389

Lecture #11 of 18(?)

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390

Mass Transfer Processes

Chapters 1 and 4

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391

Q: What's in this set of lectures?
A: B&F Chapters 1 & 4 main concepts:

- Section 1.4: Mass transfer and Semi-empirical treatment of electrochemical observations

- Chapter 4:   Mass transfer

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(UPDATED) 392

Looking forward… Section 1.4 and Chapter 4

- Mass transfer
- Diffusion
- Migration / Drift
- Convection
- Semi-empirical diffusive models
- **Conductivity**
- **Transport (Transference) number**
- **Balance sheets**
- *Ohmic drop/loss*

392

… because we are at steady-state, let's approximate the concentration gradient near the WE as a linear function: **(ADDED)** 393

RECALL:
$$N_O(x) = -D_O \frac{C_O^* - C_O(x = 0)}{\delta_O}$$

where C_O^* is the bulk concentration of O, δ is the Nernst diffusion layer thickness

the linear approximation

C_O^*

the TRUE concentration gradient

C_O

Bard & Faulkner, 2nd Ed., Figure 1.4.1

$C_O(x=0)$

stirring of the bulk solution causes δ to become well-defined, time-invariant, and a short distance to encounter bulk solution conditions

Figure 1.4.1 Concentration profiles (solid lines) and diffusion layer approximation (dashed lines). $x = 0$ corresponds to the electrode surface and δ_O is the diffusion layer thickness. Concentration profiles are shown at two different electrode potentials: (1) where $C_O(x = 0)$ is about $C_O^*/2$, (2) where $C_O(x = 0) \approx 0$ and $i = i_l$.

393

(ADDED) 394

RECALL:
$$E = E_{1/2} + \frac{RT}{nF} \ln\left(\frac{i_l - i}{i}\right)$$

… this will show up again…

Cathodic

i_l

$E_{1/2}$

E

(−) ⟶

log [(i_l − i)/i]

$E_{1/2}$

E

(−) ⟶

Anodic

(a)   (b)

Figure 1.4.2 (a) Current-potential curve for a nernstian reaction involving two soluble species with only oxidant present initially. (b) $\log[(i_l - i)/i]$ vs. E for this system.

What happens to the potential when $i \to i_l$? $E \to -\infty$
What happens to the potential when $i \to 0$? $E \to +\infty$

394

... and when $C_R^* \neq 0$... 395

RECALL: $E = E^{0\prime} - \dfrac{RT}{nF}\ln\left(\dfrac{m_O}{m_R}\right) + \dfrac{RT}{nF}\ln\left(\dfrac{i_{l,c} - i}{i - i_{l,a}}\right)$
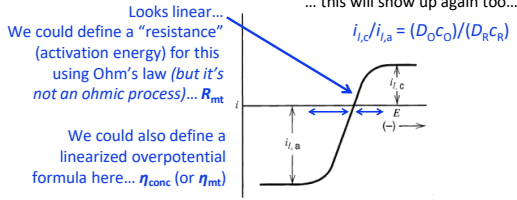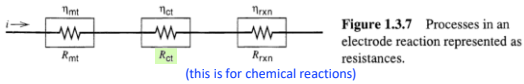
... this will show up again too...

$i_{l,c}/i_{l,a} = (D_O c_O)/(D_R c_R)$

Looks linear...
We could define a "resistance" (activation energy) for this using Ohm's law *(but it's not an ohmic process)*... $\boldsymbol{R_{mt}}$

We could also define a linearized overpotential formula here... $\boldsymbol{\eta_{conc}}$ (or $\boldsymbol{\eta_{mt}}$)

Figure 1.4.3 Current-potential curve for a nernstian system involving two soluble species with both forms initially present.

... but recall that this is all due to mass transport by <u>diffusion</u> only...
... **what if we now also include mass transport by migration/drift?**...

395

Key Slide: Summary of overpotentials due to variable resistances... 396

η_{mt} η_{ct} η_{rxn}
R_{mt} R_{ct} R_{rxn}
(this is for chemical reactions)

Figure 1.3.7 Processes in an electrode reaction represented as resistances.

