's not in an electrochemical context?

Just say no to illegal parameter fitting.

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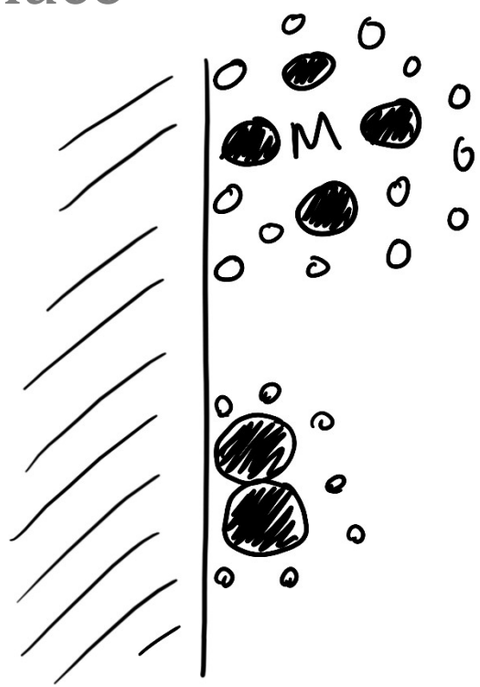
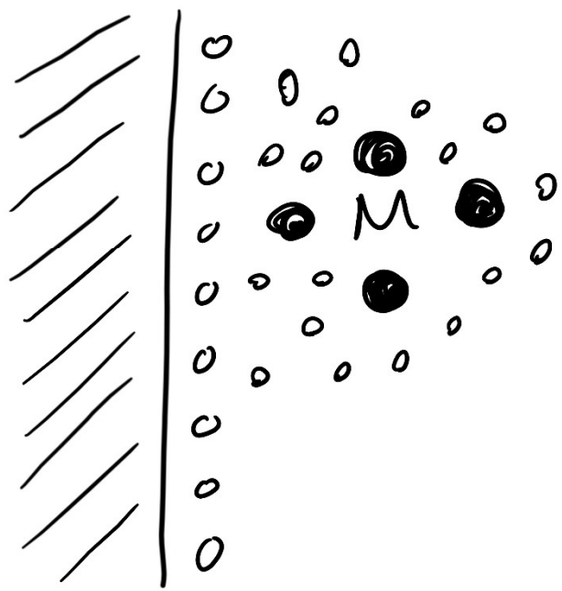
Other Kinetic Concepts

Inner/Outer Sphere Reactions

- Inner Sphere
  - Reactants and/or products interact with the electrode surface



- Outer Sphere
  - Reactants and/or products remain at least one solvent layer removed from electrode surface



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Marcus Theory

Upgrade free energy surfaces from linear to quadratic:

$$G_{Ox}^{0}(q) = \frac{k}{2}(q - q_{Ox})^2$$

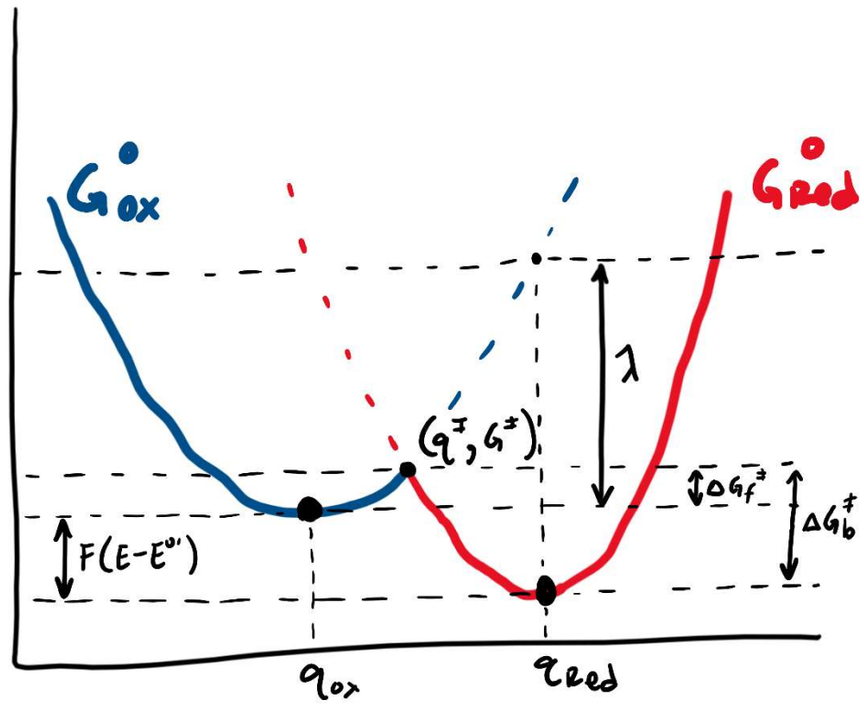
$$G_{Red}^{0}(q) = \frac{k}{2}(q - q_{Red})^2 + \Delta G^0$$

