lecture 16

Now.. Electrode Processes

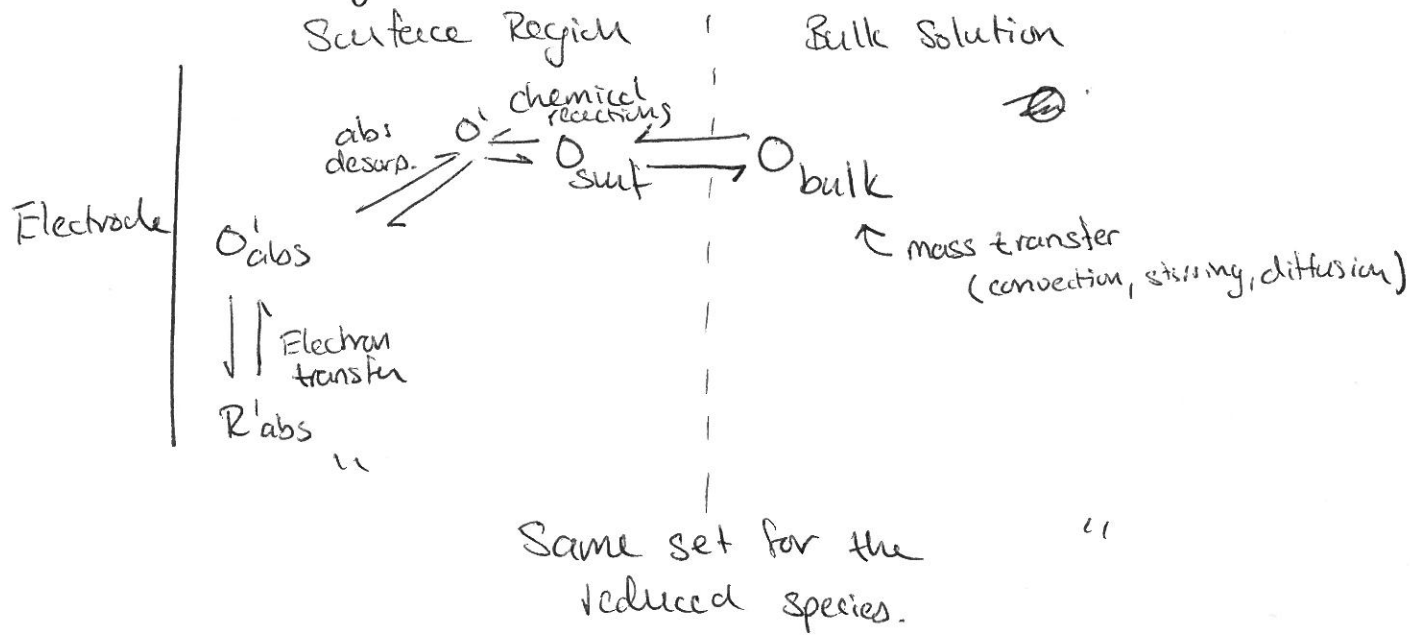
measure some process: $O + ne^- \rightarrow R$

$$i\ (\text{Amperes}) = \frac{dQ}{dt}\ (\text{coulombs/s})$$

$$\frac{Q}{nF}\ \left(\frac{\text{coulombs}}{(\text{coulombs/mol})}\right) = N\ (\text{mol electrolyzed})$$

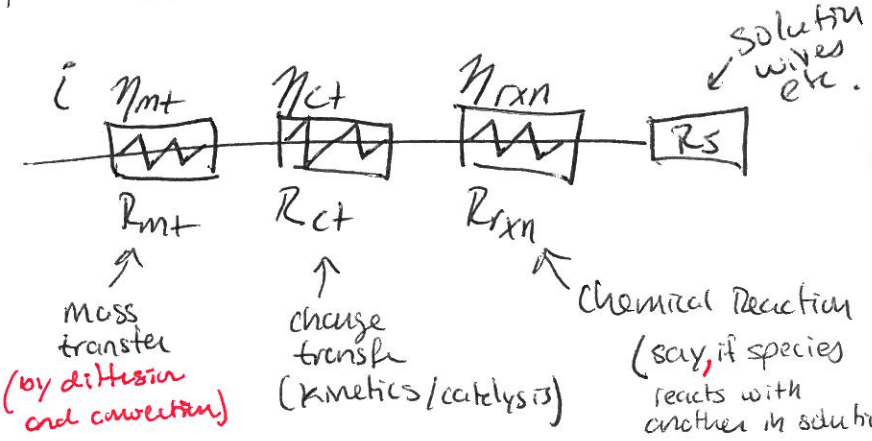
$$\text{Reaction Rate}\ (\text{mol/s}) = \frac{dN}{dt} = \frac{i}{nF}$$