The potential across an electrochemical cell must be "dropped" across the intervening media, e.g. electrodes, electrolytes, interfaces. Thus, one can model an electrochemical cell as the sum of the potential drops / differences because they are electrically in series. Each of these potential differences is a function of the steady-state current, because the current through each is the same ($I = I_1 = I_2 = I_3$), written as $E(I) = E_1(I) + E_2(I) + E_3(I)$.

The Randles equivalent circuit is very common in electrochemistry...
... why is this such a common equivalent circuit representation?

R_s c R_{ct} ... where is R_{mt}?... more on that later...

http://pubs.rsc.org/en/content/articlehtml/2013/py/c2py20613g
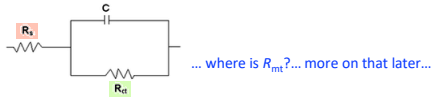
396

... Include migration/drift to capture R_s (or R_u) using Ohm's law... 397

- The Drude model starts with... a potential bias creates an electric field ($-d\phi/dx = \boldsymbol{E}$) that drives electrons preferentially in one direction
- These electrons bounce off of stationary crystal ions (and other things, e.g. other electrons) which slow the transport of the electrons and, as before, they are said to have a resulting average drift velocity, $\boldsymbol{v_d}$ (see below)
- With each bounce, these electrons lose kinetic energy to heat (*inelastic* collision) and this results in the loss of some of the thermodynamic driving force (potential)
- Thus, at this point, these electrons have less (free) energy to move ("potential drop")...

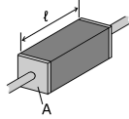... or, they are "stopped" and they start again due to the potential at this new starting location
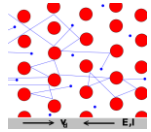
http://en.wikipedia.org/wiki/Ohm%27s_law
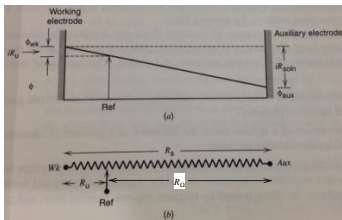
397

… so, is resistance really the optimal intrinsic property that we should be concerned with? 398

Given a resistor with resistance, R, look what you can calculate:

$\rho = \frac{RA}{l}$… which is the resistivity (Ω cm)

   … the resistivity is great because it is independent of size! …

$\sigma = \frac{1}{\rho} = \frac{l}{RA} = \frac{Gl}{A}$… which is the conductivity (Ω^{-1} cm^{-1} = mho cm^{-1} (< 1971) = S cm^{-1}) and where S stands for siemen … the conductivity is equally as great because it is also independent of size! …

… well, the conductivity (of an electrolyte) is even better, because it can be determined directly based on the properties of its constituents…
… let's see how…

398

… recall, the *simplified* Nernst–Planck equation (with "no" mixing) **(UPDATED)** 399
… for one species and as a current density…   No subscript i… species independent

$$J_i = z_i F N_i = -z_i F D_i \cdot \frac{dc_i}{dx} - |z_i| F \mu_i c_i \cdot \frac{d\phi}{dx}$$

… when little current is passing, it is assumed that the bulk concentration of species does not change much and so J_{diff} is small (~0) …
… thus, for all species $J = \sum_i J_{\text{migration},i}$… and also recall Ohm's law ($E = iR$)…

$J = -F \sum_i (|z_i| \mu_i c_i) \cdot \frac{d\phi}{dx} = \frac{E}{RA} = \frac{EG}{A}$, where G is the conductance (S)

$G = \frac{AF}{E} \mathbf{E} \sum_i (|z_i| \mu_i c_i)$, where $\mathbf{E}$ is the electric field (V/m), since $\frac{d\phi}{dx} = -\mathbf{E}$

… then, because we assumed no gradients in species concentrations ($J_{\text{diff}} \approx 0$) – meaning no diffusion component – and assuming a linear change in potential over space, l, then $\mathbf{E} = -E/l$ and so, assuming unsigned…

