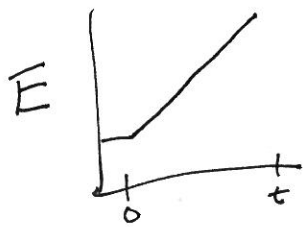
6. Potential Sweep Methods (LSV and CV)

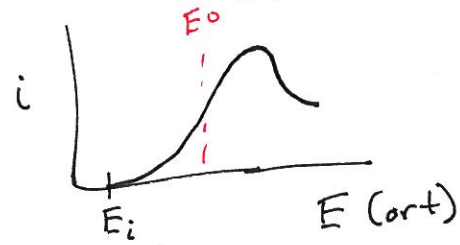
- useful to identify and quantify different species as well as the electron transfer kinetics

a. Linear Sweep Voltammetry

apply voltage sweep

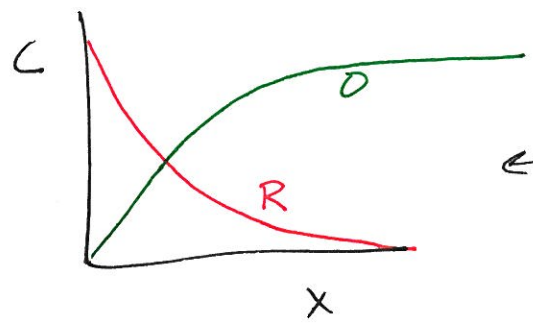


measure current response



scan st

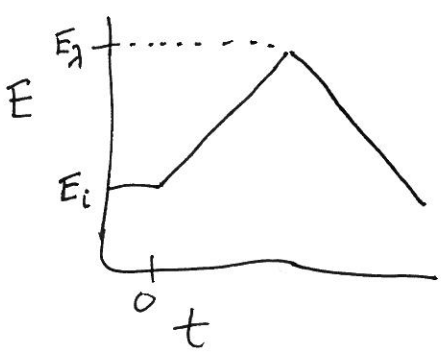
$$O + e^- \rightarrow R$$

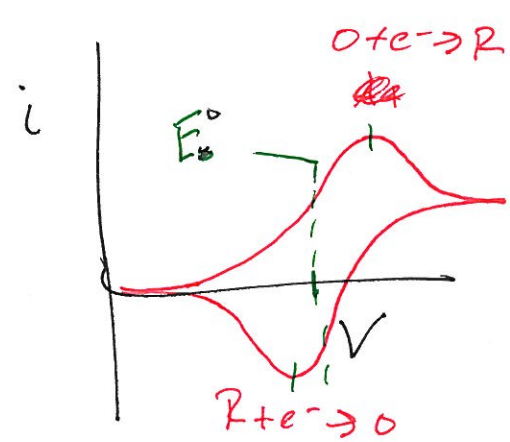


↔ concentration gradients

b. Cyclic Voltammetry

→ E° for chemical species, peak splitting due to diffusion and kinetics.





6.2 Linear Sweep Voltametry

a. Nernstian System (What does this mean?)

↓

k^0 and i_0 large

$$E(t) = E_i - vt$$

↑ scan sweep rate in V/s

initial condition:

$$C_O(x,t) = C_O^*$$

Boundary condition:

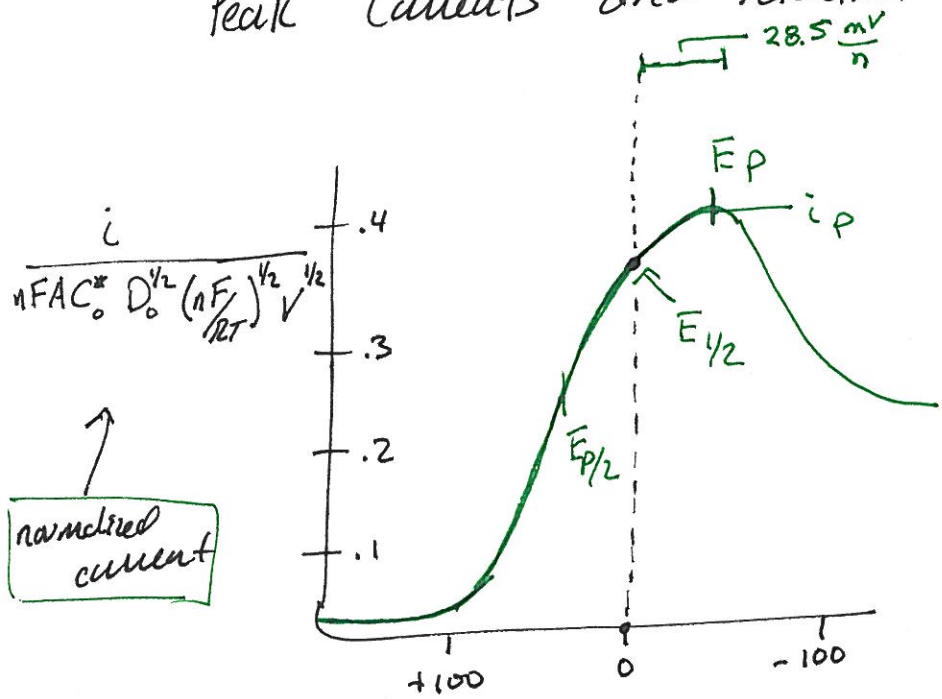
$$\frac{C_O(0,t)}{C_R(0,t)} = f(t) = \underline{\exp\left[\frac{nF}{RT}\left(E_i - vt - E^{0\prime}\right)\right]}$$