$$\lambda = \frac{k}{2}(q_{Red} - q_{Ox})^2$$

$$\Delta G_f^{\ddagger} = \frac{\lambda}{4} + \frac{\Delta w}{2} + \frac{\Delta w^2}{4\lambda} + \alpha F\left(E - E^{0'}\right)$$

$$\Delta G_b^{\ddagger} = \frac{\lambda}{4} - \frac{\Delta w}{2} + \frac{\Delta w^2}{4\lambda} - (1 - \alpha) F\left(E - E^{0'}\right)$$

$$\alpha = \frac{1}{2} + \frac{F\left(E - E^{0'}\right)}{4\lambda} + \frac{\Delta w}{2\lambda}$$



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OCP in Complex Systems

- In single redox couple systems:

$$E_{OCP} = E^{0'}_{M/M^{+n}} + \frac{RT}{nF}\ln\left(\frac{a_{M^{+n}}}{a_M}\right)$$

- In multiple redox couple systems:

$$0 = \sum_j i_j(E_{OCP}, t)$$

$$\text{where } i_j = i_{0,j}\left(e^{(1-\alpha_j)f\eta_j} - e^{-\alpha_j f\eta_j}\right)$$

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Multi-Step, Multi-Electron Transfer

- Rate Determining Step (RDS), Outer-Sphere Reaction, Irreversible First Step:

$$Ox + e^- \leftrightarrow Red'$$
$$\underline{Red' + n"e^- \leftrightarrow Red} \qquad n = n" + 1$$
$$Ox + ne^- \leftrightarrow Red$$

$$I = -nFAk^o_{RDS}\left[C_{Ox}e^{-\frac{\alpha_{RDS}F(E-E^o)}{RT}}\right]$$

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Multi-Step, Multi-Electron Transfer

- Rate Determining Step (RDS), Quasi-reversible

$$Ox + n'e^- \leftrightarrow Ox' \qquad E^{0'}_{pre}$$
$$Ox' + e^- \leftrightarrow Red' \qquad E^{0'}_{RDS} \qquad n = n' + n" + 1$$
$$\underline{Red' + n"e^- \leftrightarrow Red} \qquad E^{0'}_{post}$$
$$Ox + ne^- \leftrightarrow Red$$

$$I = -nFA\left[k_f C_{Ox} - k_b C_{Re}\right]$$

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Multi-Step, Multi-Electron Transfer

$$I = -nFA_e\left[k_f C_{Ox} - k_b C_{Re}\ \right]$$

$$k_f = \ k^o e^{\left\{\frac{F}{RT}\left[n' E^{0'}_{pre} + \alpha E^{0'}_{RDS}\right]\right\}} e^{\left\{-\frac{F}{RT}\left[(n'+\alpha)E\right]\right\}}$$

$$k_b = \ k^o e^{\left\{-\frac{F}{RT}\left[n'' E^{0'}_{post} + (1-\alpha) E^{0'}_{RDS}\right]\right\}} e^{\left\{\frac{F}{RT}\left[(n''+1-\alpha)E\right]\right\}}$$

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Questions

- How does Marcus theory upgrade the typical free-energy surface diagrams?

- How can you tell if something is an inner or outer sphere reaction?

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Questions

- How does Marcus theory upgrade the typical free-energy surface diagrams?

Treats the curves as quadratic instead of straight lines.

- How can you tell if something is an inner or outer sphere reaction?

Inner sphere reactions will be electrode substrate dependent. Outer sphere reactions will be agnostic.

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