Multistep mechanisms (B+F chapt. 12)

Single step:

$$O + e \rightarrow R$$

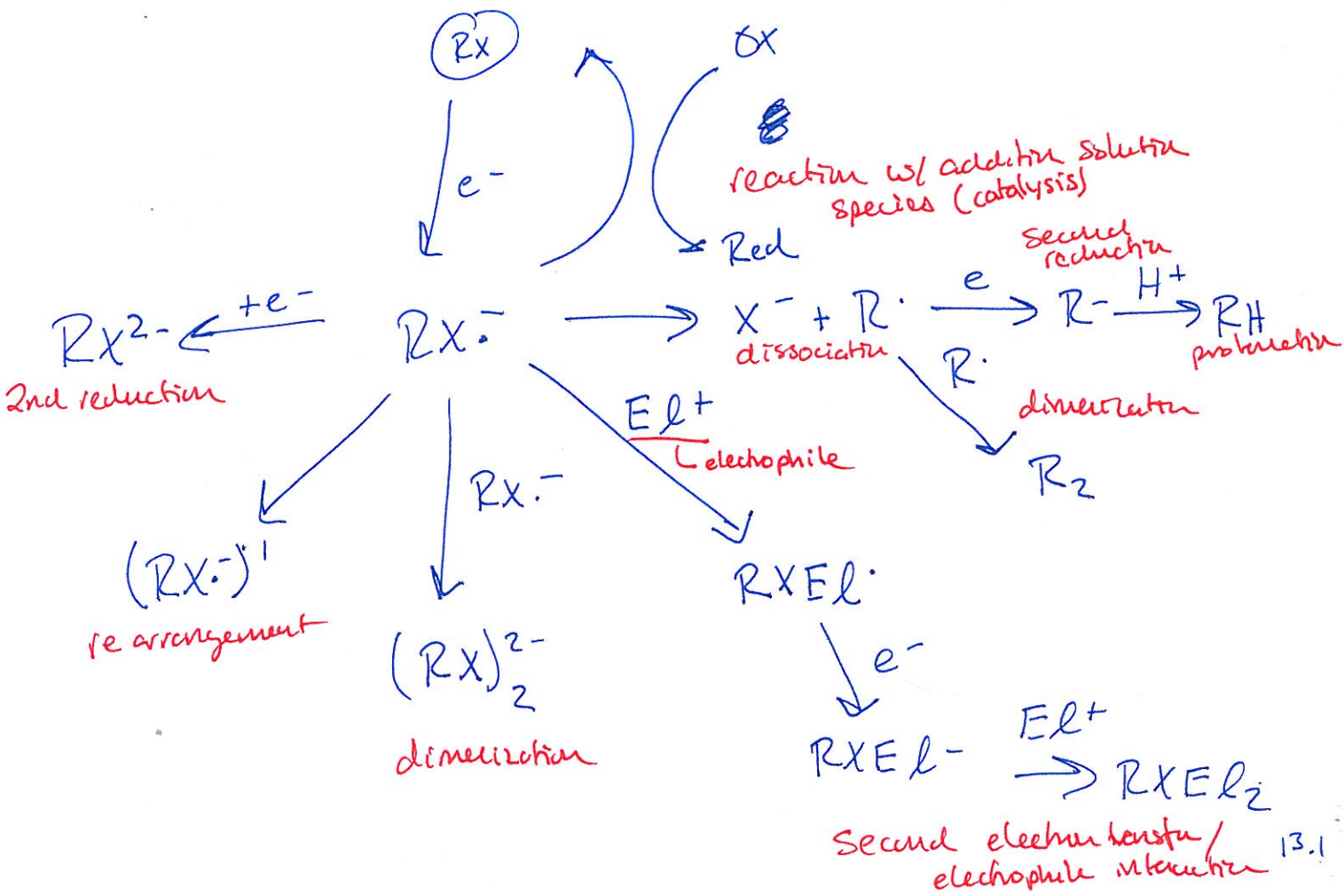
Many reactions multistep.

Consider the fate of species:

$R-X$

hydrocarbon species

functional group



Need ~~mechanistic~~ way to classify different reactions, so we can understand how to use models to interpret voltammetry data.