from the Nernst equation

time-dependence of boundary condition makes solving the dif. eq. via the Laplace transformation more difficult.

→ must be solved numerically... Book has master equation and look-up table.

Peak Currents and Potentials (For Nernstian systems)



Remember

$$\boxed{E_{1/2} = E^\circ + \frac{RT}{nF}\ln\left(\frac{D_R}{D_O}\right)^{1/2}}$$

SKIP

$$\boxed{n(E-E_{1/2})} = \left(\frac{RT}{F}\ln\xi + n(E_i - E^\circ) - \frac{RT}{F}\sigma t\right)$$

$$\boxed{\xi = \left(\frac{D_O}{D_R}\right)^{1/2}}$$

$$\sigma = \left(\frac{nF}{RT}\right)v$$

scan rate

$$i_p = 0.446\left(\frac{F^3}{RT}\right)^{1/2} n^{3/2} A D_O^{1/2} C_O^* v^{1/2}$$

independent of scan rate

$$\boxed{E_p = E_{1/2} - \boxed{1.11\frac{RT}{nF}}}$$

$$\boxed{\left(\text{or } \frac{28.5\text{ mV}}{n}\right)}$$

Sometimes the half-peak potential is used, as it can be easier to define

$$E_{p/2} = E_{1/2} + \boxed{1.09\frac{RT}{nF}} \quad \frac{28\text{ mV}}{n}$$

These can be used as

Cyclic Voltammetry

in linear sweep voltammetry we started with O and studied $O + ne \rightarrow R$.

Q. How do we study the reverse reaction?

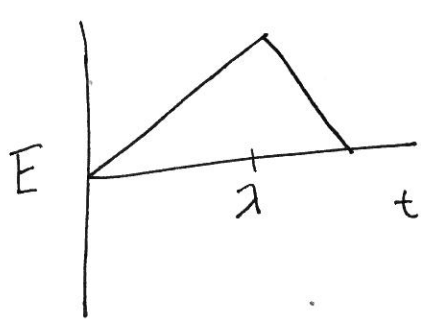
Q. What if R (or O) is unstable?

A: generate species and analize in-situ using a "reversal" technique called Cyclic Voltammetry

→ Most common technique employed

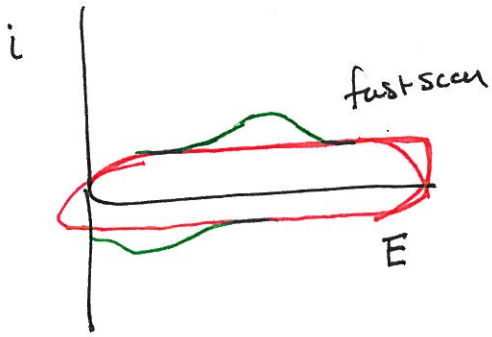
$0 < t \leq \lambda \qquad E = E_i - vt$

$t > \lambda \qquad E = E_i - 2v\lambda + vt$



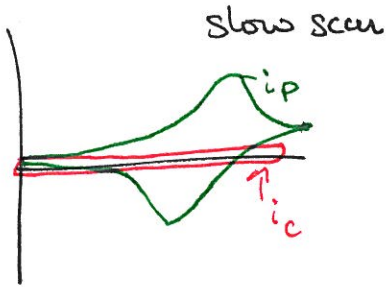
triangle wave

Double-layer Charging Effects (on CV)



Capacitive Charging gives a i-E response of a box.

$$\boxed{i_c = C_d v}$$



Scales linearly w/ voltage sweep rate

from before → $i_p \propto v^{1/2}$

At [redacted] faster scan rates, capacitive component will [redacted] contribute increasingly to the overall current.

