

# Lecture #11 of 18(?)

# Mass Transfer Processes

Chapters 1 and 4

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

## Looking forward... Section 1.4 and Chapter 4

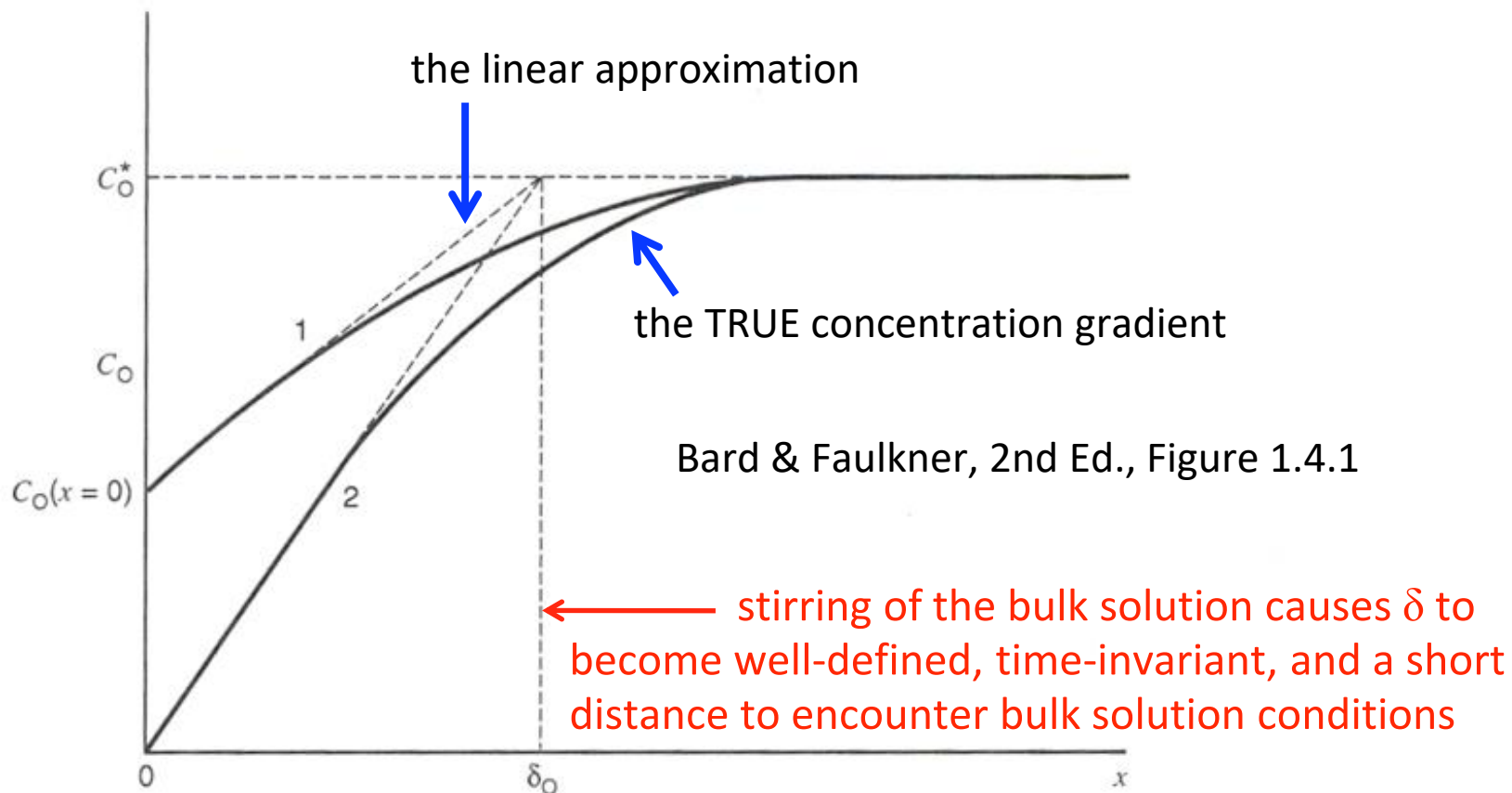
- Mass transfer
- Diffusion
- Migration / Drift
- Convection
- Semi-empirical diffusive models
- **Conductivity**
- **Transport (Transference) number**
- **Balance sheets**
- *Ohmic drop/loss*

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

**RECALL:**

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

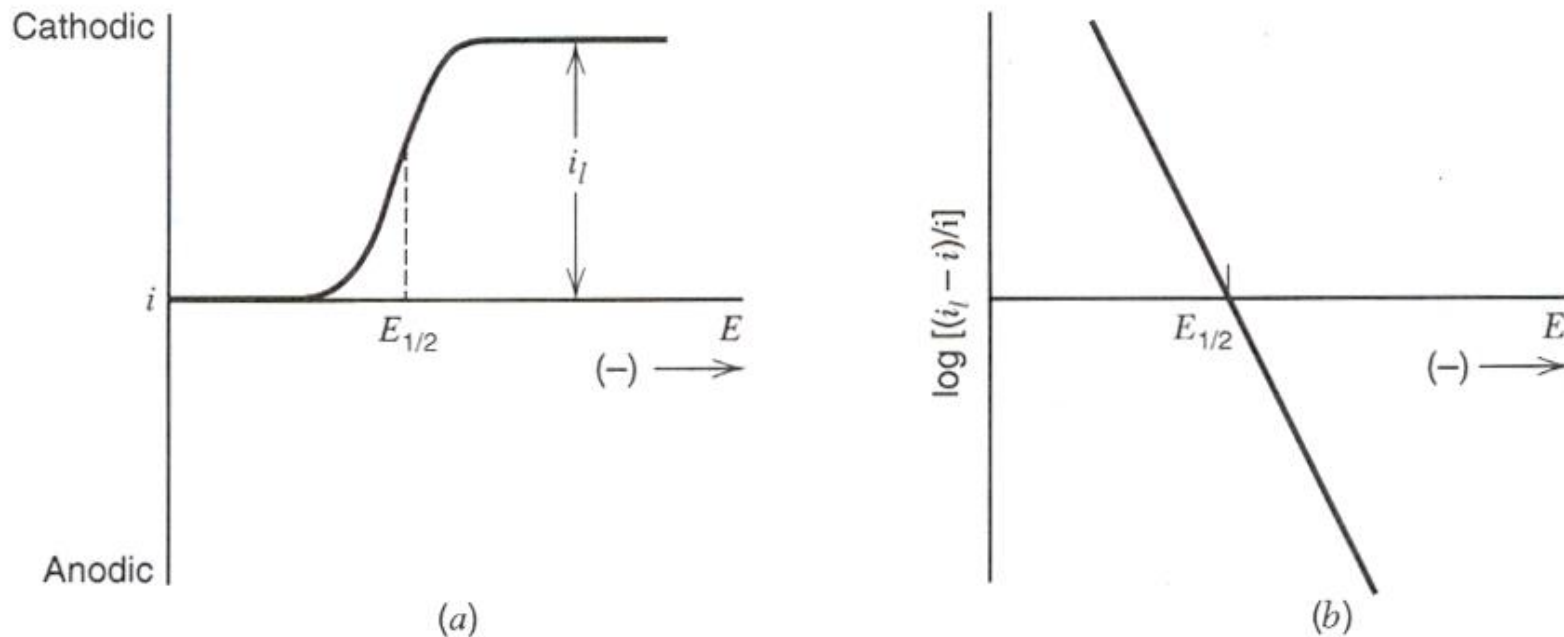
where  $C_O^*$  is the bulk concentration of O,  $\delta$  is the Nernst diffusion layer thickness



**Figure 1.4.1** Concentration profiles (solid lines) and diffusion layer approximation (dashed lines).  $x = 0$  corresponds to the electrode surface and  $\delta_O$  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  $i = i_l$ .

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

... this will show up again...



