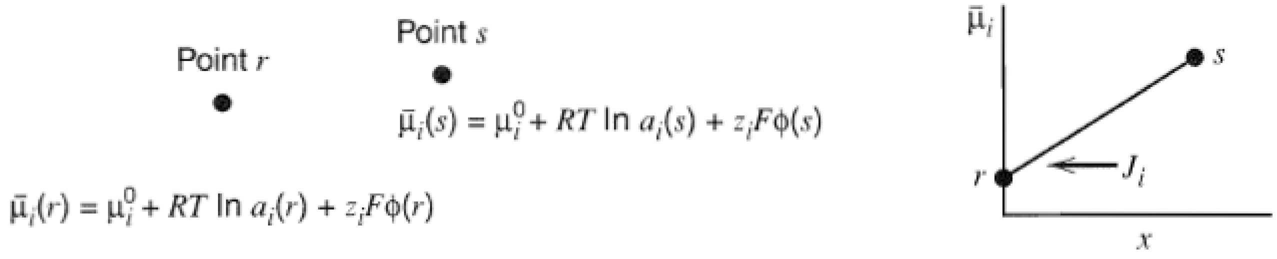
Ch. 4

MASS TRANSFER
BY MIGRATION
AND DIFFUSION

4.1 DERIVATION OF A GENERAL MASS TRANSFER EQUATION

- The difference of electrochemical potential over a distance

  → due to a concentration gradient or potential gradient



(*a*) (*b*)

Figure 4.1.1 A gradient of electrochemical potential.

- A flux of species J occurs to alleviate any difference of electrochemical potential

$$\left.\begin{aligned} J_i(x) &= -C_i u_i \frac{\partial \bar{\mu}_i}{\partial x} \\ u_i &= \frac{D_i}{RT} \end{aligned}\right\} \quad J_i(x) = -\frac{C_i D_i}{RT}\frac{\partial \bar{\mu}_i}{\partial x}$$

: Nernst-Einstein relation

4.1 DERIVATION OF A GENERAL MASS TRANSFER EQUATION

- Consider the Nernst-Planck equations

$$J_i(x) = -\frac{C_i D_i}{RT}\frac{\partial \bar{\mu}_i}{\partial x} + \underline{C_i v}$$

: if solution is moving

$$= -\frac{C_i D_i}{RT}\left[\frac{\partial}{\partial x}\left(RT \ln a_i\right) + \frac{\partial}{\partial x}\left(z_i F \phi\right)\right] + C_i v$$

When a_i = C_i

$$= -\frac{C_i D_i}{RT}\left[\frac{\partial}{\partial x}\left(RT \ln C_i\right) + \frac{\partial}{\partial x}\left(z_i F \phi\right)\right] + C_i v$$

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

4.1 DERIVATION OF A GENERAL MASS TRANSFER EQUATION

- Consider the Nernst-Planck equations

$$\boxed{\mathbf{J}_j = -D_j \nabla C_j - \frac{z_j F}{RT} D_j C_j \nabla \phi + C_j \mathbf{v}}$$

$$\boxed{J_j(x) = -\underbrace{D_j \frac{\partial C_j(x)}{\partial x}}_{\text{diffusion}} - \underbrace{\frac{z_j F}{RT} D_j C_j \frac{\partial \phi(x)}{\partial x}}_{\text{migration}} + \underbrace{C_j v(x)}_{\text{convection}}}$$

For linear mass transfer

- In this chapter, we are concerned with systems in which convection is absent.

  → Convective mass transfer (Chapter 9)

- In an unstirred or stagnant solution with no density gradients

  → solution velocity (v) = 0

  → the general flux equation for species j becomes

$$J_j(x) = -D_j\left(\frac{\partial C_j(x)}{\partial x}\right) - \frac{z_j F}{RT} D_j C_j \left(\frac{\partial \phi(x)}{\partial x}\right)$$

4.1 DERIVATION OF A GENERAL MASS TRANSFER EQUATION

$$J_j(x) = -D_j\left(\frac{\partial C_j(x)}{\partial x}\right) - \frac{z_jF}{RT}D_jC_j\left(\frac{\partial \phi(x)}{\partial x}\right)$$

- If species j is charged,

  → then the flux, J_j, is equivalent to a current density.