Information from a CV sweep:

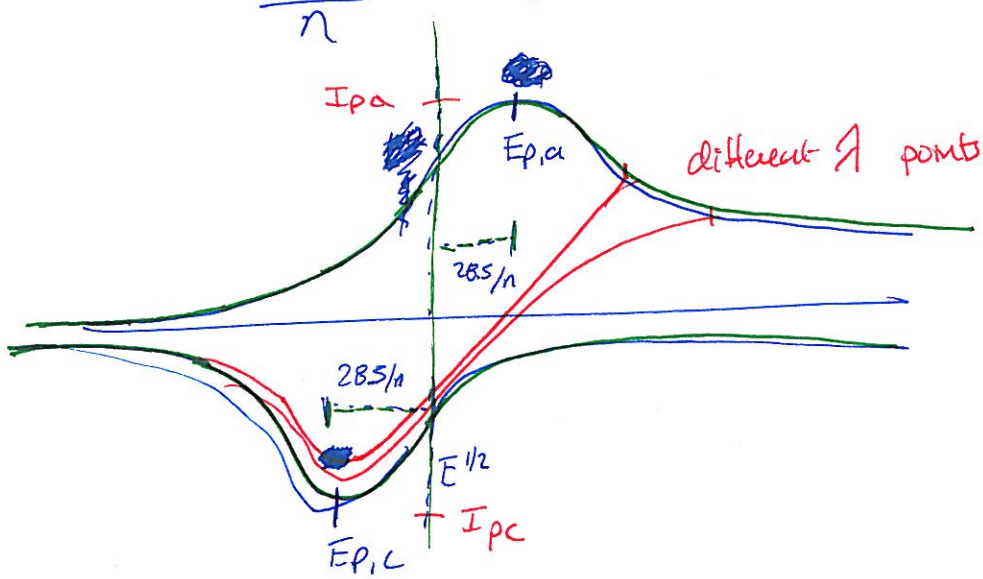
(1) if a Nernstian ~~Reaction~~ system then

$$\Delta E_p \sim 2.3RT/nF \text{ or } 59/n \text{ mV}$$

(actually a slight function of λ, the switching potential).

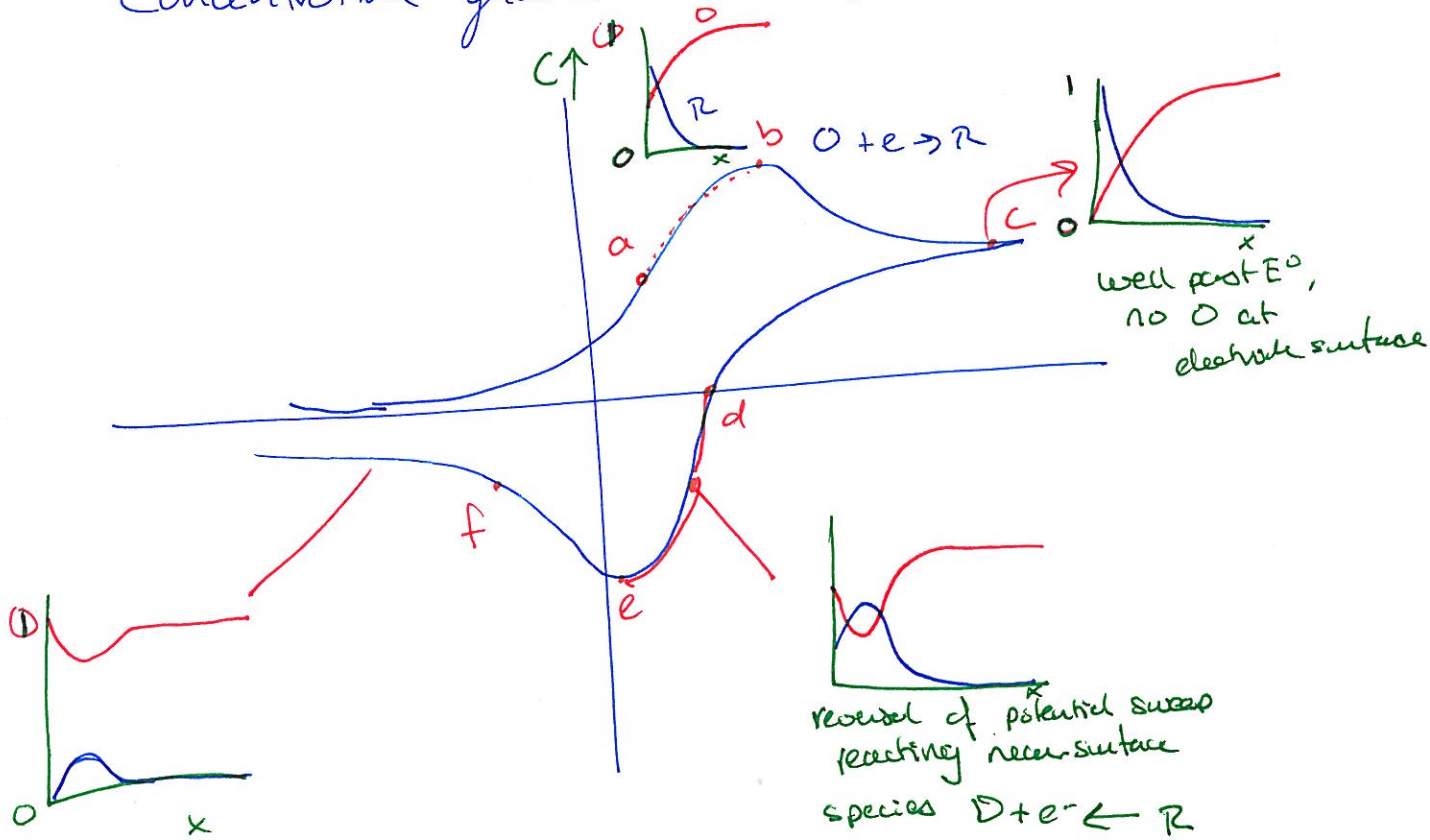
$\boxed{\text{Show example using simulation tool.}}$