**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  $i \rightarrow i_l$ ?  $E \rightarrow -\infty$

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

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

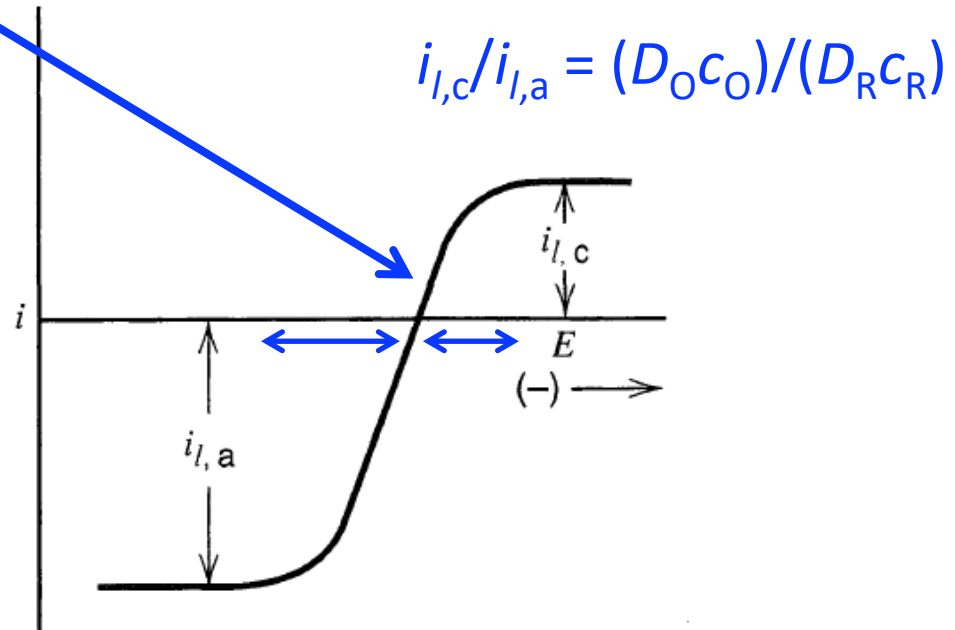
**RECALL:** 
$$E = E^{0'} - \frac{RT}{nF} \ln \left( \frac{m_O}{m_R} \right) + \frac{RT}{nF} \ln \left( \frac{i_{l,c} - i}{i - i_{l,a}} \right)$$

... this will show up again too...

Looks linear...

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

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



**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 diffusion only...

... what if we now also include mass transport by migration/drift?...

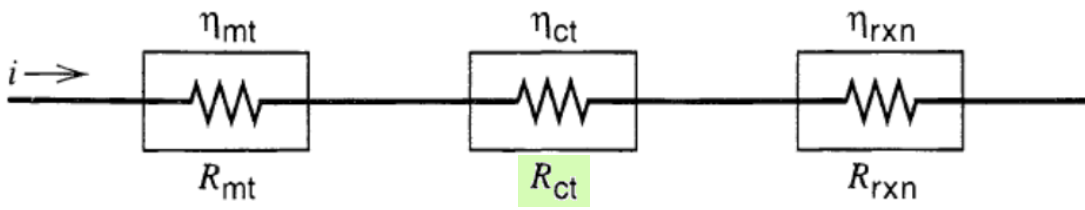
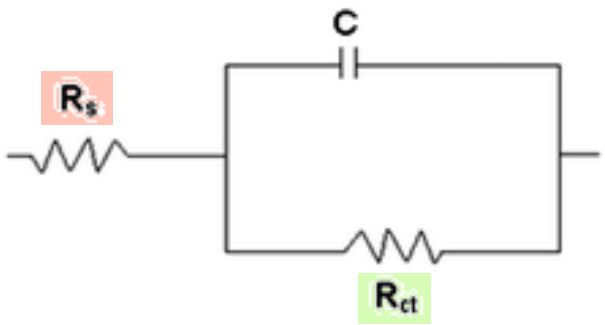


Figure 1.3.7 Processes in an electrode reaction represented as resistances.

(this is for chemical reactions)

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?



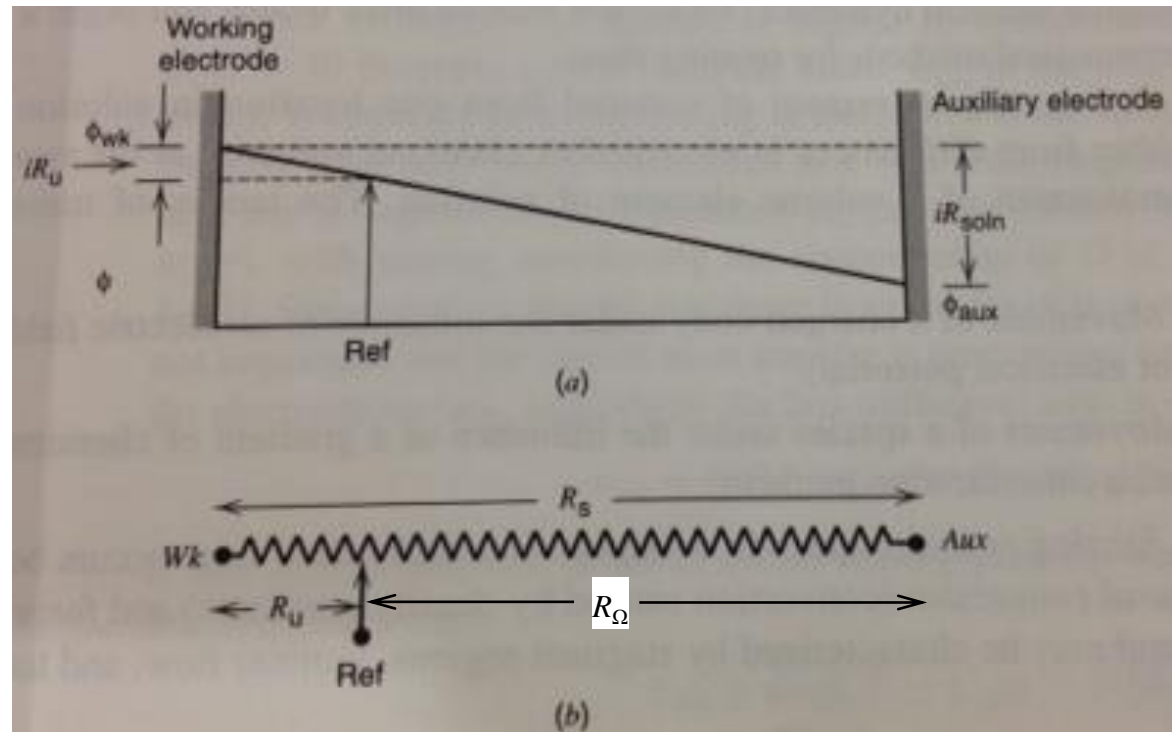
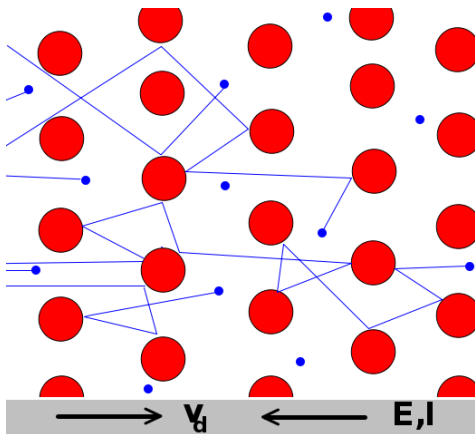
... where is  $R_{mt}$ ?... more on that later...

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

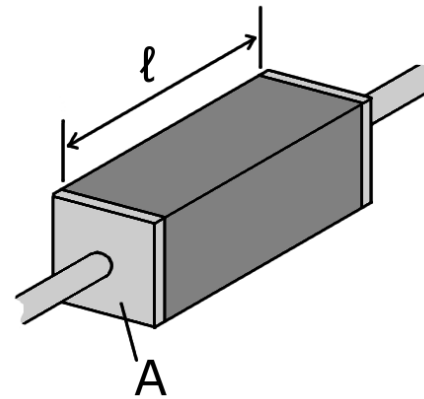


... Include migration/drift to capture  $R_s$  (or  $R_u$ ) using Ohm's law...

- The Drude model starts with... a potential bias creates an electric field ( $-\frac{d\phi}{dx} = E$ ) 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,  $v_d$  (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



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



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

$$\rho = \frac{RA}{l} \dots \text{which is the resistivity } (\Omega \text{ cm})$$

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

$$\sigma = \frac{1}{\rho} = \frac{l}{RA} = \frac{Gl}{A} \dots \text{which is the conductivity } (\Omega^{-1} \text{ cm}^{-1} = \text{mho cm}^{-1} (< 1971) = \text{S}$$

$\text{cm}^{-1}$ ) 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...**

... recall, the *simplified* Nernst–Planck equation (with “no” mixing)

... 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 ( $\sim 0$ ) ...

... thus, for all species  $J = \sum_i J_{migration,i}$ ... and also recall Ohm’s law ( $E = iR$ )...

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

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

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

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

... recall, the *simplified* Nernst–Planck equation (with “no” mixing)

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

... Wow! Simple!

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

... 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

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

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

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- *Ohmic drop/loss*

(UPDATED)

... and so let's understand the interplay of diffusion and migration...