- If we consider a linear system with a cross-sectional area, A, normal to the axis of mass flow.

  → J_j (mol s^{-1} cm^{-2}) is equal to $-i_j/z_jFA$ [C/s per (C mol^{-1} cm^2)]

  → where i_j is the current component at any value of x arising from a flow of species j

- Then,

$$-J_j = \frac{i_j}{z_jFA}$$

4.1 DERIVATION OF A GENERAL MASS TRANSFER EQUATION

$$J_j(x) = -D_j\left(\frac{\partial C_j(x)}{\partial x}\right) - \frac{z_jF}{RT}D_jC_j\left(\frac{\partial \phi(x)}{\partial x}\right)$$

⇨ $$-J_j = \frac{i_j}{z_jFA} = \frac{i_{d,j}}{z_jFA} + \frac{i_{m,j}}{z_jFA}$$

→ $i_{d,j}$: diffusion currents of species j

→ $i_{m,j}$: migration currents of species j

$$\frac{i_{d,j}}{z_jFA} = D_j\frac{\partial C_j}{\partial x}$$

$$\frac{i_{m,j}}{z_jFA} = \frac{z_jFD_j}{RT}C_j\frac{\partial \phi}{\partial x}$$

4.2 MIGRATION

1) In the bulk solution (away from the electrode)

→ concentration gradients are generally small

→ the total current is carried mainly by migration

- For species j in the bulk region of a linear mass-transfer system having a cross-sectional Area A,

→ $i_j = i_{m,j}$

$$J_j(x) = -\cancel{D_j\left(\frac{\partial C_j(x)}{\partial x}\right)} - \frac{z_jF}{RT}D_jC_j\left(\frac{\partial \phi(x)}{\partial x}\right) \Rightarrow \frac{i_{m,j}}{z_jFA} = \frac{z_jFD_j}{RT}C_j\frac{\partial \phi}{\partial x}$$

$$i_j = \frac{z_j^2F^2AD_jC_j}{RT}\cdot\frac{\partial \phi}{\partial x}$$

- Einstein-Smoluchowski equation

→ relationship between the mobility of species j and the diffusion coefficient

$$\boxed{u_j = \frac{|z_j|FD_j}{RT}}$$

4.2 MIGRATION

$$i_j = \frac{z_j^2 F^2 A D_j C_j}{RT} \cdot \frac{\partial \phi}{\partial x}$$

$$u_j = \frac{|z_j| F D_j}{RT}$$

$$i_j = |z_j| F A u_j C_j \frac{\partial \phi}{\partial x}$$

- For a linear electric field

$$\frac{\partial \phi}{\partial x} = \frac{\Delta E}{l}$$

$$i_j = \frac{|z_j|\, F A u_j C_j\, \Delta E}{l}$$

: where ΔE/l is the gradient (V/cm) arising from the change in potential ΔE over distance l.

- The total current in bulk solution is given by

$$i = \sum_j i_j = \frac{FA\,\Delta E}{l} \sum_j |z_j| u_j C_j$$

4.2 MIGRATION

- The conductance of the solution, L (Ω^{-1}),

  → the reciprocal of the resistance, R (Ω),

  → given by Ohm's law

$$i = \sum_j i_j = \frac{FA\,\Delta E}{l} \sum_j |z_j| u_j C_j \quad \Rightarrow \quad L = \frac{1}{R} = \frac{i}{\Delta E} = \frac{FA}{l} \sum_j |z_j| u_j C_j = \frac{A}{l}\kappa$$