Factors Affecting Electrode Reaction Rate:



each process can be thought of as step w/ a corresponding resistance to flow of current

often one of these is Rate-Limiting



we will discuss all of these in this course

6.1

Today we talk about the "mass transport" component:

$$\text{rate} = i/nFA$$ → need to describe rate of reaction at electrode surface

Mass transfer limited current:

(1) kinetics of charge transfer at the electrode surface are fast, therefore concentrations of species (O/R) at electrode surface are determined by the Nernst eqn.

in the next lecture we will consider when this is not true!

$$E = E^0 - \frac{kT}{ne} \ln \frac{[Red]}{[Ox]} \quad \text{for } Ox + ne^- \rightarrow Red$$

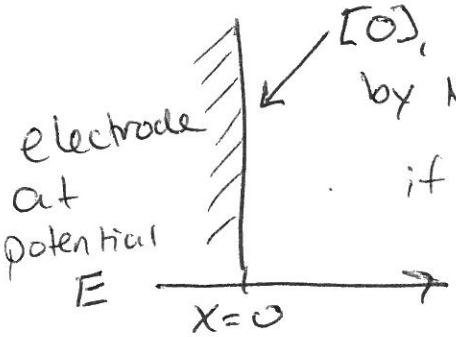
$\uparrow$ or $\frac{RT}{nF}$

- comes directly from general case of Gibbs free energy:

$$\left\{ \begin{array}{l} \Delta G = \Delta G^0 + kT \ln Q \\ \text{where } \Delta G = -nFE \end{array} \right\}$$

$$\left\{ Q \stackrel{\text{def}}{=} \frac{[Y]^y [Z]^z}{[A]^a [B]^b} \right.$$

(Echem directly measures thermodynamic quantities!)



[O], [R] determined by Nernst EQ at $x = \phi$

if kinetics are fast then i will be determined by diffusion / convection of species to the electrode surface.

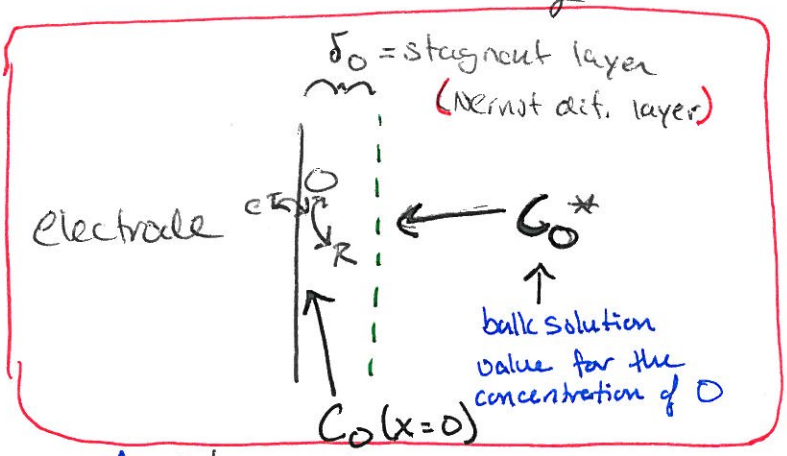
Mass Transport

→ governed by the Nernst-Planck Eq. (here in 1D)