Why is it ~59 mV? → consider two linear sweep voltammetry curves, each peak is shifted $\frac{28.5}{n}$ mV from E.



different λ points affect $E_{p,c}$, but not greatly → do affect, however, $I_{p,c}$

Concentration gradients during a CV scan.

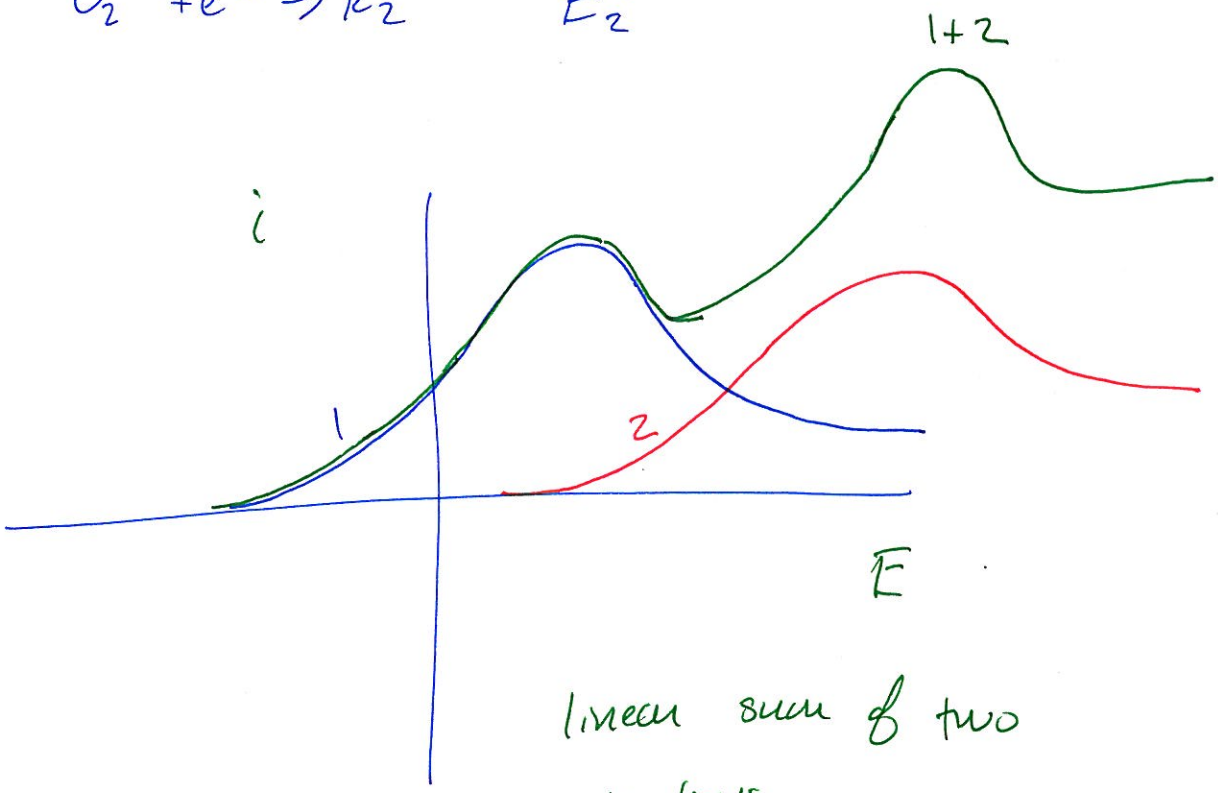


Diffusion now forms only O at electrode surface, but some R remains in solution.

Multiple Redox Species in Solution

$O_1 + e^- \rightarrow R_1 \qquad E_1^\circ$

$O_2 + e^- \rightarrow R_2 \qquad E_2^\circ$



linear sum of two reactions.