: where κ, the conductivity (Ω^{-1} cm^{-1}) is given by

$$\kappa = F \sum_j |z_j| u_j C_j$$

(discussed in Ch. 2)

- The fraction of the total current that a given ion j carries

→ t_j, the transference number of j

$$i = \sum_j i_j = \frac{FA\,\Delta E}{l} \sum_j |z_j| u_j C_j \quad \Rightarrow \quad \boxed{t_j = \frac{i_j}{i} = \frac{|z_j| u_j C_j}{\sum_k |z_k| u_k C_k} = \frac{|z_j|\, C_j \lambda_j}{\sum_k |z_k|\, C_k \lambda_k}}$$

4.3 MIXED MIGRATION AND DIFFUSION NEAR AN ACTIVE ELECTRODE

2) Near the electrode,

: an electroactive substance is transported by both diffusion and migration processes.

- That current can be separated into diffusion and migration currents

→ reflect the diffusive and migrational components to the flux of the electroactive species at the surface:

$$i = i_d + i_m$$

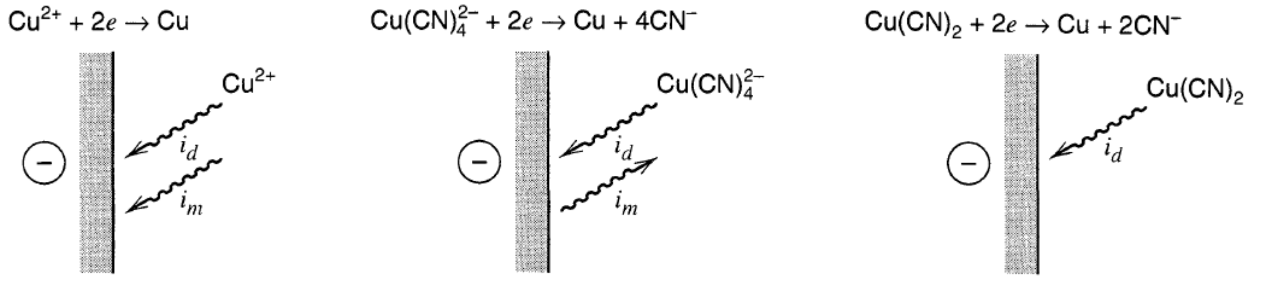
- Note that i_m and i_d may be in the same or opposite directions

→ depending on the direction of the electric field and the charge on the electroactive species.

4.3 MIXED MIGRATION AND DIFFUSION NEAR AN ACTIVE ELECTRODE

- Examples of three reductions

  : a positively charged, a negatively charged, and an uncharged substance



(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.

$$i = i_{\mathrm{d}} + i_{\mathrm{m}}$$

- The migrational component is always in the same direction as i_d for cationic species reacting at cathodes and for anionic species reacting at anodes.

- It opposes i_d when anions are reduced at cathodes and when cations are oxidized at anodes.

4.3.1 Balance Sheets for Mass Transfer During Electrolysis

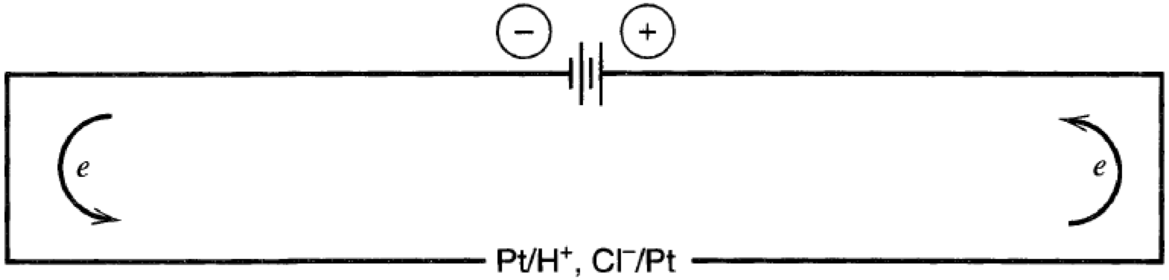
- For many electrochemical systems, the mathematical treatments can be simplified if the migrational component to the flux of the electroactive substance is made negligible.
→ discuss the conditions under which that approximation holds.