$G = \frac{AF}{l} \sum_i (|z_i| \mu_i c_i) = \frac{A}{l} \sigma$, where σ **is the conductivity (S cm^{-1})**

399

… recall, the *simplified* Nernst–Planck equation (with "no" mixing) **(UPDATED)** 400
… for one species and as a current density…   No subscript i… species independent

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$G = \frac{AF}{l} \sum_i (|z_i| \mu_i c_i) = \frac{A}{l} \sigma$ $\sigma = F \sum_i (|z_i| \mu_i c_i)$

… Wow! Simple!

400

… so, who can tell me what the transport (transference) number is? 401

$$t_i = \frac{|z_i|u_i C_i}{\displaystyle\sum_j |z_j|u_j C_j}$$

… It is the fraction of the conductivity that each ion carries…
… and thus, the t_i must sum to one!

… it is the fraction of the current (density) that each ion carries

$J = -F\sum_i(|z_i|\mu_i c_i)\cdot\frac{d\phi}{dx} = \frac{E}{RA} = \frac{EG}{A}$, where G is the conductance (S)

$$\sigma = F\sum_i(|z_i|\mu_i c_i)$$

401

(UPDATED) 402

Looking forward… Section 1.4 and Chapter 4

- Mass transfer
- Diffusion
- Migration / Drift
- Convection
- Semi-empirical diffusive models
- Conductivity
- Transport (Transference) number
- **Balance sheets**
- *Ohmic drop/loss*

402

… and so let's understand the interplay of diffusion and migration… 403
… again, the Nernst–Planck equation… **(UPDATED)**

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

diffusion   migration   convection

… and let's continue to suppose that we do not stir at the electrode surface…

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

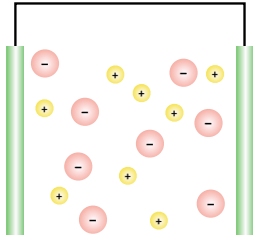diffusion   migration   convection

Question: How can we analyze an electrochemical experiment in order to ascertain whether migration has been reduced to the point where it can be completely neglected?

current   flux

$$i = i_{d(\text{iffusion})} + i_{m(\text{igration})} = nFAN(x)$$

403

So, $i_{m(igration)}$ can reinforce $i_{d(iffusion)}$… or oppose it…   404

404

So, $i_{m(igration)}$ can reinforce $i_{d(iffusion)}$… or oppose it…   405
… in, for example, an electrolytic cell…
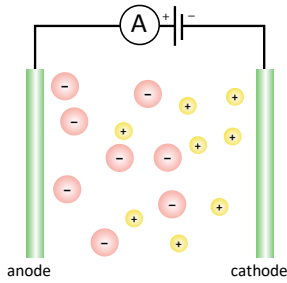
anode   cathode

○− i_m adds to the current (anode); i_d subtracts from the current (cathode)

○+ i_m adds to the current (cathode); i_d subtracts from the current (anode)

405

So, $i_{m(igration)}$ can reinforce $i_{d(iffusion)}$… or oppose it…   406
… in, for example, an electrolytic cell…

- cathodes "source" negative charge; anodes "sink" it
- so, migration drives anions from the cathode to the anode, and cations from the anode to the cathode
- neutral species are not affected… Huh?

… *examples:*

Don't forget about us!

$Cu^{2+} + 2e \rightarrow Cu$ $Cu(CN)_4^{2-} + 2e \rightarrow Cu + 4CN^-$ $Cu(CN)_2 + 2e \rightarrow Cu + 2CN^-$

Cu^{2+} $Cu(CN)_4^{2-}$ $Cu(CN)_2$

i_d i_d i_d
i_m i_m

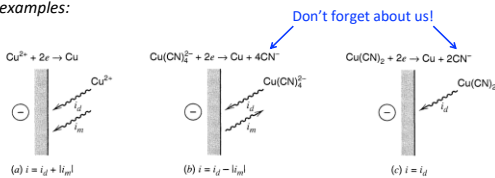(a) $i = i_d + |i_m|$ (b) $i = i_d - |i_m|$ (c) $i = i_d$

Figure 4.3.1   Examples of reduction processes with different contributions of the migration current: (a) positively charged reactant, (b) negatively charged reactant, (c) uncharged reactant.