... again, the Nernst–Planck equation...

$$\mathbf{N}_i(x) = \underbrace{-D_i \frac{\partial C_i(x)}{\partial x}}_{\text{diffusion}} \underbrace{- \frac{z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x}}_{\text{migration}} + \underbrace{C_i v(x)}_{\text{convection}}$$

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

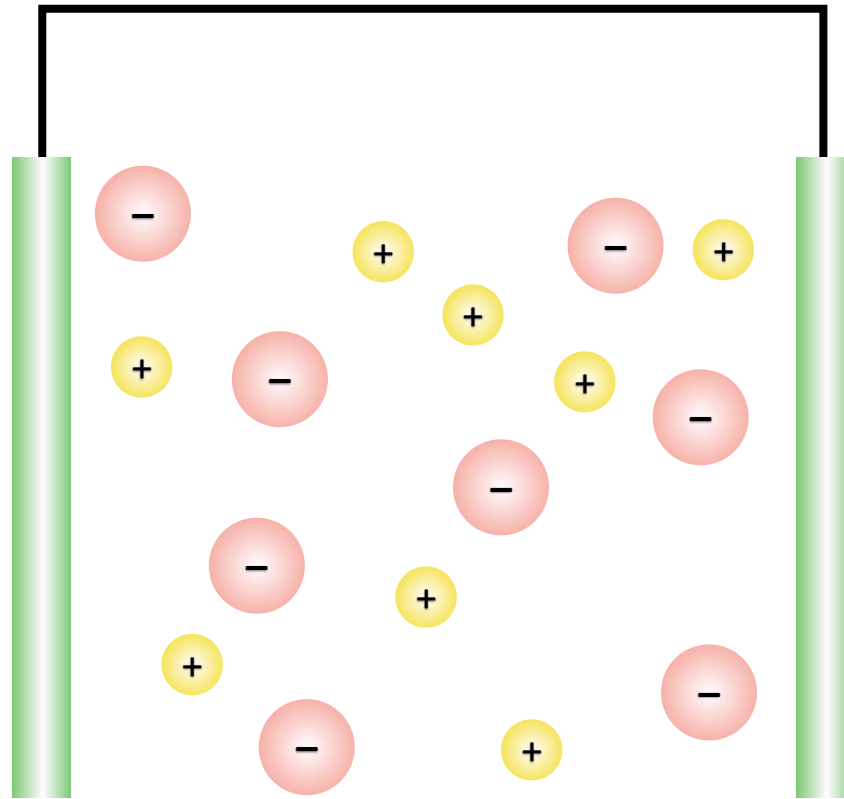
$$\mathbf{N}_i(x) = \underbrace{-D_i \frac{\partial C_i(x)}{\partial x}}_{\text{diffusion}} \underbrace{- \frac{z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x}}_{\text{migration}} + \cancel{C_i v(x)}_{\text{convection}}$$

**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  $\swarrow$   $\searrow$  flux

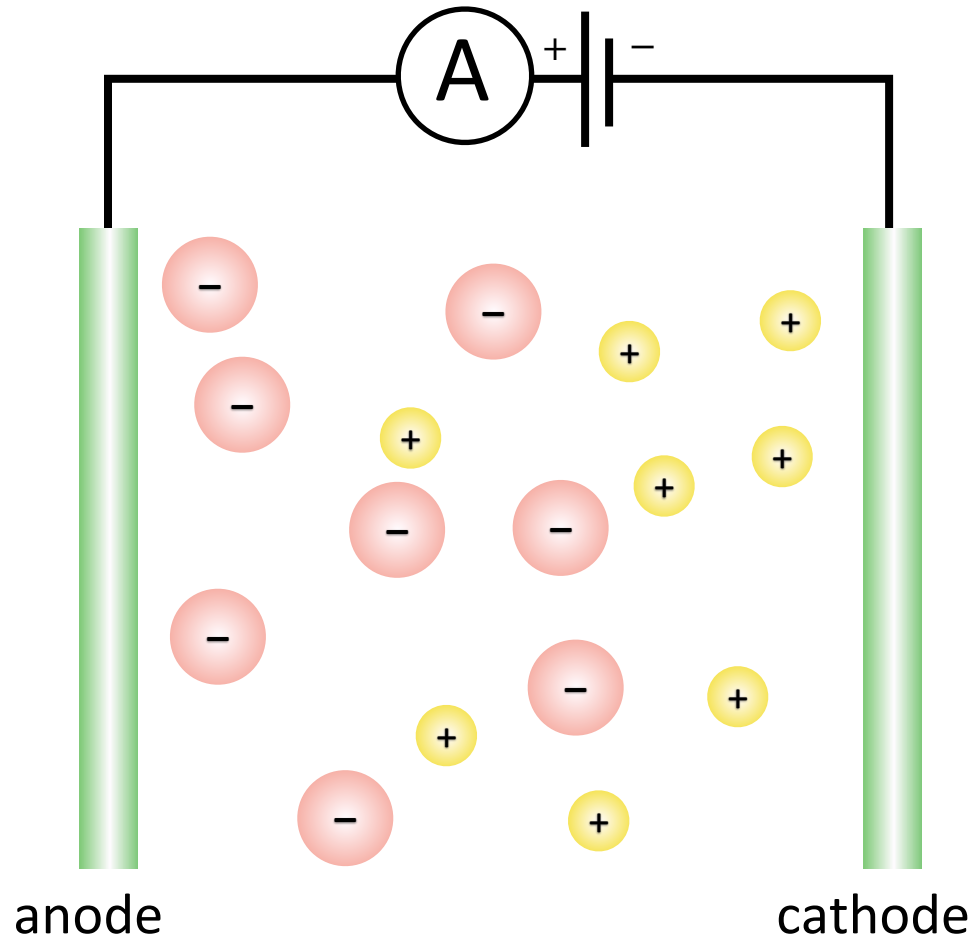
$$\mathbf{i} = \mathbf{i}_{d(\text{iffusion})} + \mathbf{i}_{m(\text{igration})} = nFAN(x)$$

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





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

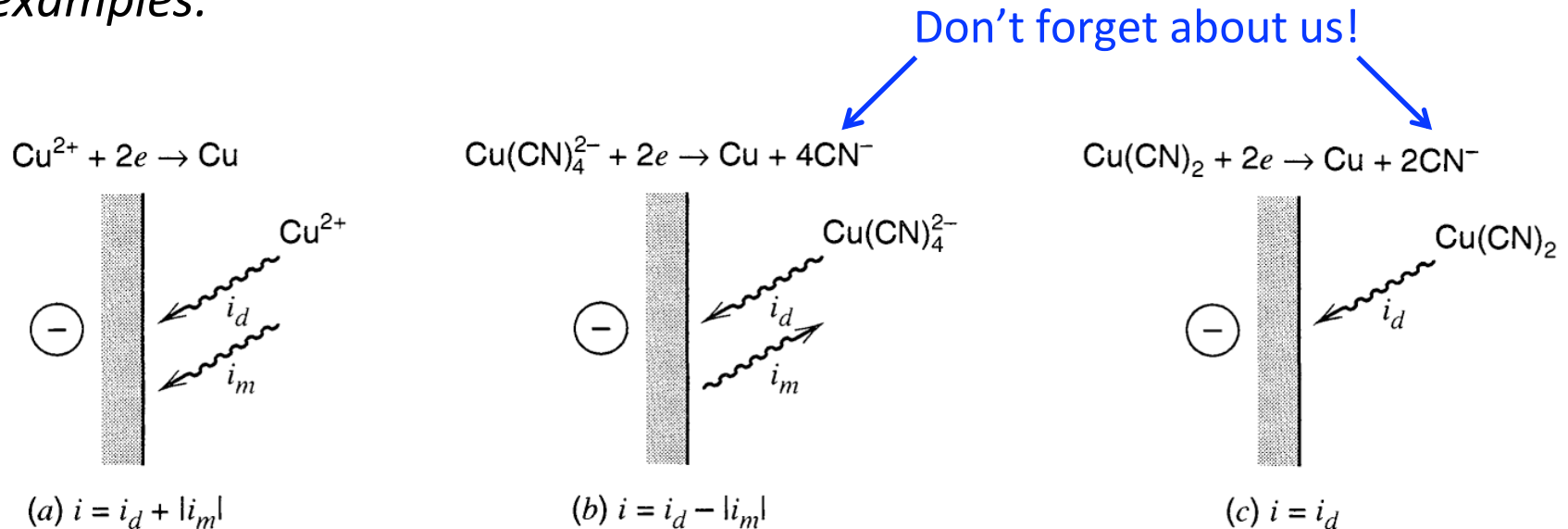


- $i_m$  adds to the current (anode);  $i_d$  subtracts from the current (cathode)
- +  $i_m$  adds to the current (cathode);  $i_d$  subtracts from the current (anode)

So,  $i_{m(\text{igration})}$  can reinforce  $i_{d(\text{iffusion})}$ ... or oppose it...  
 ... 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:

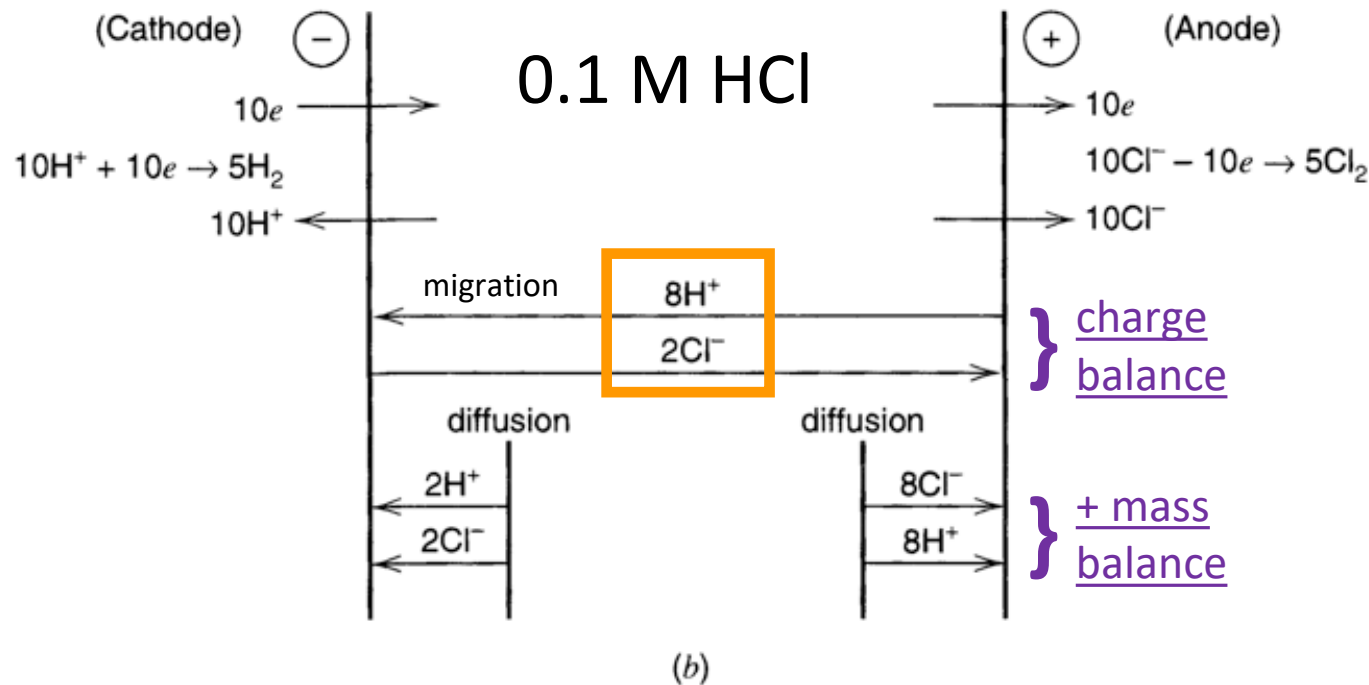


**Figure 4.3.1** Examples of reduction processes with different contributions of the migration current: (a) positively charged reactant, (b) negatively charged reactant, (c) uncharged reactant.

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

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

$$t_i = \frac{|z_i|u_iC_i}{\sum_j |z_j|u_jC_j}$$



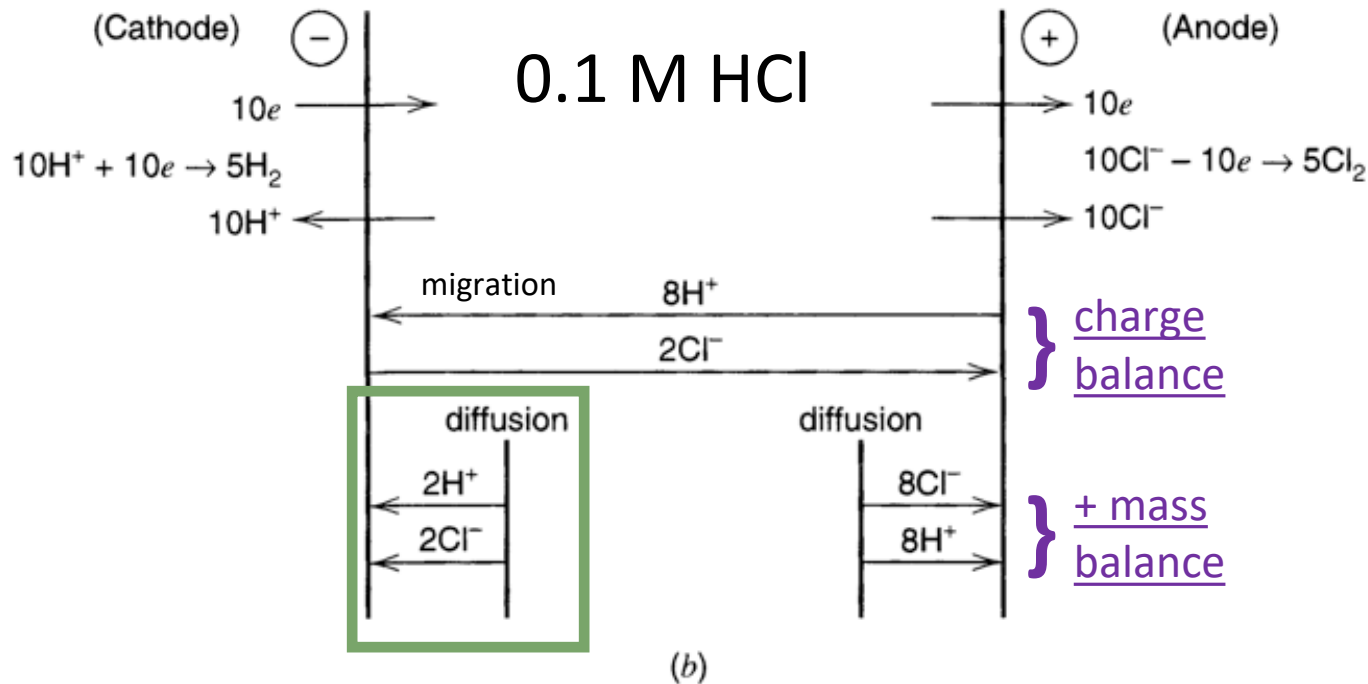
**Figure 4.3.2** Balance sheet for electrolysis of hydrochloric acid solution. (a) Cell schematic. (b) Various contributions to the current when  $10e^-$  are passed in the external circuit per unit time.

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

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

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

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.

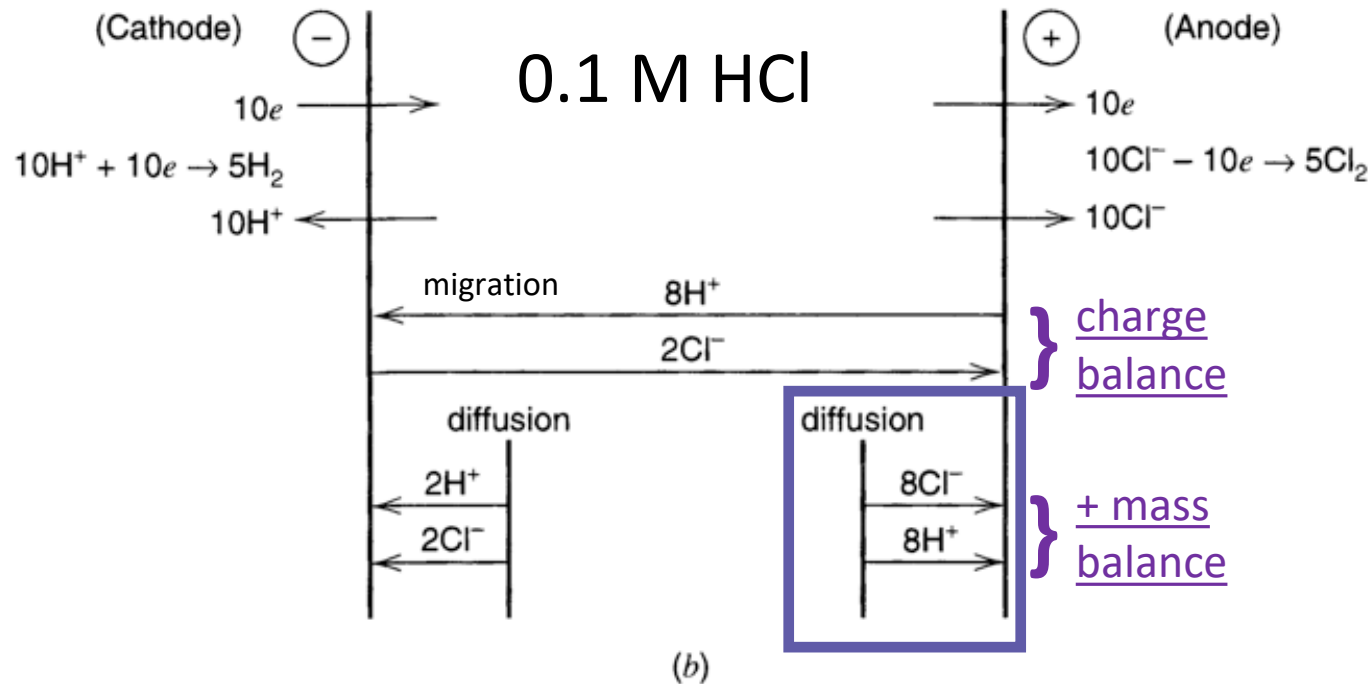
these coefficients are the values necessary to satisfy the steady-state condition of  $i = i_m + i_d$ ... for example, at the *cathode* (left):

$10\text{H}^+(\text{needed}) = 8\text{H}^+(\text{migration}) + 2\text{H}^+(\text{diffusion})$ ...

