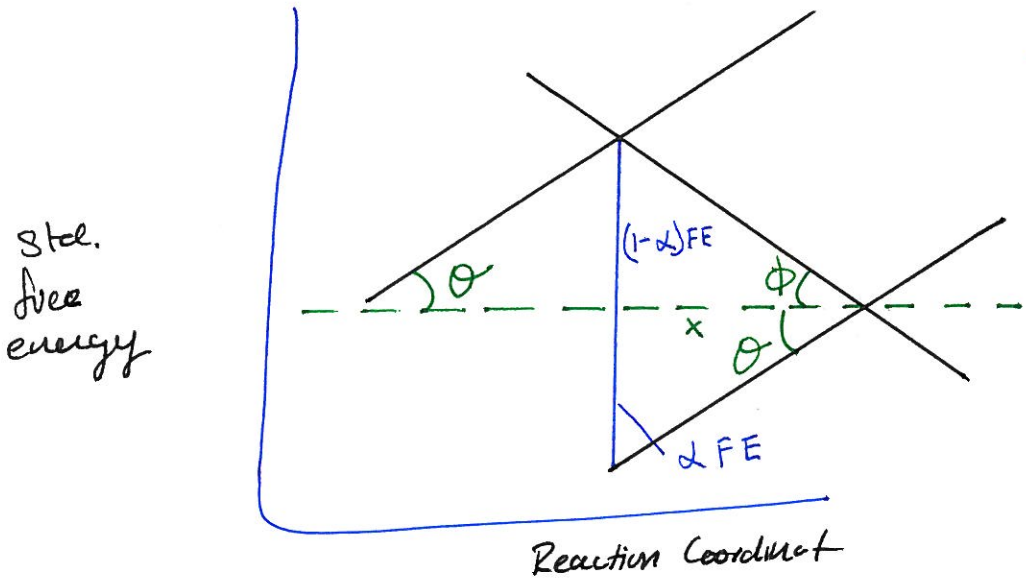
3.3.4 The transfer coefficient : a measure of the symmetry of the energy barrier



$$\tan\theta = \alpha FE / x$$

$$\tan\phi = (1-\alpha)FE / x$$

Solve algebra:

$$\alpha = \frac{x \tan\theta}{\alpha FE} \qquad x = \frac{\alpha FE}{\tan\theta}$$

$$\Rightarrow \tan\phi = \frac{(1-\alpha)\cancel{FE}\tan\theta}{\alpha \cancel{FE}}$$

$$\frac{\tan\phi}{\tan\theta} = \frac{1-\alpha}{\alpha} \quad = \quad \alpha = \frac{1}{\frac{\tan\phi}{\tan\theta}+1} = \boxed{\frac{\tan\theta}{\tan\phi+\tan\theta}}$$

$$\alpha\frac{\tan\phi}{\tan\theta} = 1-\alpha$$

$$\alpha\left(\frac{\tan\phi}{\tan\theta}+1\right) = 1$$

3.4 - Implications of the Butler-Volmer Model

at E.Q. the net current is $\emptyset$,

electrode should adopt a potential

given by the C_O^* and C_R^* (bulk concentrations)

Using Butler Volmer Expression:

$$i = 0 \Rightarrow \cancel{FAk^\circ} C_O(0,t) e^{-\alpha f (E_{eq} - E^\circ)}$$

$$= \cancel{FAk^\circ} C_R(0,t) e^{(1-\alpha) f (E_{eq} - E^\circ)}$$

at E.Q. bulk concentrations are found near the surface...

so

$$\frac{C_O^*}{C_R^*} = \frac{e^{(1-\alpha) f (E_{eq} - E^\circ)}}{e^{-\alpha f (E_{eq} - E^\circ)}} = e^{f (E_{eq} - E^\circ)}$$

which is simply the exponential form of the Nernst Equation:

$$\ln\left(\frac{C_O^*}{C_R^*}\right) = f (E_{eq} - E^\circ)$$

What is this?

$$E_{eq} = E^\circ + \frac{RT}{nF} \ln\left(\frac{C_O^*}{C_R}\right)$$

exchange current → even though net current is ϕ, we still envision balanced faradaic activity that can be expressed in terms of

i_0 → is = to either i_a or i_c at E.Q.