"E" = electron transfer step <u>across</u> the electrode surface

"C" = <u>homogeneous</u> chemical reaction (or electrochemical)

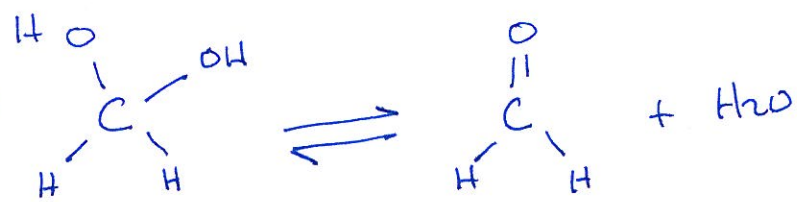
Some examples:

(a) CE reaction (preceding reaction)

$$Y \rightleftharpoons O \qquad C$$

$$O + ne \rightarrow R \qquad E$$

"hydrated" Formaldehyde



↑ <u>non-reducible</u> ↑ <u>reducible</u>

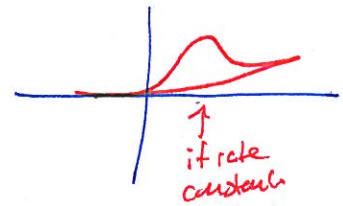
b.

EC Reaction (Following Reaction)

$$O + ne \rightleftharpoons R$$

$$R \underset{k_b}{\overset{k_f}{\rightleftharpoons}} X$$

Q: what do we expect the resulting CV to look like in this case?



↑ if rate constant is fast enough no reverse sweep (irreversible CV curve)

R reacts to species that is <u>not electroactive</u>

p-aminophenol

quinone imine

benzoquinone

↑ not redox active

c. Catalytic (EC') reaction

$$O + ne \rightleftharpoons R$$

$$R + Z \rightarrow O + Y$$

→ O/R couple is catalyst for reduction of Z to Y! (many water splitting type folks investigating these things)

(c) Catalytic (EC') Reaction

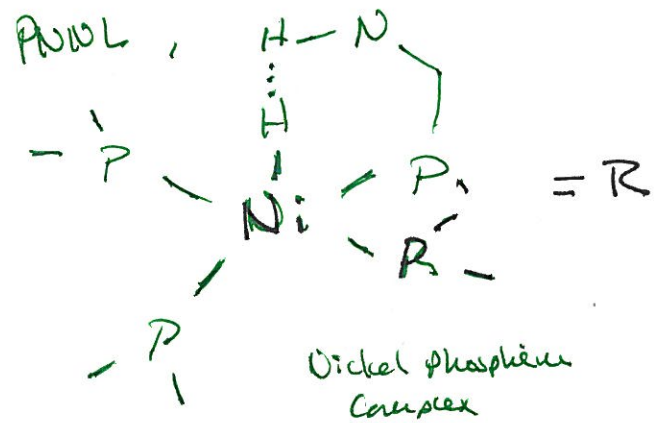
Nernstian →

$$O + ne^- \rightleftarrows R$$

$$R + Z \xrightarrow{k'} O + Y$$

k' = forward rate constant, can assume irreversible

Example Dan DuBois

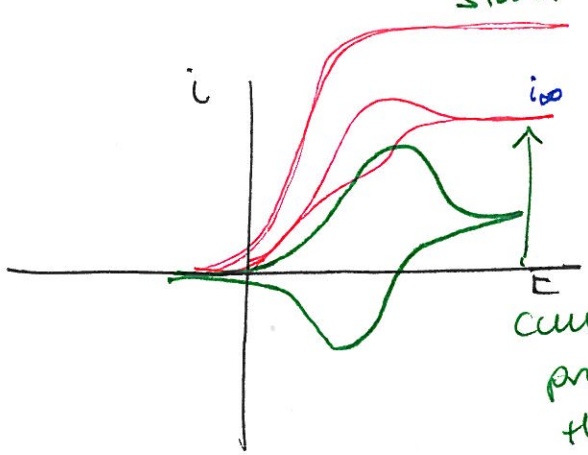


Nickel-Based active site

→ decays to give H_2 + O-form of the homogeneous electrocatalyst.

Can we predict what the CV curves would look like in this case?

unstirred solution, assume only O to start and the R reacts w/ protons to make H_2



← Bare redox wave

current is proportional to the rate constant for the catalytic reaction

at large potentials the current limits at $\underline{i_\infty}$ → this is the so-called catalytic current. It is independent of the applied potential. and is independent of the scan rate v.