406

... B&F's "balance sheets" help us understand the role of migration in steady-state electrolytic mass transport. *Let's break them down:* 407

all ions in the bulk of the cell contribute to migration *by an amount proportional to their transport number...*

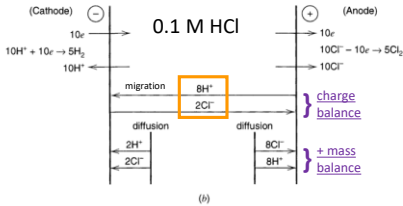$$t_i = \frac{|z_i| u_i C_i}{\sum_j |z_j| u_j C_j}$$

Figure 4.3.2 Balance sheet for electrolysis of hydrochloric acid solution. (*a*) Cell schematic. (*b*) Various contributions to the current when $10e$ are passed in the external circuit per unit time.

$$t_{H^+} = \frac{|1|(3.6 \times 10^{-3}\ \text{cm}^2\text{s}^{-1}\text{V}^{-1})(0.1 \times 10^{-3}\ \text{mol/cm}^3)}{|1|(3.6 \times 10^{-3}\ \text{cm}^2\text{s}^{-1}\text{V}^{-1})(0.1 \times 10^{-3}\ \text{mol/cm}^3) + |1|(7.9 \times 10^{-4}\ \text{cm}^2\text{s}^{-1}\text{V}^{-1})(0.1 \times 10^{-3}\ \text{mol/cm}^3)} = \boxed{0.82} \approx 8$$

$$t_{Cl^-} = \boxed{0.18} \approx 2$$

B&F Example #1 (of 3)

407

... B&F's "balance sheets" help us understand the role of migration in steady-state electrolytic mass transport. *Let's break them down:* 408

diffusion occurs only in regions where a concentration gradient exists... near the electrodes...

Figure 4.3.2 Balance sheet for electrolysis of hydrochloric acid solution. (*a*) Cell schematic. (*b*) Various contributions to the current when $10e$ are passed in the external circuit per unit time.

these coefficients are the values necessary to satisfy the steady-state condition of $i = i_m + i_d$... for example, at the *cathode (left)*:

$10H^+$(needed) = $8H^+$(migration) + $2H^+$(diffusion)...
$+ 2Cl^-$(diffusion) for charge balance

B&F Example #1 (of 3)

408

... B&F's "balance sheets" help us understand the role of migration in steady-state electrolytic mass transport. *Let's break them down:* 409

Figure 4.3.2 Balance sheet for electrolysis of hydrochloric acid solution. (*a*) Cell schematic. (*b*) Various contributions to the current when $10e$ are passed in the external circuit per unit time.

and at the *anode (right)*:

$10Cl^-$(needed) = $2Cl^-$(migration) + $8Cl^-$(diffusion)...
$+ 8H^+$(diffusion) for charge balance

B&F Example #1 (of 3)

409

… B&F's "balance sheets" help us understand the role of migration in steady-state electrolytic mass transport. *Let's break them down:* 410

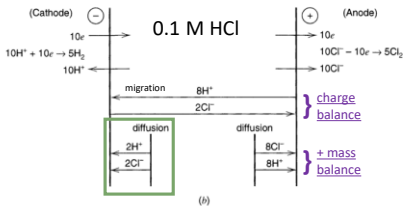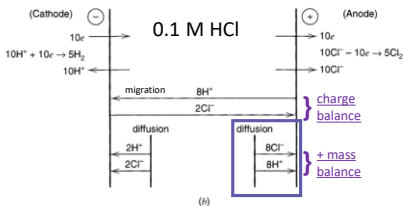If we focus on the **cathode H⁺ current** and **anode Cl⁻ current**…
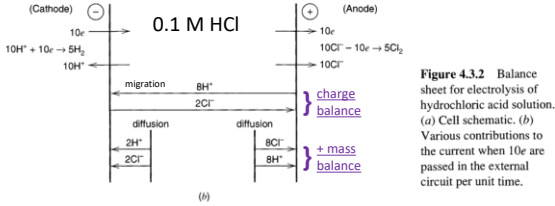
Figure 4.3.2 Balance sheet for electrolysis of hydrochloric acid solution. (*a*) Cell schematic. (*b*) Various contributions to the current when 10e are passed in the external circuit per unit time.