(1) $$\boxed{i_0 = FAk^0 C_0^* e^{-\alpha f(E_{eq} - E^0)}}$$

note exchange current depends on difference between E_{eq} and E^0

use Nernst Equation to generalize this expression:

also:

$$e^{f(E_{eq} - E^0)} = \frac{C_0^*}{C_R^*}$$ (exp. form of Nernst Eq.)

$$= e^{-\alpha f(E_{eq} - E^0)} = \left(\frac{C_0^*}{C_R^*}\right)^{-\alpha}$$ (~~multiply~~ raise to power of α)

$$C_0^* e^{-\alpha(E_{eq} - E^0)} = (C_R^*)^{\alpha}(C_0^*)^{-(\alpha-1)}$$

plug into (1) above

$$\boxed{i_0 = FAk^0 (C_R^*)^{\alpha} (C_0^*)^{1-\alpha}}$$

When is i_0 maximized?

if $\alpha = 1/2$?

$C_R^* = C_0^*$

3.4.2 The current-overpotential Equation

we want to now write the Butler Volmer expression in terms of $\eta = E - E_{eq}$ and i_0 instead of E^0 and k^0

η and i_0 are experimentally controllable and measurable parameters.

dividing Butler volmer expression by i_0 we have

FAK^0 terms cancel out

$$\frac{i}{i_0} = \frac{C_O(0,t)\, e^{-\alpha f(E-E^0)}}{C_O^{*(1-\alpha)}\, C_R^{*\alpha}} - \frac{C_R(0,t)\, e^{(1-\alpha) f(E-E^0)}}{C_O^{*(1-\alpha)}\, C_R^{*(\alpha)}}$$

$C_R^{*\alpha} = C_R^{*}\, C_R^{*\alpha-1}$

$$= \frac{C_O(0,t)}{C_O^{*}}\, e^{-\alpha f(E-E^0)} \left(\frac{C_O^*}{C_R^*}\right)^{\alpha} - \frac{C_R(0,t)}{C_R^*}\, e^{(1-\alpha) f(E-E^0)} \left(\frac{C_O^*}{C_R^*}\right)^{-(1-\alpha)}$$

we've factored out these terms

now From the Nernst Equation

we can write that $\left(\frac{C_O^*}{C_R^*}\right)^{\alpha} = e^{+\alpha f(E_{eq} - E^0)}$

Standard Potential

Equilibrium Potential of solution

and $\left(C_O^*/C_R^*\right)^{-(1-\alpha)} = e^{-(1-\alpha) f(E_{eq} - E^0)}$

now plugging into previous expression.