- Although migration carries the current in the bulk solution during electrolysis, diffusional transport also occurs in the vicinity of the electrodes, because concentration gradients of the electroactive species arise there.
→ Under some circumstances, the flux of electroactive species to the electrode is due almost completely to diffusion.
→ To illustrate these effects, let us apply the "balance sheet" approach to transport in several examples.

4.3.1 Balance Sheets for Mass Transfer During Electrolysis

Example 4.1

- Consider the electrolysis of a solution of hydrochloric acid at platinum electrodes



(*a*)

- Since the equivalent ionic conductance of H^+, λ^+, and of Cl^-, λ^-, relate as $\lambda^+ \approx 4\lambda^-$

$$\boxed{t_j = \frac{i_j}{i} = \frac{|z_j|u_j C_j}{\sum_k |z_k|u_k C_k} = \frac{|z_j|\, C_j \lambda_j}{\sum_k |z_k|\, C_k \lambda_k}}$$

$$t_{H^+} = \frac{\lambda_{H^+}}{\lambda_{H^+} + \lambda_{Cl^-}} = \frac{4}{4+1} = 0.8$$

$t_{H+} = 0.8$ and $t_{Cl-} = 0.2$

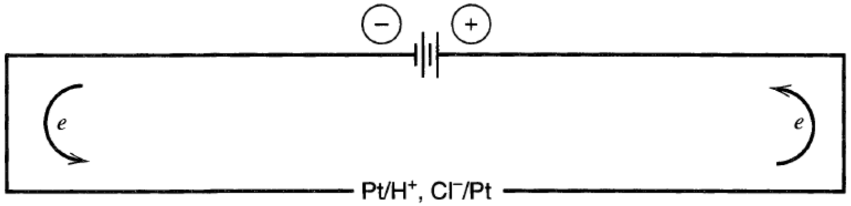
4.3.1 Balance Sheets for Mass Transfer During Electrolysis

- Assume that a total current equivalent to 10e per unit time is passed through the cell,

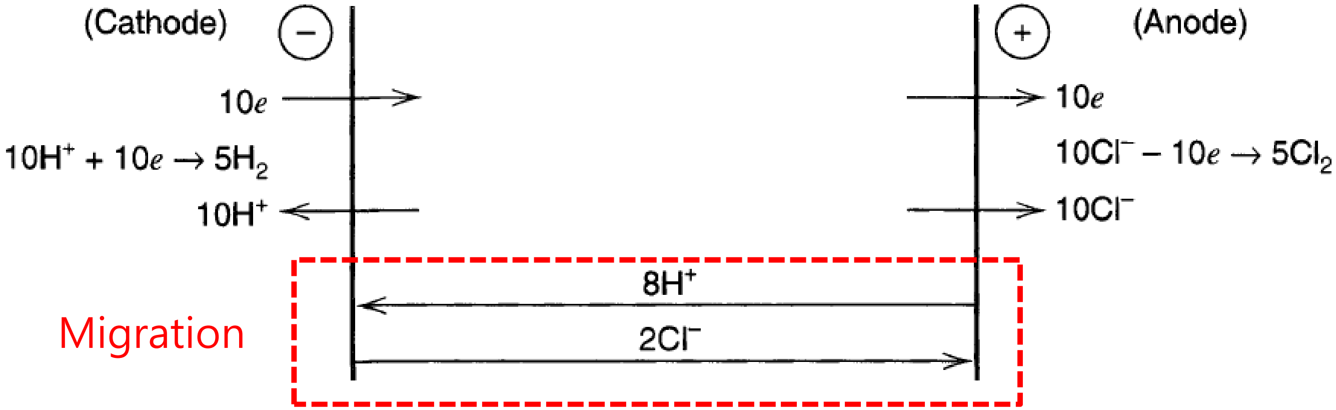
→ producing five H_2 molecules at the cathode and five Cl_2 molecules at the anode.