… we can also estimate the relative contribution of i_d and i_m at each electrode:

cathode (for H⁺): $i = -10$; $i_d = -2$, $i_m = -8$ *(80% of the H⁺ current is migration)*
anode (for Cl⁻): $i = +10$; $i_d = 8$, $i_m = 2$ *(20% of the Cl⁻ current is migration)*

410

… again, at steady-state, ionic migration current must equal electronic current (due to KCL!) 411

This is a negative current…

6e⁻ need 6 "+"s, whose fractional conductivities are t_i

… and so is this!

Figure 4.3.3 Balance sheet for electrolysis of the Cu(II), Cu(I), NH₃ system. (*a*) Cell schematic. (*b*) Various contributions to the current when 6e are passed in the external circuit per unit time; $i = 6$, $n = 1$. For Cu(II) at the cathode, $|i_m| = (1/2)(1/3)(6) = 1$ (equation 4.3.3), $i_d = 6 - 1 = 5$ (equation 4.3.4). For Cu(I) at the anode, $|i_m| = (1/1)(1/6)(6) = 1$, $i_d = 6 + 1 = 7$.
B&F Example #2 (of 3)

411

… again, at steady-state, counterions move to maintain electroneutrality in diffusion layers 412

This is a negative current…

6e⁻ need 6 "+"s, whose fractional conductivities are t_i

… and so is this!

$-5(2) + 7(1) = -3$

$= 3(1) = +3$
… neutral!

Figure 4.3.3 Balance sheet for electrolysis of the Cu(II), Cu(I), NH₃ system. (*a*) Cell schematic. (*b*) Various contributions to the current when 6e are passed in the external circuit per unit time; $i = 6$, $n = 1$. For Cu(II) at the cathode, $|i_m| = (1/2)(1/3)(6) = 1$ (equation 4.3.3), $i_d = 6 - 1 = 5$ (equation 4.3.4). For Cu(I) at the anode, $|i_m| = (1/1)(1/6)(6) = 1$, $i_d = 6 + 1 = 7$.
B&F Example #2 (of 3)

412

… again, at steady-state, counterions move to maintain electroneutrality in diffusion layers   413

… and this is a positive current (at that electrode)…

(Cathode) ⊖	0.001 M Cu(II)Cl₂/Cu(I)Cl	⊕ (Anode)

$6e$ → $6e$

$6Cu(II) + 6e \rightarrow 6Cu(I)$ $6Cu(I) - 6e \rightarrow 6Cu(II)$

6Cu(II)   6Cu(II)
6Cu(I)   6Cu(I)

migration   3Cl⁻

6e⁻ need 6 "+"s, whose fractional conductivities are t_i … and so is this!

1Cu(II)
1Cu(I)