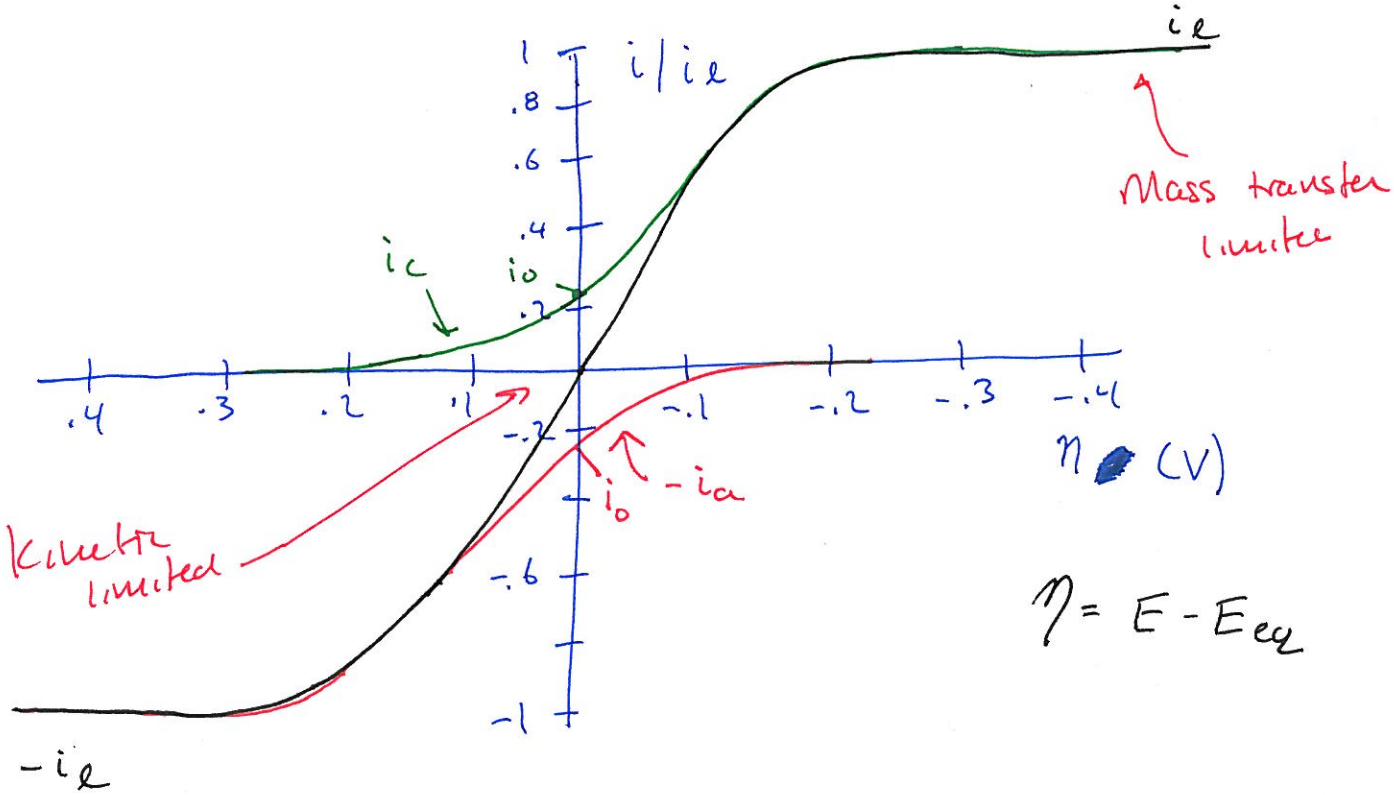
$$\frac{i}{i_0} = \frac{C_O(0,t)}{C_O^*} \underbrace{e^{-\alpha f (E-E^\circ)} e^{\alpha f (E_{eq}-E^\circ)}} - \frac{C_R(0,t)}{C_R^*} e^{(1-\alpha) f (E-E^\circ)} \cdot e^{-(1-\alpha) f (E_{eq}-E^\circ)}$$

simplifying these terms leads to

$$\boxed{i = i_0 \left[\frac{C_O(0,t)}{C_O^*} e^{-\alpha f \frac{(E-E_{eq})}{\eta}} - \frac{C_R(0,t)}{C_R^*} e^{(1-\alpha) f \frac{(E-E_{eq})}{\eta}} \right]}$$

- this is the current-over potential equation

- exponential kinetic factors are moderated by the mass-transport limitations $\left(\frac{C(0,t)}{C^*} \right)$ factor!



$\eta = E - E_{eq}$

Current - overpotential curves, $O + e \rightleftharpoons R$

$\alpha = 0.5$

$T = 298K$

$i_{\ell,a} = i_{\ell,c} = i_\ell$, $\frac{i_0}{i_\ell} = 0.2$

Approximate Forms of the i-E curves:

(a) no mass transfer effects → $\boxed{i = i_o\left[e^{-\alpha f \eta} - e^{(1-\alpha) f \eta}\right]}$