- The total current is carried in the bulk solution by the movement of $8H^+$ toward the cathode and $2C^-$ toward the anode

→ $t_+ = 0.8$ and $t_- = 0.2$



(a)



Migration

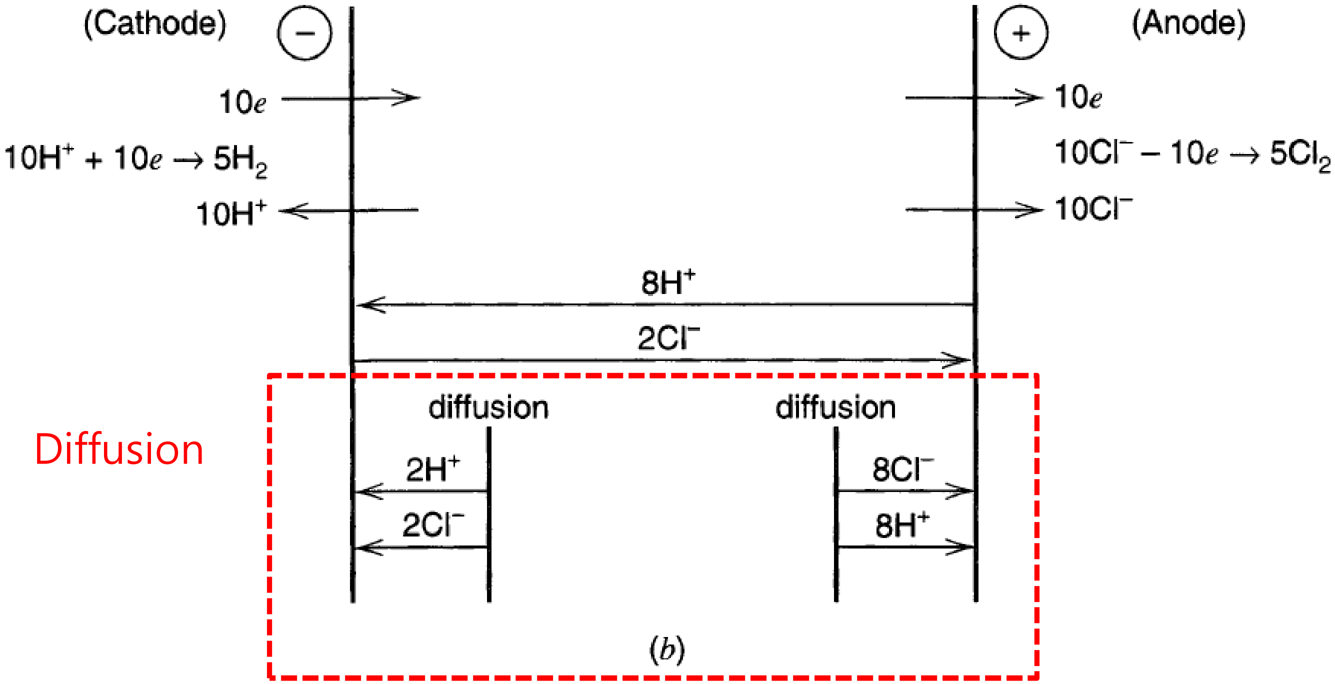
4.3.1 Balance Sheets for Mass Transfer During Electrolysis

- To maintain a steady current,

  → $10H^+$ must be supplied to the cathode per unit time,

  → so an additional $2H^+$ must diffuse to the electrode, along with $2Cl^-$
- Similarly at the anode, to supply $10Cl^-$ per unit time,

  → $8Cl^-$ must arrive by diffusion, along with $8H^+$.