**B&F Example #1 (of 3)**

+  $2\text{Cl}^-(\text{diffusion})$  for charge balance

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



**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.

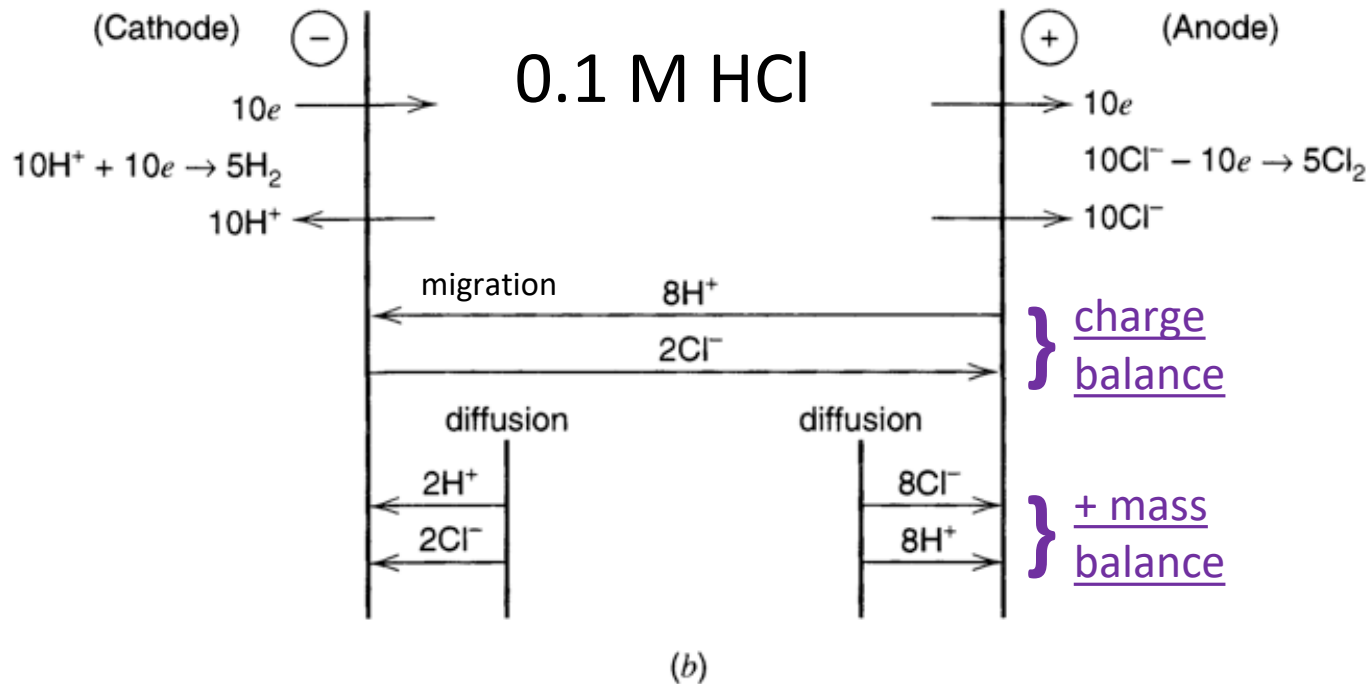
and at the *anode* (right):

$$10Cl^-(\text{needed}) = 2Cl^-(\text{migration}) + 8Cl^-(\text{diffusion})...$$

$$+ 8H^+(\text{diffusion}) \text{ for charge balance}$$

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

If we focus on the **cathode  $H^+$  current** and **anode  $Cl^-$  current**...

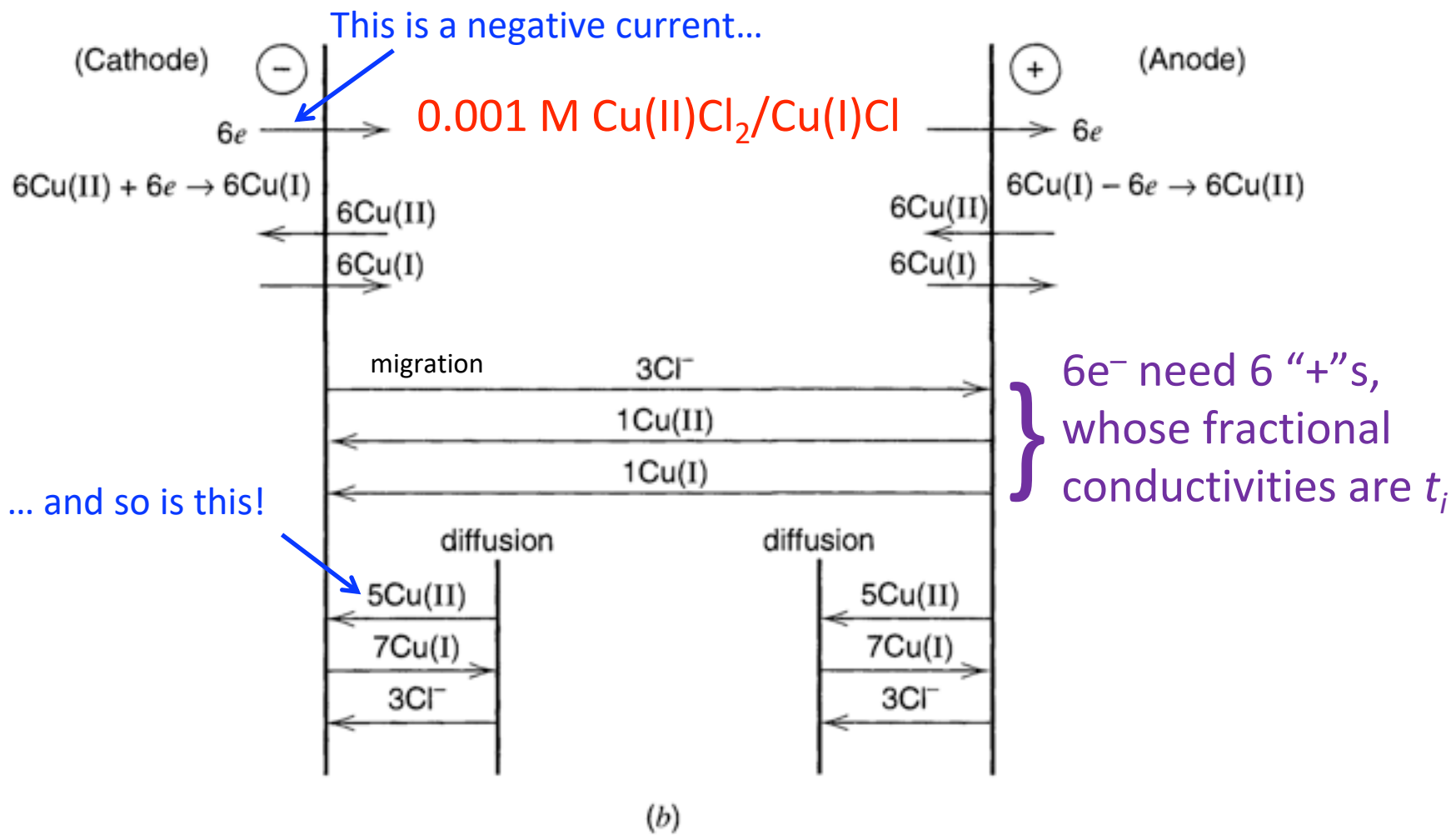


**Figure 4.3.2** Balance sheet for electrolysis of hydrochloric acid solution. (a) Cell schematic. (b) Various contributions to the current when  $10e$  are passed in the external circuit per unit time.