because, $C(0,t) = C^*$,

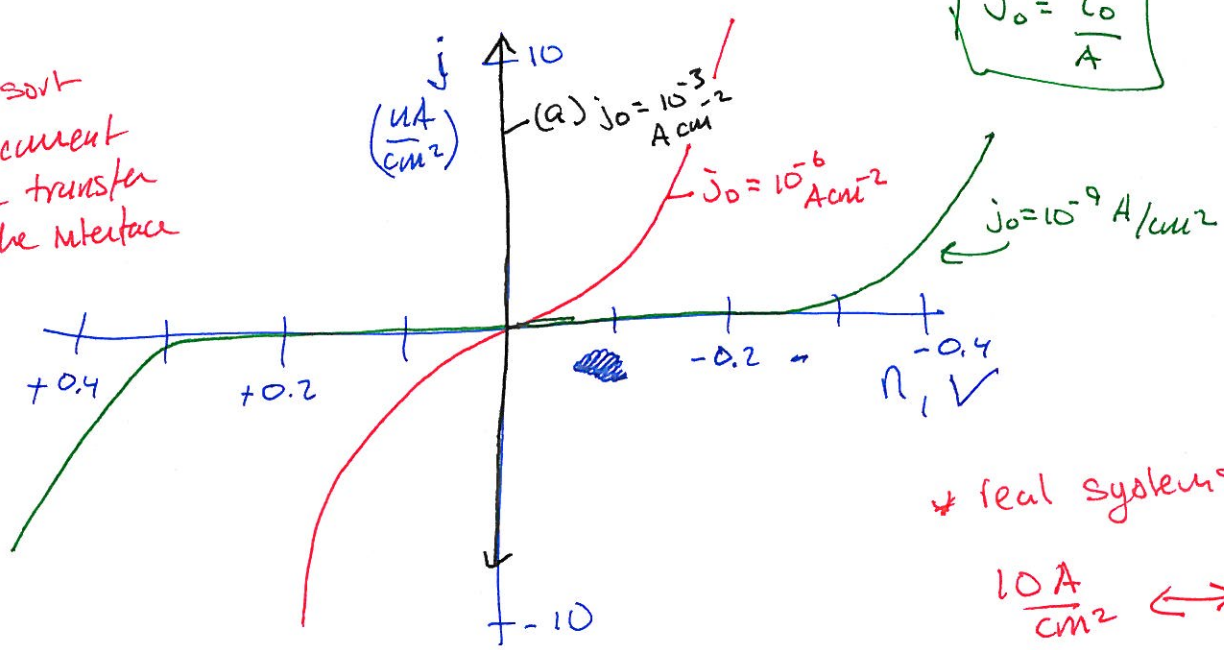
Surface concentration same as in the bulk

good approximation when i is ~ 10% of smaller limiting current.

– curves dominated by "activation overpotential"

$\boxed{j_o = \frac{i_o}{A}}$

* exchange current is sort of "idle" current for charge transfer across the interface



* real systems

$10 \frac{A}{cm^2} \longleftrightarrow < 1 \frac{pA}{cm^2}$

effect of the exchange current density on i-E in the absence of mass transport.

b linear characteristics at small η

for small x, $e^x \cong 1 + x$

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

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

$$i = i_0 \left[-\cancel{\alpha f \eta} - f\eta + \cancel{\alpha f \eta} \right] = \boxed{-i_0 f \eta}$$

which is linear.

Hence, the definition of the "charge-transfer Resistance"

$R = -\eta / i$ (voltage divided by current - ohm's law)

$$\boxed{R_{CT} = \frac{1}{f i_0} = \frac{RT}{F i_0}}$$

R_{CT}

any exponential looks linear over a small Δ

(C) Tafel behavior at large η

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

what happens for large ~~or~~ η (either positive or negative)?

~~small η~~

- One term dominates.
- considered totally irreversible kinetics.

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

and, $\eta = \underbrace{\frac{RT}{\alpha F} \ln i_0}_{a} - \underbrace{\boxed{\frac{RT}{\alpha F}}}_{b} i$

which matches experimentally observed:

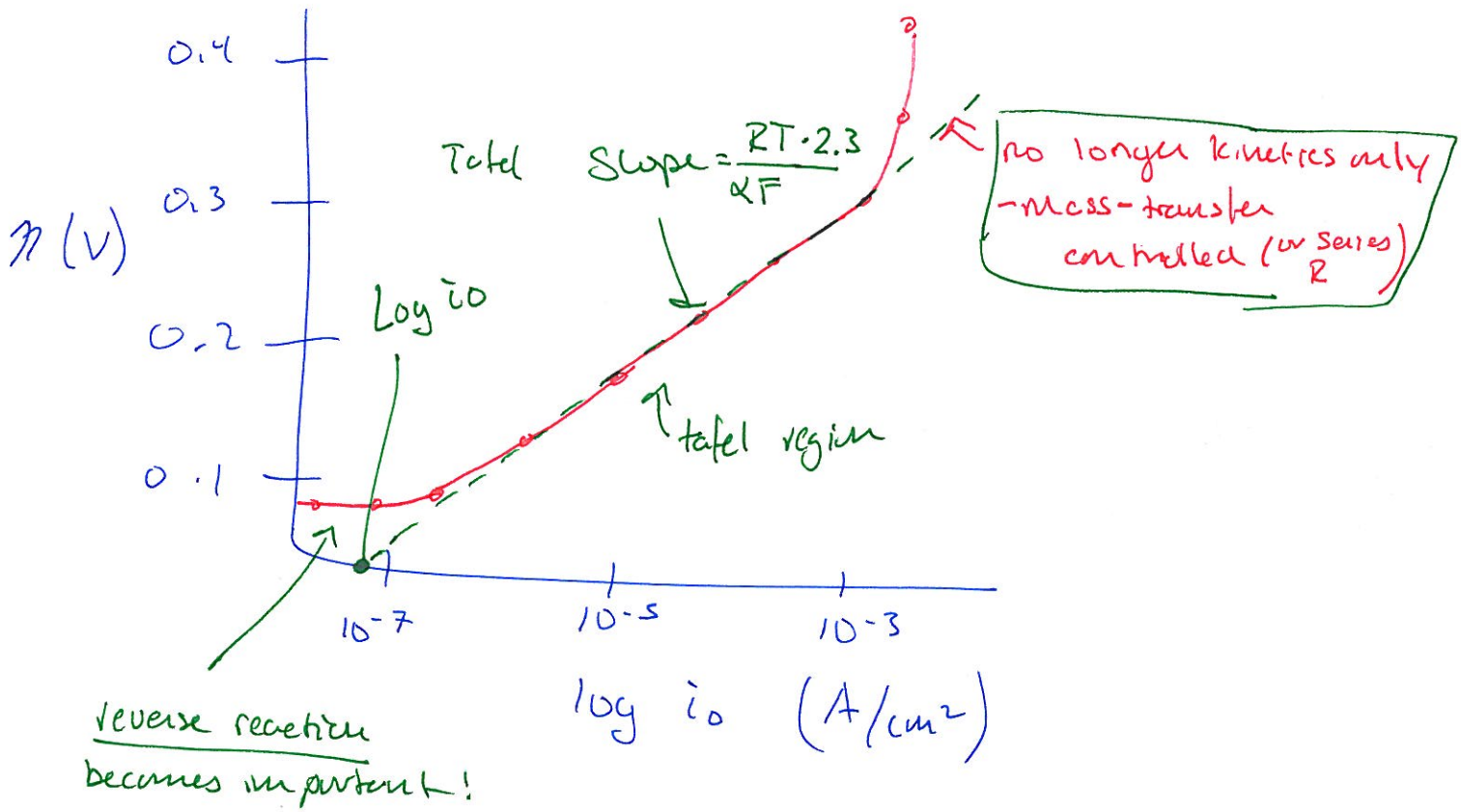
$$\eta = a + b \log i$$

tafel slope

tafel intercept

rewrite in terms of tafel slope or intercept

Tafel Plots



Note for a $1e^-$ transfer with a symmetric barrier ($\alpha = 0.5$)

$$\text{tafel slope} = \frac{RT \cdot 2.3}{(0.5) \cdot F} = 120\ mV\left(/dec\right)$$

often written per decade.