4.3.1 Balance Sheets for Mass Transfer During Electrolysis

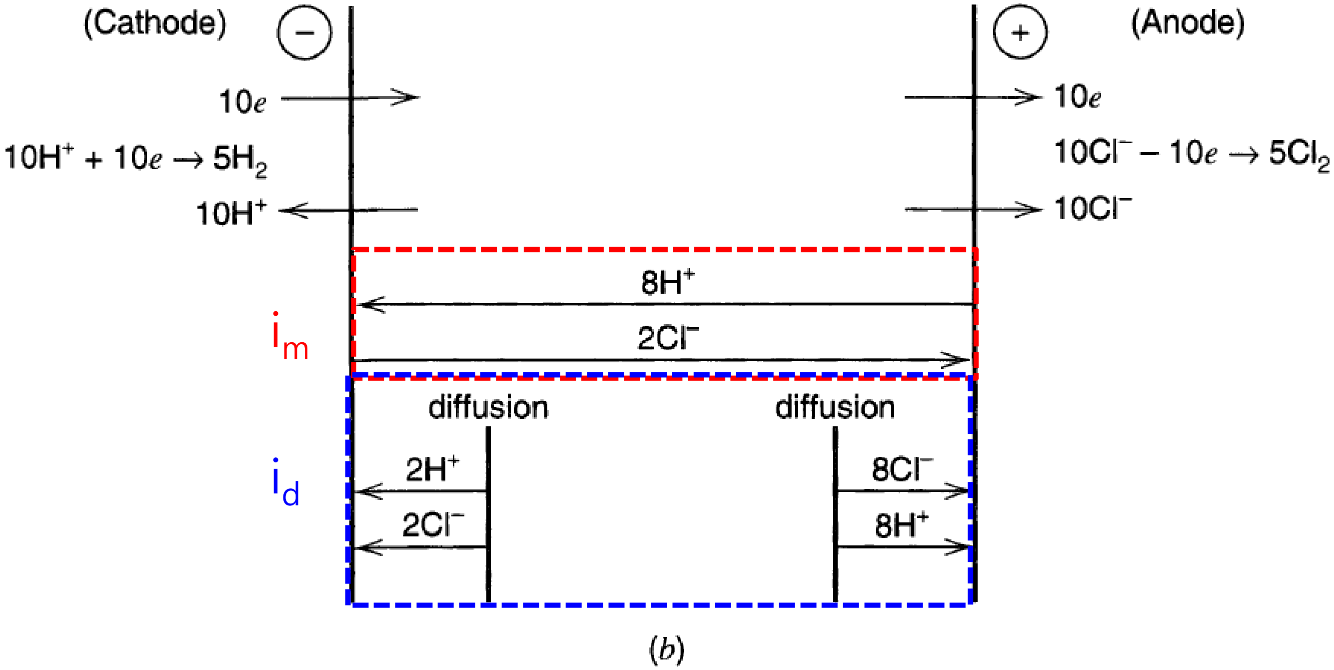
- Thus,

→ the current for H^+: $i_d = 2$, $i_m = 8$ at the cathode

→ the current for Cl^-: $i_d = 8$, $i_m = 2$ at the anode

➔ The total current, i = 10.