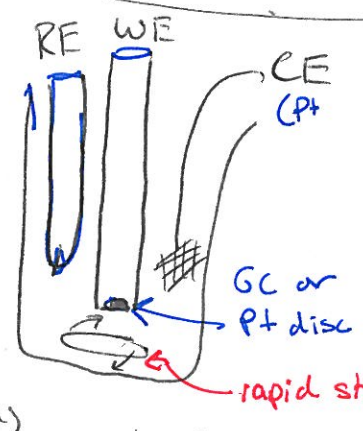
$$J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i v(x)$$

- $J_i(x)$: flux of species i ($mol\, s^{-1} cm^{-2}$); x: position
- D_i: diffusion coefficient (cm^2/s)
- $\frac{\partial C_i(x)}{\partial x}$: concentration gradient
- z_i: charge of ion; $\frac{\partial \phi(x)}{\partial x}$: potential gradient (i.e. $\vec{E}$)
- C_i: concentration [mol/cm³]
- $v(x)$: velocity of sol. element cm/s

A. $O + ne^- \rightleftharpoons R$ (assume rapid stirring)



B. E.G. $\left(Fe(CN)_6^{3-} / Fe(CN)_6^{4-} \right)$ in 0.1 M K_2SO_4



sup. electrolyte (to minimize R_s)

+ also assume high supporting electrolyte concentration so $\frac{\partial \phi(x)}{\partial x} \sim \emptyset$ except over double-layer with a few 10's of nm of electrode surface. (migration not important... will discuss later)

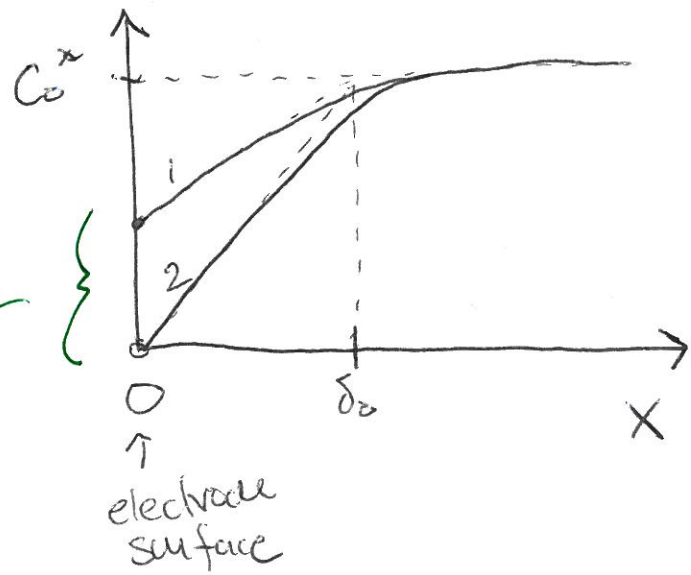
C. So

$$v_{mt} \propto \left(\frac{\partial C_O}{\partial x}\right)_{x=\emptyset} = D_O \left(\frac{\partial C_O}{\partial x}\right)_{x=0}$$

v_{mt}: mass transfer controlled rate of reaction

↳ rate of reaction is just rate of diffusion of species directly next to the electrode.

$ne^- + O \rightarrow R$



this value at the electrode surface is dictated by the potential of the Electrode, E, and the Nernst EQn.

consider two cases:

(1) $C_O(x=0) = C_O^*/2$

(2) $C_O(x=0) \approx 0$

$$\boxed{i = i_\ell}$$

when $C_O(x=0) = \emptyset$ current is completely M.T. controlled $\rightarrow i = i_\ell$

* limiting current.