3.4.5 Very Facile Kinetics and Reversible Behavior

Current overpotential equation from before:

$$\left[\frac{i}{i_0} = \frac{C_O(0,t)}{C_O^*} e^{-\alpha f \eta} - \frac{C_R(0,t)}{C_R^*} e^{(1-\alpha) f \eta} \right.$$

if $\underline{i_0}$ gets huge compared to $\underline{i}$ (i.e. kinetics are fast)

then $\frac{i}{i_0} \rightarrow \phi$

So $$\frac{C_O(0,t)}{C_O^*} e^{-\alpha f \eta} = \frac{C_R(0,t)}{C_R^*} e^{(1-\alpha) f \eta}$$

$$= \frac{C_O(0,t)}{C_R(0,t)} = \frac{C_O^*}{C_R^*} e^{(1-\alpha) f \eta} \cdot e^{\alpha f \eta}$$

$$= \frac{C_O^*}{C_R^*} e^{f \eta} = \frac{C_O^*}{C_R^*} e^{f(E - E_{eq})}$$

From before,

the exponential form of the Nernst equation: (from Equilibrium state)

$$e^{f(E_{eq} - E^\circ)} = \frac{C_O^*}{C_R^*}$$

Reversible, Nernstian System. Surface at EQ w/ Electrode. Net current Flows due to Mass trans.

plug in to ~~Eq~~ find:

$$\frac{C_O(0,t)}{C_R(0,t)} = e^{f(E_{eq} - E^\circ)} e^{f(E - E_{eq})} = e^{f(E - E^\circ)}$$

independent of current ~~flow if~~

$$\Rightarrow \boxed{E = E^\circ + \frac{RT}{F} \ln \frac{C_O(0,t)}{C_R(0,t)}}$$

important! now electrode potential and SURFACE O/R are linked by Nernst Form EQN!

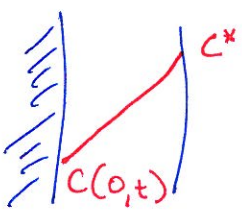
3.4.6 Effects of Mass Transfer

general form of the current overpotential equation:

$$i = i_0 \left[\boxed{\frac{C_O(0,t)}{C_O^*}} e^{-\alpha f \eta} - \boxed{\frac{C_R(0,t)}{C_R^*}} e^{(1-\alpha) f \eta} \right.$$

mass transfer terms → important when $C^* \neq C(0,t)$!

But, we have already ~~substituted~~ ~~derived~~ derived expression for mass-transport in simple case



Bulk stirred solution

Stagnant layer d_0

$$\boxed{\frac{C_O(x=0)}{C_O^*} = 1 - \frac{i}{i_{l,c}}} \qquad \boxed{\frac{C_R(x=0)}{C_R^*} = 1 - \frac{i}{i_{l,a}}}$$

~~Expressions~~ ~~for~~ surface concentration ~~in terms~~ to ~~of~~ Bulk concentration ratio related to current versus the limiting current.

You will "derive" this in the homework.

3.5 Multistep Mechanisms

- previously we considered simple one-step, one-electron reactions.
- many reactions are multistep

$2H^+ + 2e^- \rightarrow H_2$ → highly dependent on metal electrode
→ must go through surface intermediate

$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$ → Is it reasonable to assume that the reaction goes through Sn^{3+} intermediate? Unlikely that $2e^-$ simultaneously tunnel from electrode into the Sn^{4+} ion!

3.51 Rate Determining Electron Transfer

rate determining step ≡ R.D.S.

assumed that truly elementary electron transfer reactions involve only $1e^-$. n electrons, at least n steps

$O + ne^- \rightarrow R$ $\qquad n = n' + n'' + 1$

(1) $O + n'e \leftrightharpoons O'$ (net result of all steps prior to RDS)

(2) $O' + e \underset{k_b}{\overset{k_f}{\rightleftharpoons}} R'$ ~~(net result of all steps~~ RDS

(3) $R' + n''e \rightleftharpoons R$ (net result of all steps after RDS) leave as current bound

$$i = nFAk^\circ_{rds}\left[C_{O'}(0,t)e^{-\alpha f(E-E^\circ_{rds})} - C_{R'}(0,t)e^{(1-\alpha)f(E-E^\circ_{rds})}\right]$$

total n for rxn $\qquad$ intermediates $\qquad$ for rds n=1 $\qquad$ E° for RDS.

How to find $C_{O'}(0,t)$, $C_{R'}(0,t)$?

3.5.2 Multi-Step Processes at Equilibrium

$\Rightarrow \underline{i = 0}$ (definition of E.Q.)