diffusion   diffusion

-5(2) + 7(1) = -3

5Cu(II)   5Cu(II)   5(2) + -7(1) = +3
7Cu(I)   7Cu(I)
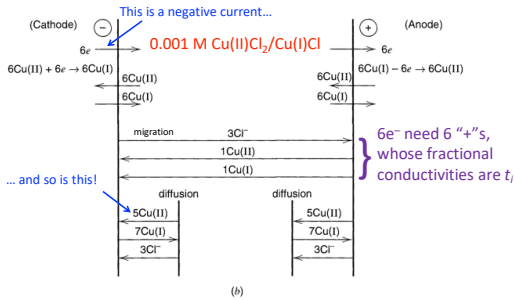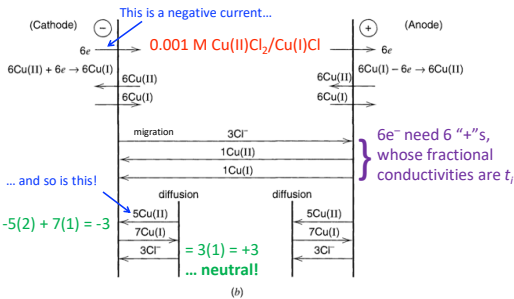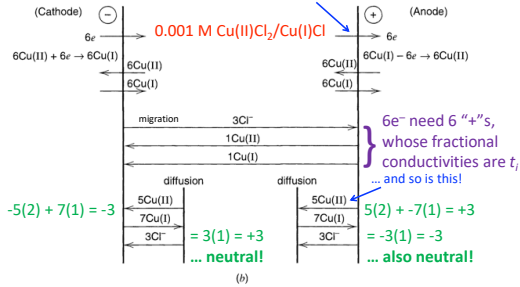3Cl⁻   = 3(1) = +3   3Cl⁻   = -3(1) = -3
… neutral!   … also neutral!

(b)

Figure 4.3.3 Balance sheet for electrolysis of the Cu(II), Cu(I), NH₃ system. (a) Cell schematic. (b) Various contributions to the current when $6e$ are passed in the external circuit per unit time; $i = 6, n = 1$. For Cu(II) at the cathode, $|i_m| = (1/2)(1/3)(6) = 1$ (equation 4.3.3), $i_d = 6 - 1 = 5$ (equation 4.3.4). For Cu(I) at the anode, $|i_m| = (1/1)(1/6)(6) = 1$, $i_d = 6 + 1 = 7$.

B&F Example #2 (of 3)

413

… adding a supporting electrolyte reduces the original i_m values   414

(Cathode) ⊖	0.001 M Cu(II)Cl₂/Cu(I)Cl 0.1 M NaClO₄	⊕ (Anode)

$6e$ → $6e$

$6Cu(II) + 6e \rightarrow 6Cu(I)$ $6Cu(I) - 6e \rightarrow 6Cu(II)$

6Cu(II)   6Cu(II)
6Cu(I)   6Cu(I)

migration   2.91 Na⁺

Na⁺ClO₄⁻ dominates because it carries the most current; its contribution to σ is large, and thus its components have the largest values of t_i

2.91 ClO₄⁻
0.0291 Cu(II)
0.0291 Cu(I)
0.0873 Cl⁻

But this is actually much more complex because of the…

diffusion   diffusion

5.97Cu(II)   5.97Cu(II)
6.029Cu(I)   6.029Cu(I)

… diffusion effects here →

2.92Na⁺   2.92Na⁺
2.92ClO₄⁻   2.92ClO₄⁻

Na⁺, ClO₄⁻, **and Cl⁻** must share charge balance responsibilities… **… and so this is incorrect!**

B&F Example #3 (of 3)   (b)

Figure 4.3.4 Balance sheet for the system in Figure 4.3.3, but with excess NaClO₄ as a supporting electrolyte. (a) Cell schematic. (b) Various contributions to the current per unit time $(i = 6, n = 1)$. $t_{Cu(II)} = [(2 \times 10^{-3})\lambda/(2 \times 10^{-3} + 10^{-3} + 3 \times 10^{-3} + 0.2)\lambda] = 0.0097$. For Cu(II) at the cathode, $|i_m| = (1/2)(0.0097)(6) = 0.03$, $i_d = 6 - 0.03 = 5.97$.