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

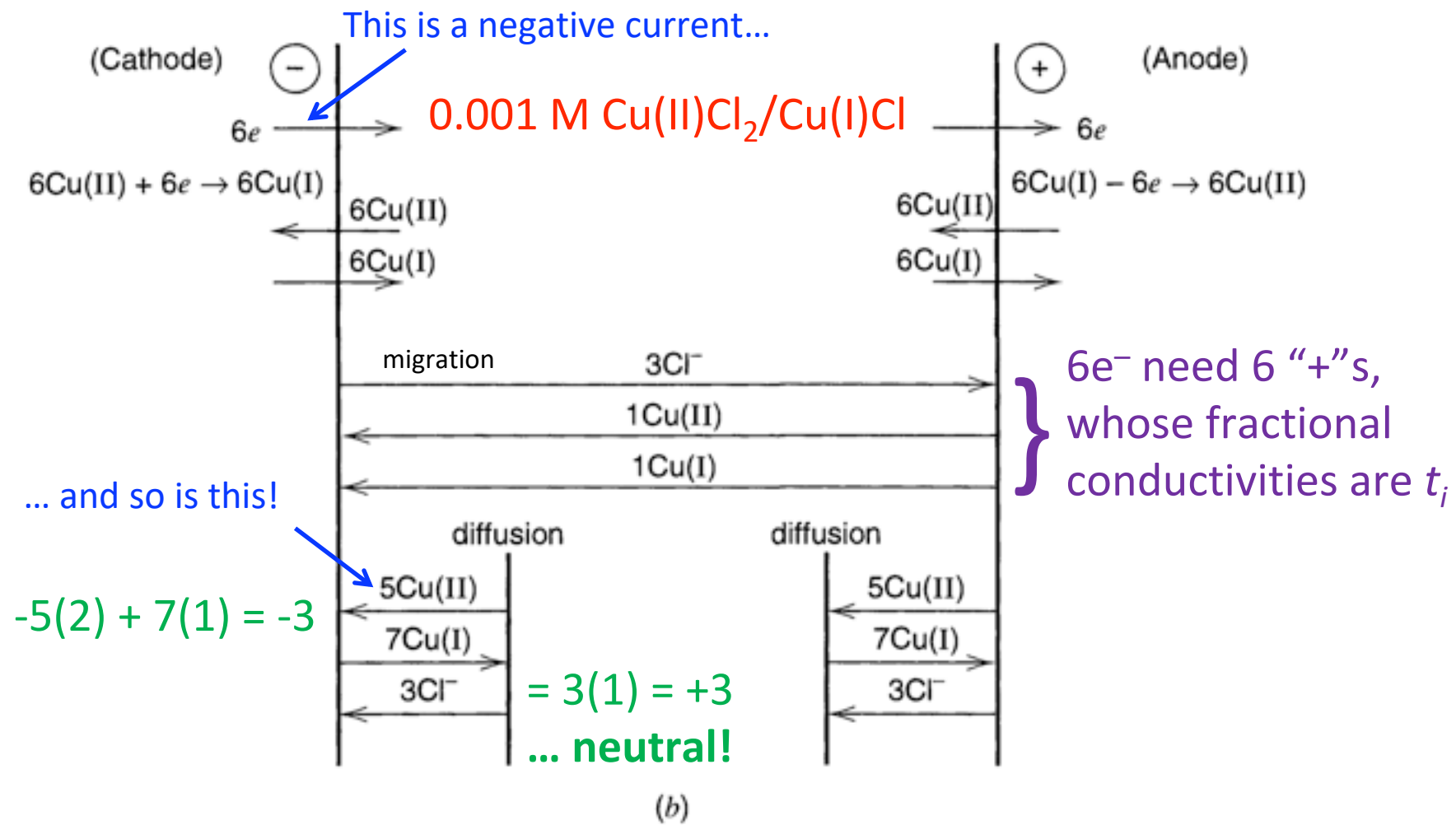
cathode (for  $H^+$ ):  $i = -10; i_d = -2, i_m = -8$  (80% of the  $H^+$  current is migration)  
 anode (for  $Cl^-$ ):  $i = +10; i_d = 8, i_m = 2$  (20% of the  $Cl^-$  current is migration)

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



**Figure 4.3.3** Balance sheet for electrolysis of the Cu(II), Cu(I), NH<sub>3</sub> 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,  $|i_m| = (1/1)(1/6)(6) = 1$ ,  $i_d = 6 + 1 = 7$ .

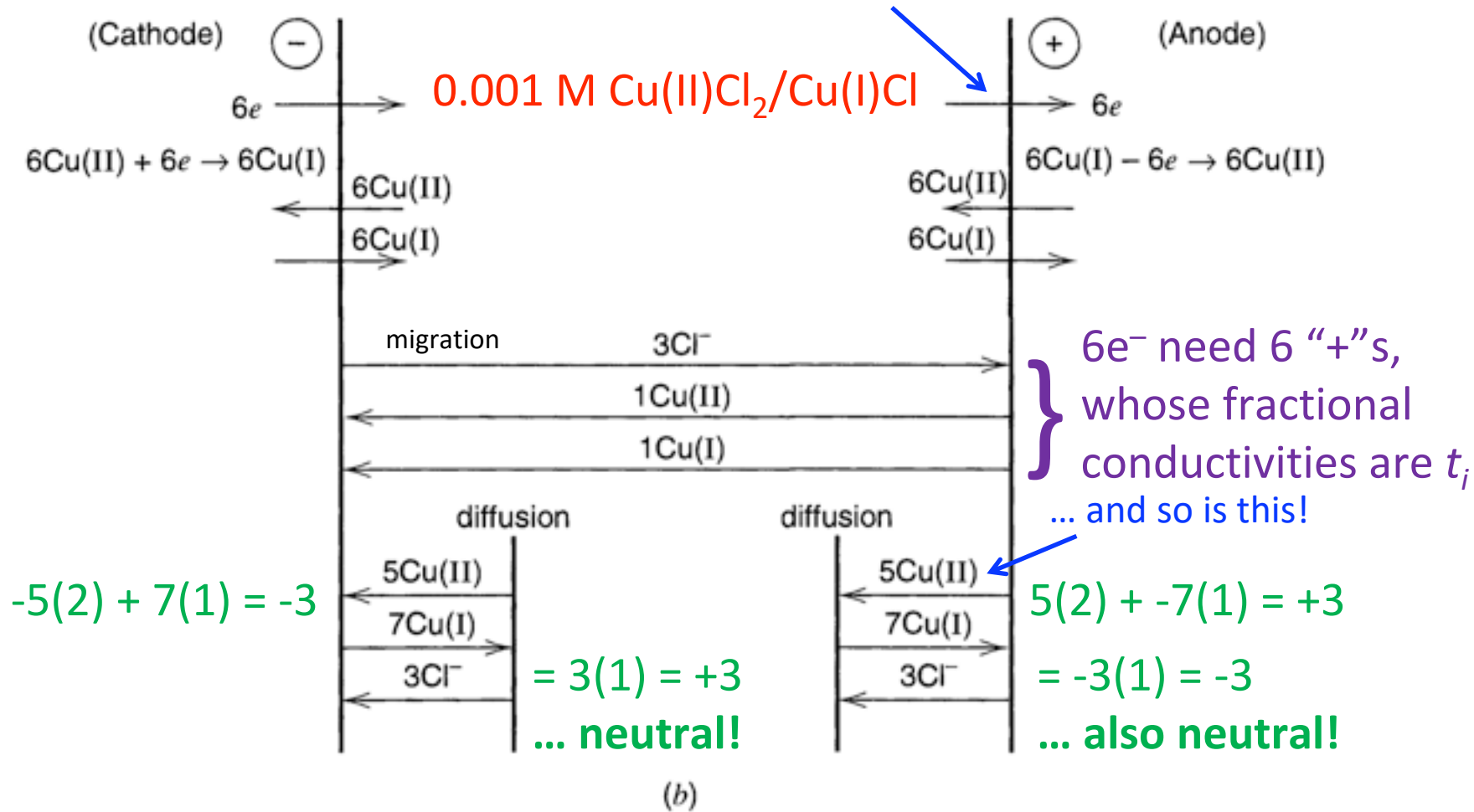
**B&F Example #2 (of 3)**



**Figure 4.3.3** Balance sheet for electrolysis of the Cu(II), Cu(I), NH<sub>3</sub> 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,  $|i_m| = (1/1)(1/6)(6) = 1$ ,  $i_d = 6 + 1 = 7$ .