Note → could skip this, net result is that Deviation Response is maintained at E.Q. ie $i \to \phi$

* all individual steps must also therefore be at EQ.!

we can therefore write the Nernstian relationships to define each equilibrium for each reaction step: (keep previous rxn steps on the board, 1, 2, 3)

① $$e^{n' f (E_{eq} - E^{o}_{pre})} = \frac{C_O^*}{(C_{O'})_{eq}}$$

result of pre-reaction steps (since all steps at ϕ do not need to account for individual step kinetics)

② $$e^{f (E_{eq} - E^{o}_{rds})} = \frac{(C_{O'})_{eq}}{(C_{R'})_{eq}}$$

primes indicate concentration of the intermediates

R.D.S.!

③ $$e^{n'' f (E_{eq} - E^{o}_{post})} = \frac{(C_{R'})_{eq}}{C_R^*}$$

result of post reaction steps

Substitute ① and ③ into ② to get:

④ $$e^{f (E_{eq} - E^{o}_{rds})} \, e^{n' f (E_{eq} - E^{o}_{pre})} \, e^{n'' f (E_{eq} - E^{o}_{post})} = \frac{C_O^*}{C_R^*}$$

now since $$E^{o} = \frac{E^{o}_{rds} + n' E^{o}_{pre} + n'' E^{o}_{post}}{n}$$

④ reduces back to

$$e^{n f (E_{eq} - E^{o})} = \frac{C_O^*}{C_R}$$

so at equilibrium, $i \to 0$, nernst equation comes out of BV equation.

Note: this can be described by a simple ex:

		ΔG
1.	$A + e^- \Rightarrow B$	$\Delta G_1 = -FE_1$
2	$B + e^- \Rightarrow C$	$\Delta G_2 = -FE_2$
	$3A + 2e^- \Rightarrow C$	ΔG

$-nFE_3 = \Delta G_1 + \Delta G_2$

$-nFE_3 = -F(E_1 + E_2)$

$E_3 = \frac{E_1 + E_2}{2}$

....

3.5.3 Nernstian Multistep Processes, under current flow

Note: could skip this...

Key concept → net result is, if $i_0 \gg i$ for all steps, then surface concentrations of initial reactant and final product are in local Nernstian balance at all times, regardless of the mechanism!

derivation: if $i_{0,rds} \gg i$

then Nernstian description of RDS leads to

$$\frac{C_O'(0,t)}{C_R'(0,t)} = e^{f(E-E^\circ_{rds})} \qquad f = \frac{F}{RT}$$

(this is just from the Butler-Volmer equation in the limit of $\frac{i}{i_0} \to 0$, now written out for a single RDS)

Same as we just did for the equilibrium on the last page of notes

we can derive that

$$e^{nf(E_{eq}-E^\circ)} = \frac{C_O(0,t)}{C_R(0,t)}$$

meaning as $i < i_0$ (for all steps) surface EQ. holds.

3.5.4 Quasi reversible and irreversible multistep Processes

→ not Nernstian

→ not at Equilibrium

→ measure current-potential behavior in terms of controllable parameters. → use info to test kinetic hypothesis

* if RDS is an electron transfer:

|| Note: best if left with smart bound from initial |

$$i = nFAk^{\circ}_{rds}\left[C_O'(0,t)\, e^{-\alpha f(E-E_{rds})} - C_R'(0,t)\, e^{(1-\alpha) f(E-E_{rds})}\right]$$

Is this form of the equation useful?

Not really → how can we know what $C_O'(0,t)$ and $C_R'(0,t)$ are?

We can write intermediate in terms of products + reactants (O, R) as before, because we can assume that the pre- and post reactions are in equilibrium since i is much less than i_0, for not RDS's

$$C_O'(0,t) = e^{-n' f(E-E^{\circ}_{pre})} \cdot C_O(0,t)$$

$$C_R'(0,t) = e^{n'' f(E-E^{\circ}_{post})}\, C_R(0,t)$$

just the Nernst equ.