414

… adding a supporting electrolyte reduces the original i_m values   415

(Cathode) ⊖	0.001 M Cu(II)Cl₂/Cu(I)Cl 0.1 M NaClO₄	⊕ (Anode)

$6e$ → $6e$

$6Cu(II) + 6e \rightarrow 6Cu(I)$ $6Cu(I) - 6e \rightarrow 6Cu(II)$

6Cu(II)   6Cu(II)
6Cu(I)   6Cu(I)

migration   2.91 Na⁺

Balance sheet now balances after corrections here, which are "underlined"

2.91 ClO₄⁻
0.0291 Cu(II)
0.0291 Cu(I)
0.0873 Cl⁻   0.0927, so sum is 6

This has a challenging sign convention, so don't worry about it… Just use absolute numbers!

diffusion   diffusion

5.97Cu(II)   5.9709   5.9709   5.97Cu(II)
6.029Cu(I)   6.0291   6.0291   6.029Cu(I)
2.92Na⁺   2.91   2.91   2.92Na⁺
2.92ClO₄⁻   2.91   2.91   2.92ClO₄⁻

PRECISION: -5.9709(2) + 6.0291(1) = -5.9127… +2.91(1) + 2.91(1) = 5.82… **so, +0.0927 for Cl⁻ toward the cathode**

Figure 4.3.4 Balance sheet for the system in Figure 4.3.3, **… and -0.0927 for Cl⁻ away from the anode** electrolyte. (a) Cell schematic. (b) Various contributions to the current when $6e$ are passed in the external circuit per unit time $(i = 6, n = 1)$. $t_{Cu(II)} = [(2 \times 10^{-3})\lambda/(2 \times 10^{-3} + 10^{-3} + 3 \times 10^{-3} + 0.2)\lambda] = 0.0097$. For Cu(II) at the cathode, $|i_m| = (1/2)(0.0097)(6) = 0.03$, $i_d = 6 - 0.03 = 5.97$.

415

Now, do the following trends make sense? Reaction is **Tl⁺ + e⁻ ⇌ Tl⁰**   416

We derived the following equation considering diffusive transport only *(i.e. in the presence of large amounts of supporting electrolyte)…*

$$i_l = nFAm_O C_O^*$$
$$m_O \approx D_O/\delta_O$$

… but this cannot explain the behavior here as none of these variables is changing

cathodic reaction

increasing supporting electrolyte

Figure 4.3.5 Voltammograms for reduction of 0.65 mM Tl$_2$SO$_4$ at a mercury film on a silver ultramicroelectrode (radius, 15 μm) in the presence of (*a*) 0, (*b*) 0.1, (*c*) 1, and (*d*) 100 mM LiClO$_4$. The potential was controlled *vs.* a Pt wire QRE whose potential was a function of solution composition. This variability is the basis for the shifts in wave position along the potential axis. [Reprinted with permission from M. Ciszkowska and J. G. Osteryoung, *Anal. Chem.*, **67**, 1125 (1995). Copyright 1995, American Chemical Society.]

416

Now, do the following trends make sense? Reaction is **Tl⁺ + e⁻ ⇌ Tl⁰**   417

… why are the diagonal trends not changing like in the lab?… see next slide…

(UPDATED)

cathodic reaction

increasing supporting electrolyte

$I_{m\text{-}Tl+}$, to bring Tl⁺ to the electrode

$I_{d\text{-}Tl+}$, to bring Tl⁺ to the electrode

… and this shift in current onset is curious… more on that later…

Figure 4.3.5 Voltammograms for reduction of 0.65 mM Tl$_2$SO$_4$ at a mercury film on a silver ultramicroelectrode (radius, 15 μm) in the presence of (*a*) 0, (*b*) 0.1, (*c*) 1, and (*d*) 100 mM LiClO$_4$. The potential was controlled *vs.* a Pt wire QRE whose potential was a function of solution composition. This variability is the basis for the shifts in wave position along the potential axis. [Reprinted with permission from M. Ciszkowska and J. G. Osteryoung, *Anal. Chem.*, **67**, 1125 (1995). Copyright 1995, American Chemical Society.]

417

(UPDATED) 418

Looking forward… Section 1.4 and Chapter 4

- Mass transfer
- Diffusion
- Migration / Drift
- Convection
- Semi-empirical diffusive models
- Conductivity
- Transport (Transference) number
- Balance sheets
- *Ohmic drop/loss*

418