This is

$$i_\infty = nFAC_0^* \left(D_0 k' C_Z^*\right)^{1/2}$$

(assumes $C_Z^* \gg C_0^*$

recall back to the unstirred CV derivation:

$$i_p = (2.69 \times 10^5)\, n^{3/2} A D_0^{1/2} C_0^* v^{1/2}$$

→ can then take the ratio of the currents to find

$$i_\infty / i_p = \frac{\cancel{n} F \cancel{A} \cancel{C_0^*} \cancel{D_0^{1/2}} k'^{1/2} C_Z^{*1/2}}{2.69 \times 10^5\, n^{\cancel{3/2}} \cancel{A} \cancel{D_0^{1/2}} \cancel{C_0^*} v^{1/2}} = \frac{F k'^{1/2} C_Z^{*1/2}}{n^{1/2} v^{1/2} \cdot 2.69 \times 10^5}$$

$$\boxed{= \left(\frac{k' C_Z^*}{n v}\right)^{1/2} \frac{F}{2.69 \times 10^5}}$$

a way to evaluate homogeneous electron transfer kinetics w/o worrying about the diffusion coefficients

12.1.2 Reactions w/ 2 or more E steps

(a) EE reaction

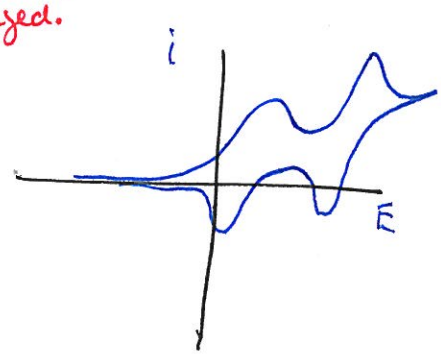
$$A + e \rightleftharpoons B \quad E_1^\circ$$

$$B + e \rightleftharpoons C \quad E_2^\circ$$

* What does the corresponding voltamogram look like?

A: it depends on the relative position of E_1° and E_2°!

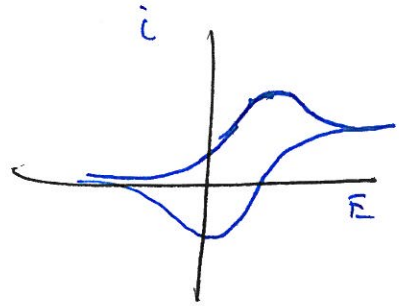
normally $E_2^\circ < E_1^\circ$; i.e. it is harder to add the second electron than the first, because the molecule is already charged.



well separated waves. ($\Delta E \sim 200mV$)

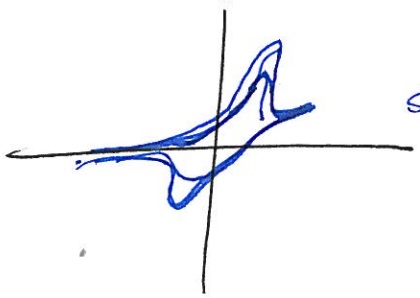
$E_2^\circ - E_1^\circ = -200mV$

Show simulation given enough time.



broadened → not well separated

$E_2^\circ - E_1^\circ$ ($\Delta E \approx 75mV$)



$E_2^\circ - E_1^\circ = +100mV$

sharpend peak and shifted

Many Electrochemical reactions that one conventially may call a $2e^-$ - transfer reaction are actually a series of 1 electron transfers in an <u>EE</u> type reaction

$$Zn \rightarrow Zn^+ + e^-$$

↑ highly unstable

$$Zn^+ \rightarrow Zn^{2+} + 2e^-$$

↑ much more stable.

because Zn^+ is easier to reduce than Zn^0, the reaction proceeds by an apparent $2e^-$ pathway.

(b) ECE reaction

$$O_1 + n_1 e^- \rightleftharpoons R_1 \quad \text{at } E_1^\circ$$

$$R_1 \xrightarrow{(+Z)} O_2$$

$$O_2 + n_2 e^- \rightleftharpoons R_2$$

* Some chemical reactions reactivates the R_1 species for a second electron transfer in the same potential range.

for example, see book, reduction of halo aromatic compounds

(c) $\vec{E}C\overleftarrow{E}$ Reactions

products of chemical reaction following reduction are <u>oxidized</u> at potentials associated with the <u>1st</u> reduction reaction!

$$A + e^- \rightleftharpoons A^-$$

$$A^- \rightarrow B^-$$

$$B^- \rightleftharpoons B + e^-$$

overall reaction simply

$\underline{A \rightarrow B}$ w/ no net transfer of e^-!

electron-transfer-catalyzed reaction.