Substitute these expressions into the multi step i - E expression to yield

$$\boxed{i = nFA\,k^{\circ}_{rds}\,C_O(0,t)\,e^{-n' f(E - E^{\circ}_{pre})}\,e^{-\alpha f(E - E^{\circ}_{rds})} - nFAk^{\circ}_{rds}\,C_R(0,t)\,e^{n'' f(E - E^{\circ}_{post})}\,e^{(1-\alpha) f(E - E^{\circ}_{rds})}}$$

But... this is not yet useful, because we want i - E relationship in terms of η and i_o!

The exchange current for the R.D.S. is

$$i_{o,rds} = FA\,k^{\circ}_{rds}\,(C_{O'})_{eq}\,e^{-\alpha f(E_{eq} - E^{\circ}_{rds})}$$

intermediate concentration at eq (where i_o is defined)

E_{eq} defined by Nernstian relationship

But $\boxed{i_o = n\,i_{o,rds}}$

(because all electron exchange reactions are going on in parallel for each step)

Pre-reactions are at equilibrium so that:

$$(C_{O'})_{eq} = C_O^{*}\,e^{-n' f(E_{eq} - E^{\circ}_{pre})}$$

(nernstian response holds)

$$\Rightarrow \quad i_o = nFAk^o_{ids} C_o^* e^{-n' f(E_{eq} - E^o_{pre})} e^{-\alpha f(E_{eq} - E^o_{ids})}$$

multiply both sides by $1 = e^{(n'+\alpha) f (E^o - E^o)}$

we get

$$i_o = nFA\, k^o_{ids} C_o^* e^{+n' f(E^o_{pre} - \bar{E}^o)} e^{-n' f(E_{eq} - \bar{E}^o)}$$

these are combined in the book...

$$\cdot e^{-\alpha f(E_{eq} - \bar{E}^o)} e^{+\alpha f(E^o_{rds} - \bar{E}^o)}$$

these terms can be described in terms of the Nernst Equation for the overall process

this is term we want to factor out the expression

$$\boxed{e^{-(n'+\alpha) f (E_{eq} - E^o)}} = \left(e^{nf(E_{eq} - E^o)}\right)^{-\frac{n'+\alpha}{n}}$$

$$\boxed{= \left(\frac{C_o^*}{C_R^*}\right)^{-\frac{n'+\alpha}{n}}}$$

putting all together

$$i_o = nFA\underbrace{k^o_{rds}\, e^{n' f(E^o_{pre} - E^o)}\, e^{\alpha f(E^o_{rds} - E^o)}}_{= k^o_{app}} C_O^{*\left(1 - \frac{n'+\alpha}{n}\right)} C_R^{*\left(\frac{n'+\alpha}{n}\right)}$$

$= k^o_{app}$ the apparent rate constant.

Note that the exponential terms are <u>constants</u> of the system at given T and P

$$\boxed{i_o = nFA\, k^o_{app}\, C_O^{*\left(1 - \frac{n'+\alpha}{n}\right)} C_R^{*\left(\frac{n'+\alpha}{n}\right)}}$$

Now we can continue to develop the <u>current-overpotential expression</u>

general method involves again multiplying the general Butler-Volmer Expression for a multistep reaction by factors of "1" (i.e. with $e^{(E_{eq} - E_{eq})}$ & to get and $e^{(E^o - E^o)}$

$$\boxed{\eta = E - E_{eq}}$$

then rewrite in terms of i_o which we derived earlier...

* the result turns out to be quite useful:

$$\frac{i}{i_0} = \frac{C_O(0,t)}{C_O^*} e^{-(n'+\alpha)f\eta} - \frac{C_R(0,t)}{C_R^*} e^{(n''+1-\alpha)f\eta}$$

$$\boxed{n = n' + n'' + 1}$$

* which is analogous to the equations we derived earlier for a single e^- transfer reaction.

when the current is small or the mass transfer is good...

$$i = i_0 \left[e^{-(n'+\alpha)f\eta} - e^{(n''+1-\alpha)f} \right]$$

when the overpotential η is large then only one term dominates

$$i = i_0 e^{-(n'+\alpha)f\eta}$$

or $\ln i = \ln i_0 - (n'+\alpha)f\underline{\eta}$

so a plot of $\log i$ vs η or η vs $\log i$ has a <u>slope</u> that depends on n'!

so the Tafel slope tells you something about the mechanism of charge transfer! (see HW)