Solve: - assume linear conc. gradient

$$V_{mt} = D_O[C_O^* - C_O(x=0)]/\delta_O$$

↑ slope of line, $\partial C_O/\partial x$

Define $\rightarrow$ $\boxed{D_O/\delta_O = m_O}$ $\rightarrow m_O$ = mass transfer coefficient

$cm^3 s^{-1} cm^{-2}$

since $V_{mt} = i/nFA$ (n = # of electrons / molecule, A = area)

(1) $$\boxed{\frac{i}{nFA} = m_O[C_O^* - C_O(x=\emptyset)]}$$

R is of course produced at the electrode surface:

← derive this

$$\frac{i}{nFA} = m_R[C_R(x=0) - C_R^*]$$

if initially no R $C_R^* = 0$

$C_O(x=)$ and $C_R(x=0)$ are $f(E)$! The Electrode potential.

again largest M.T. occurs when

$$\underline{C_O \cong \emptyset}$$

(2) $$\boxed{i_\ell = nFAm_O C_O^*}$$ expression for i_ℓ

m_O → depends on electrode/cell geometry and convection (stirring)

O reduced as fast as ~~as~~ possible.

now: combine (1) and (2):

(3) $$\boxed{C_O(x=0) = \frac{i_\ell - i}{nFAm_O}}$$ expression for concentration of species at surface w.r.t i and i_ℓ (both measureable)

again we can assume, if the ~~kinetic~~ kinetics at electrode surface are rapid,

$$\boxed{E = E^{o'} + \frac{RT}{nF} \ln \frac{C_O(x=0)}{C_R(x=0)}}$$ Nernst eqn.

* nernstian reaction

Derive i-E curves
for special cases (that one might measure in the lab!)

R initially absent: $\longrightarrow \left\{ O + ne^- \rightarrow R \right.$ at Electrode surface

$$C_R^* = \emptyset$$ bulk concentration

From before: $$\frac{i}{nFA} = M_R \left[C_R(x=0) - C_R^* \right]$$

$$\boxed{C_R(x=0) = i / nFAM_R}$$

Now start with the Nernst Equation:

$$\boxed{E = E^\circ + \frac{RT}{nF} \ln \frac{C_O(x=0)}{C_R(x=0)}}$$

Side note: technically we should use the formal potential here $E^{\circ\prime}$, instead of the standard potential E°

we know from before that:

$$\boxed{C_O(x=0) = \frac{i_\ell - i}{nFAM_O}}$$ (3)

Combining:

$$E = E^\circ + \frac{RT}{nF} \ln \frac{i_\ell - i / (\cancel{nFA} M_O)}{i / (\cancel{nFA} M_r)}$$

take M_O / M_r out of log expression

$$\cancel{E = E^\circ + \frac{RT}{nF} \ln \frac{M_O}{M_r} + i_\ell - i}$$

$$E = E^{\circ} - \frac{RT}{nF} \ln \frac{M_O}{M_R} + \frac{RT}{nF} \ln \frac{i_\ell - i}{i}$$

note that when $i = i_\ell/2$, second term goes to $\emptyset$

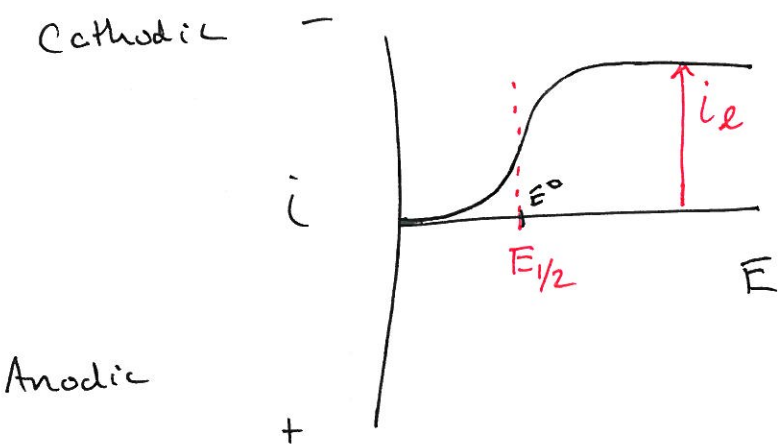
$$E = E_{1/2} = E^{\circ} - \frac{RT}{nF} \ln \frac{M_O}{M_R}$$

→ so,

if $M_O = M_R$

then $E_{1/2} = E^{\circ}$

thus, this half-wave potential $E_{1/2}$ is a good estimate of E° in nernstian systems!



Nernstian system

mass-transfer controlled current response.