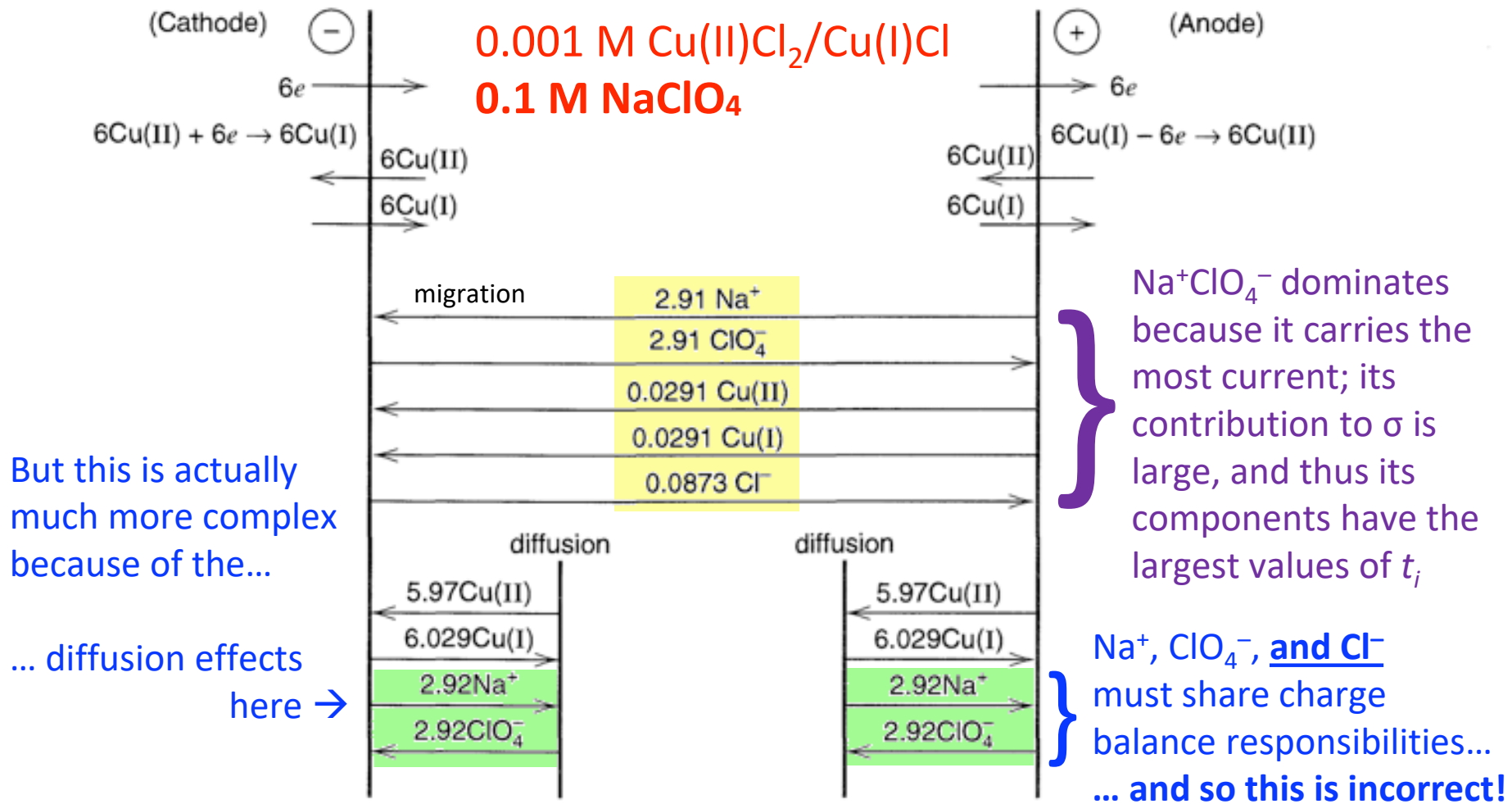


... and this is a positive current (at that electrode)...



**Figure 4.3.3** Balance sheet for electrolysis of the Cu(II), Cu(I), NH<sub>3</sub> 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,  $|i_m| = (1/1)(1/6)(6) = 1$ ,  $i_d = 6 + 1 = 7$ .

... adding a supporting electrolyte reduces the original  $i_m$  values

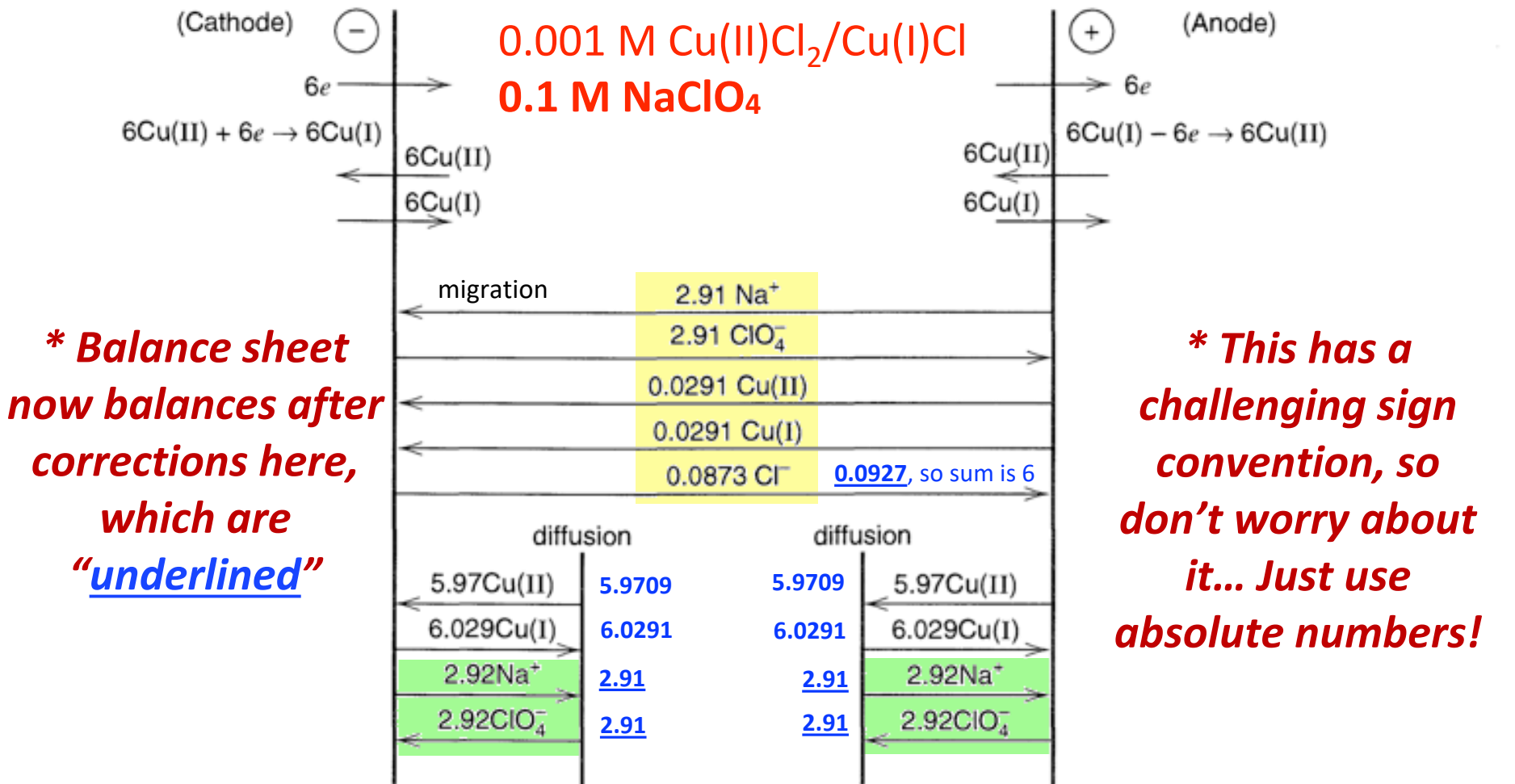


### B&F Example #3 (of 3)

(b)

**Figure 4.3.4** Balance sheet for the system in Figure 4.3.3, but with excess NaClO<sub>4</sub> as a supporting electrolyte. (a) Cell schematic. (b) Various contributions to the current when  $6e$  are passed in the external circuit per unit time ( $i = 6, n = 1$ ).  $t_{\text{Cu(II)}} = [(2 \times 10^{-3})\lambda / (2 \times 10^{-3} + 10^{-3} + 3 \times 10^{-3} + 0.2)\lambda] = 0.0097$ . For Cu(II) at the cathode,  $|i_m| = (1/2)(0.0097)(6) = 0.03$ ,  $i_d = 6 - 0.03 = 5.97$ .