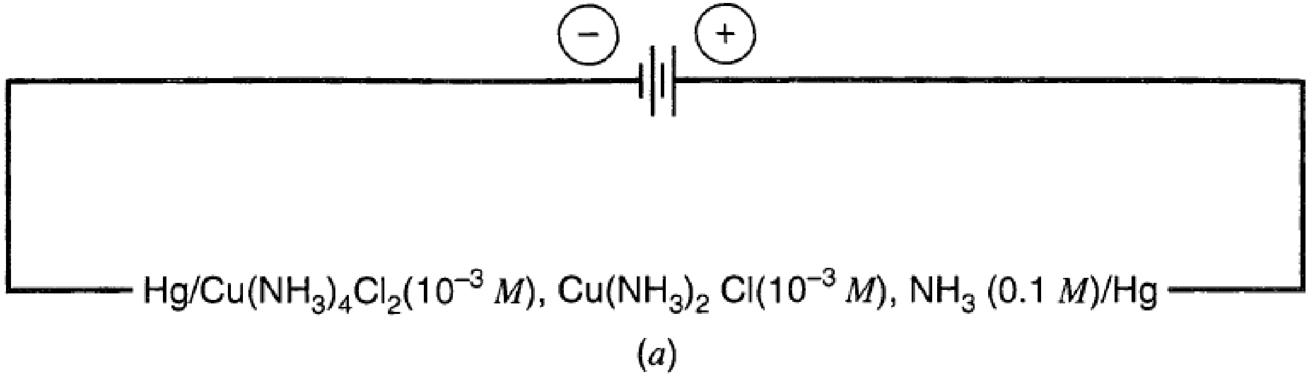
: the migration current is in the same direction as the diffusion current



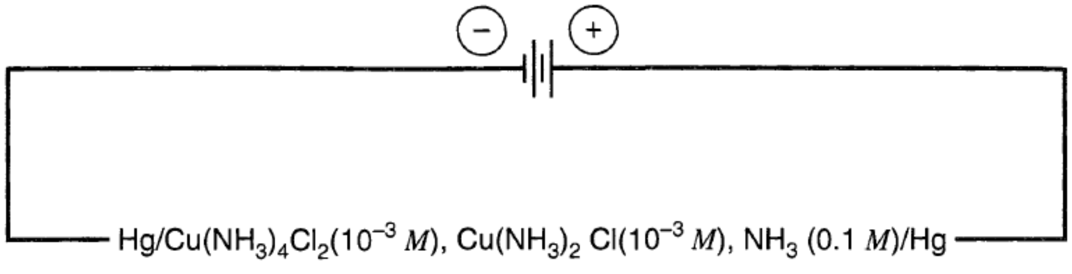
4.3.1 Balance Sheets for Mass Transfer During Electrolysis

Example 4.2

- Consider the electrolysis of a solution of 10^{-3} *M* $Cu(NH_3)_4^{2+}$, 10^{-3} *M* $Cu(NH_3)_2^{+}$, and 3 X 10^{-3} *M* Cl^- in 0.1 M NH_3 at two Hg electrodes



4.3.1 Balance Sheets for Mass Transfer During Electrolysis



(*a*)

- Assuming the limiting equivalent conductances of all ions are equal, that is,

$$\lambda_{\mathrm{Cu(II)}} = \lambda_{\mathrm{Cu(I)}} = \lambda_{\mathrm{Cl^-}} = \lambda$$

$$\boxed{t_{\mathrm{j}} = \frac{i_{\mathrm{j}}}{i} = \frac{|z_{\mathrm{j}}|u_{\mathrm{j}}C_{\mathrm{j}}}{\sum_{\mathrm{k}} |z_{\mathrm{k}}|u_{\mathrm{k}}C_{\mathrm{k}}} = \frac{|z_{\mathrm{j}}|\, C_{\mathrm{j}}\lambda_{\mathrm{j}}}{\sum_{\mathrm{k}} |z_{\mathrm{k}}|\, C_{\mathrm{k}}\lambda_{\mathrm{k}}}}$$

$$t_{\mathrm{Cu^{2+}}} = \frac{|z_{\mathrm{Cu^{2+}}}|c_{\mathrm{Cu^{2+}}}}{|z_{\mathrm{Cu^{2+}}}|c_{\mathrm{Cu^{2+}}} + |z_{\mathrm{Cu^{+}}}|c_{\mathrm{Cu^{+}}} + |z_{\mathrm{Cl^{-}}}|c_{\mathrm{Cl^{-}}}} = \frac{2}{2+1+3} = \frac{2}{6} = \frac{1}{3}$$