Case 2: both O and R initially present

now must distinguish between cathodic limiting current ($i_{l,c}$)

and anodic " " ($i_{l,a}$)

$$i_{l,a} = -nFAm_R C_R^*$$

(again defined by $C_R(x=0) = \phi$)

for potentials away from those that give the $i_{l,a}$

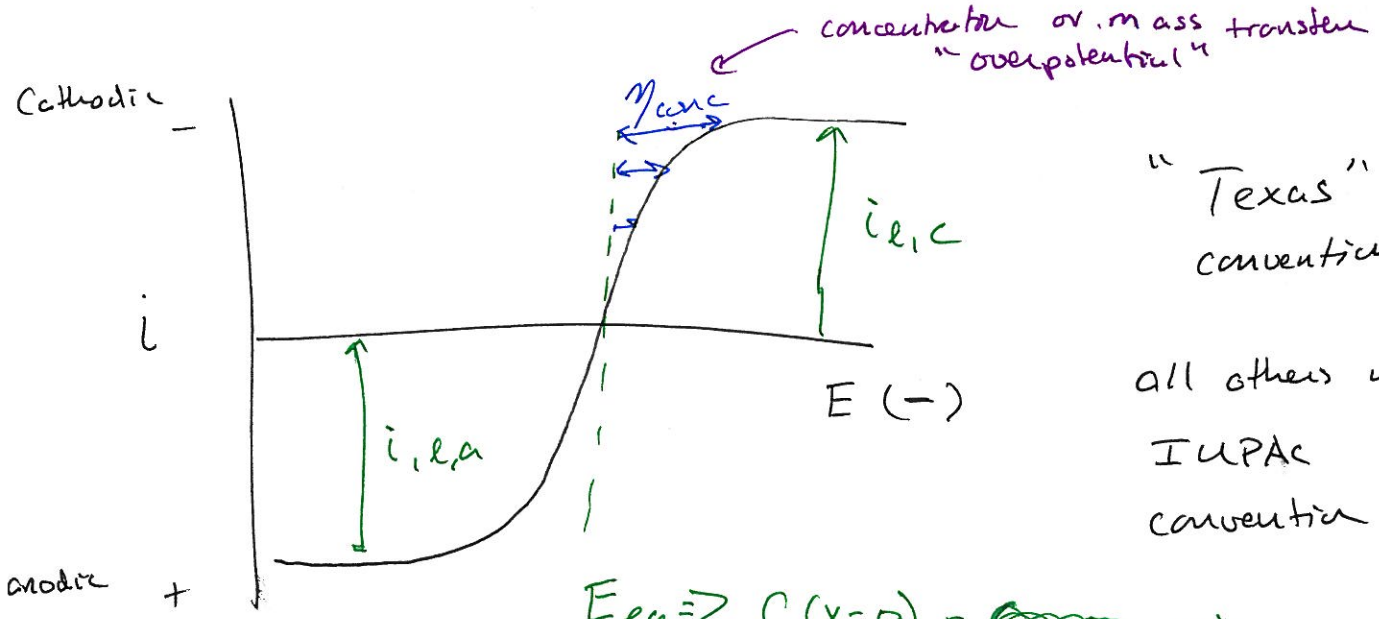
$$C_R(x=0) = \frac{i - i_{l,a}}{nFAm_R}$$

(identical to that given previously for the anodic current)

Again, start with the Nernst Equation:

$$E = E^o + \frac{RT}{nF} \ln \frac{C_O(x=0)}{C_R(x=0)} = E^o + \frac{RT}{nF} \ln \frac{(i_{l,c} - i)/nFAm_O}{(i - i_{l,a})/nFAm_R}$$

$$E = E^o + \frac{RT}{nF} \ln \frac{i_{l,c} - i}{i - i_{l,a}} - \frac{RT}{nF} \ln \frac{m_O}{m_R}$$



"Texas" convention

all others use IUPAC convention

$E_{eq} \Rightarrow C_O(x=0) = C_O^*$

$C_R(x=0) = C_R^*$

↳ this is the equilibrium potential

→ what you measure if you simple put an electrode in the solution!