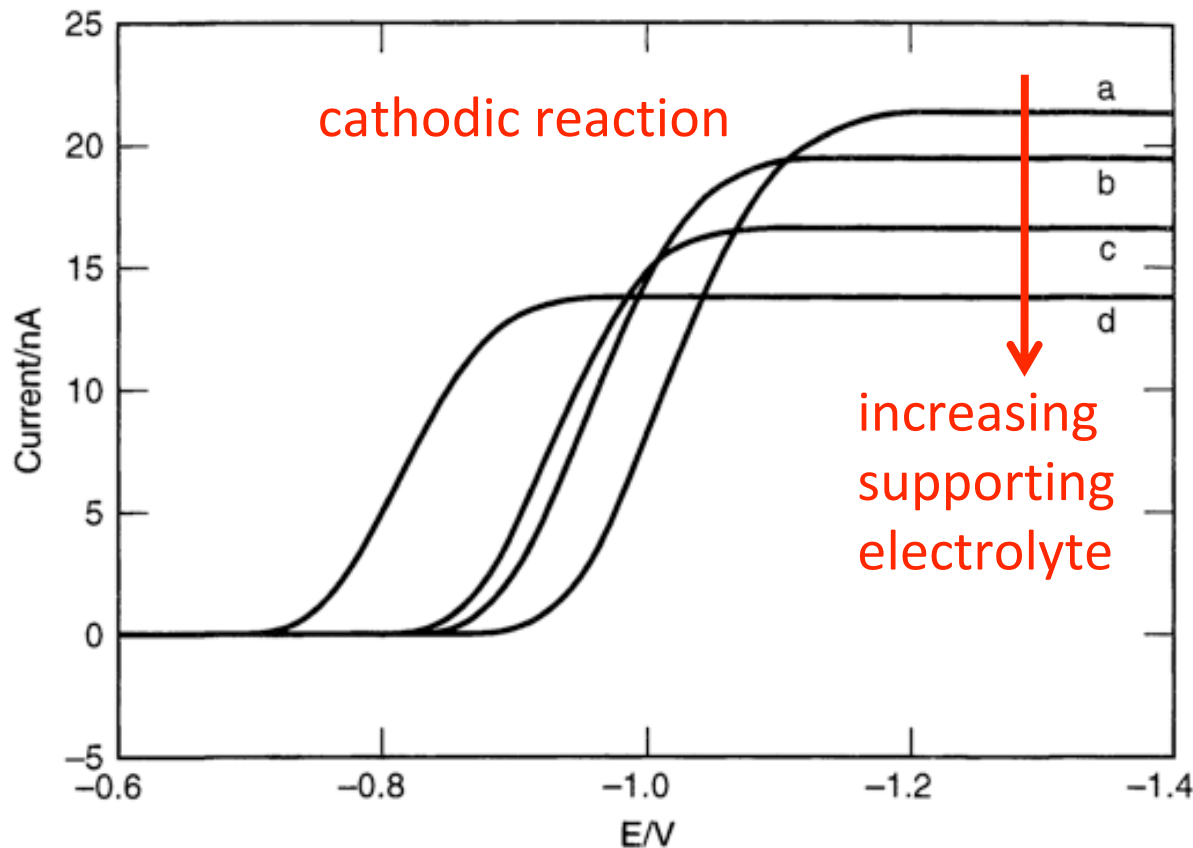
... adding a supporting electrolyte reduces the original  $i_m$  values



**PRECISION:**  $-5.9709(2) + 6.0291(1) = -5.9127... + 2.91(1) + 2.91(1) = 5.82... \text{ so, } +\underline{0.0927}$  for Cl<sup>-</sup> toward the cathode

**Figure 4.3.4** Balance sheet for the system in Figure 4.3.3, ... and  $-\underline{0.0927}$  for Cl<sup>-</sup> 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 ( $i = 6, n = 1$ ).  $t_{\text{Cu(II)}} = [(2 \times 10^{-3})\lambda / (2 \times 10^{-3} + 10^{-3} + 3 \times 10^{-3} + 0.2)\lambda] = 0.0097$ . For Cu(II) at the cathode,  $|i_m| = (1/2)(0.0097)(6) = 0.03, i_d = 6 - 0.03 = 5.97$ .

Now, do the following trends make sense? Reaction is  $\text{Tl}^+ + \text{e}^- \rightleftharpoons \text{Tl}^0$



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

$$i_l = nF A m_0 C_O^*$$

$$m_0 = D_O / \delta_O$$

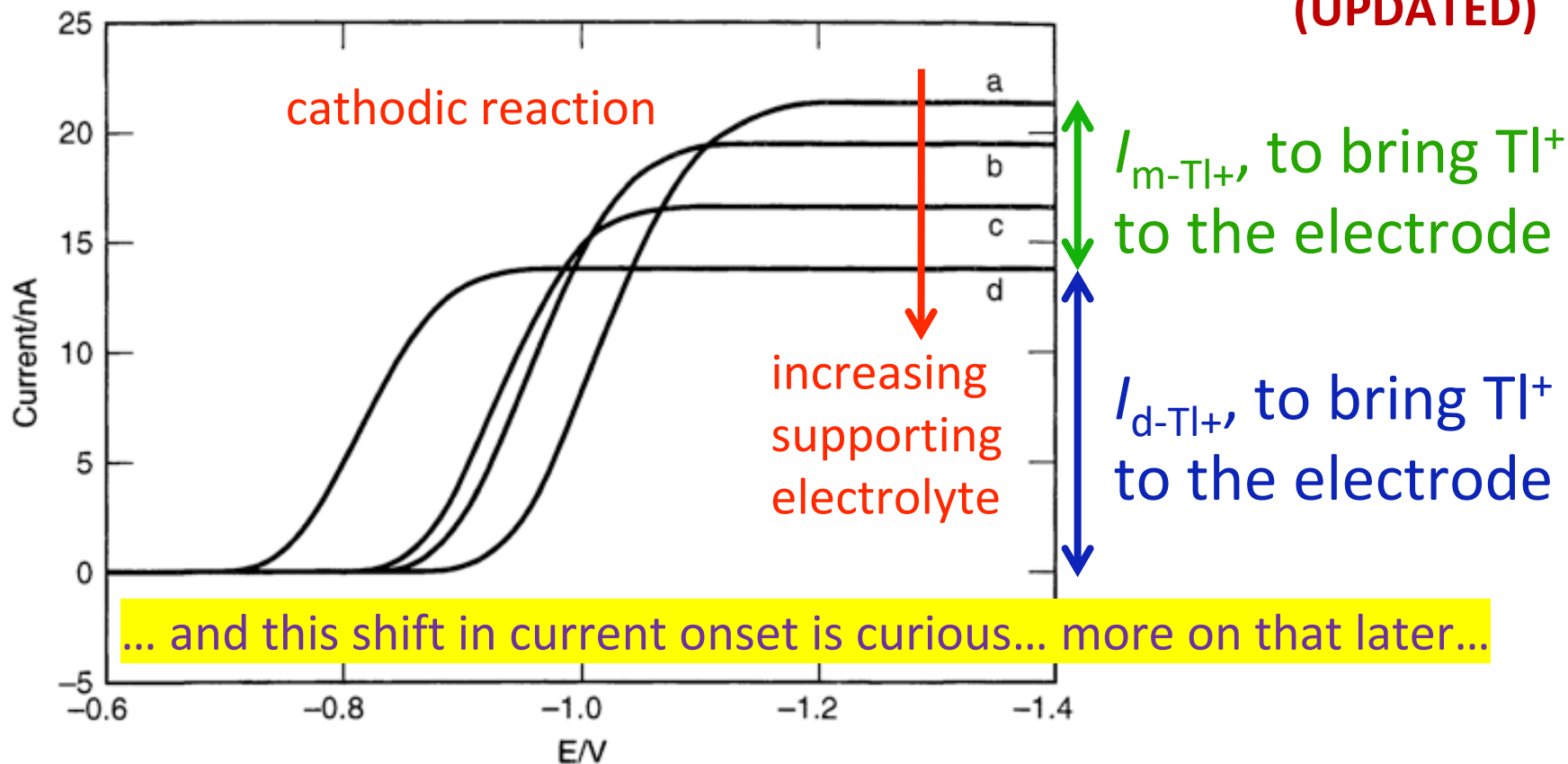
... but this cannot explain the behavior here as none of these variables is changing

**Figure 4.3.5** Voltammograms for reduction of 0.65 mM  $\text{Tl}_2\text{SO}_4$  at a mercury film on a silver ultramicroelectrode (radius, 15  $\mu\text{m}$ ) in the presence of (a) 0, (b) 0.1, (c) 1, and (d) 100 mM  $\text{LiClO}_4$ . 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. Ciszowska and J. G. Osteryoung, *Anal. Chem.*, **67**, 1125 (1995). Copyright 1995, American Chemical Society.]

Now, do the following trends make sense? Reaction is  $\text{Tl}^+ + \text{e}^- \rightleftharpoons \text{Tl}^0$

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

(UPDATED)



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