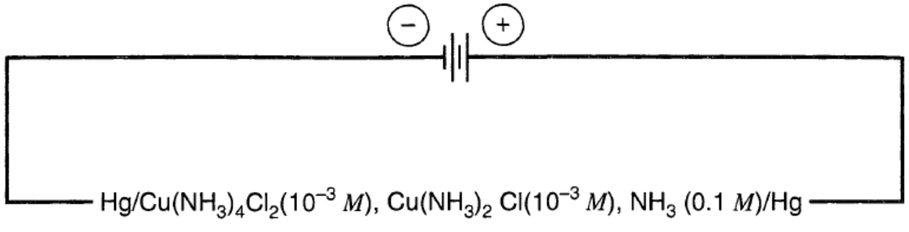
$$t_{\mathrm{Cu^{+}}} = \frac{1}{2+1+3} = \frac{1}{6}$$

$$t_{\mathrm{Cl^{-}}} = 1 - t_{\mathrm{Cu^{2+}}} - t_{\mathrm{Cu^{+}}} = 1 - \frac{1}{3} - \frac{1}{6} = \frac{1}{2}$$

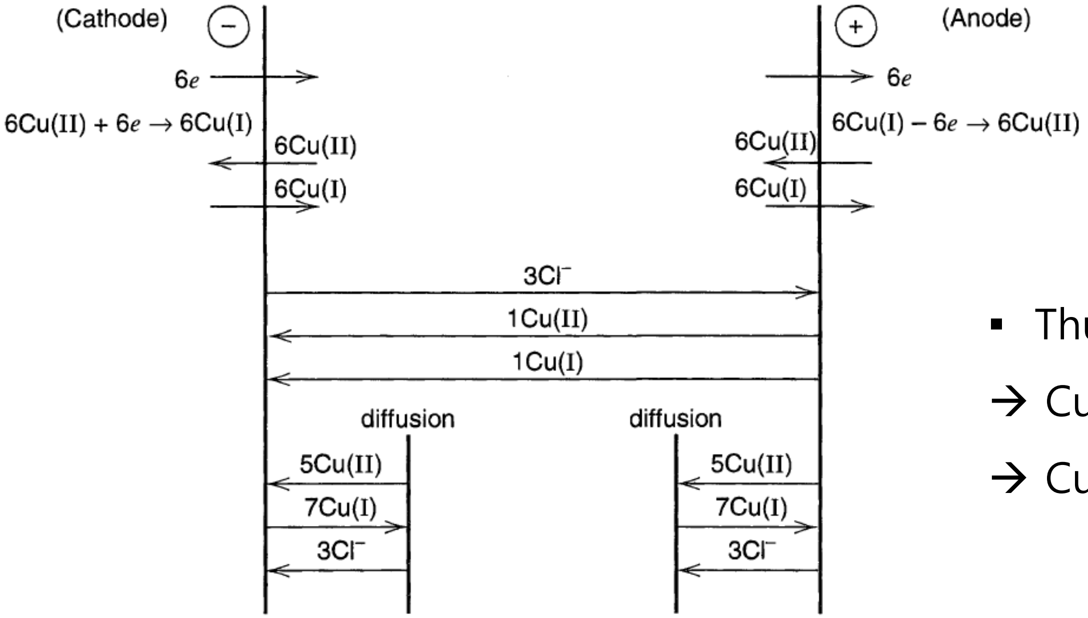
4.3.1 Balance Sheets for Mass Transfer During Electrolysis

- With an arbitrary current of 6e per unit time being passed,

  → the migration current in bulk solution is carried by movement of one Cu(II) and one Cu(I) toward the cathode, and three Cl^- toward the anode.



(a)



- Thus,

→ Cu(II): i_d = 5, i_m = 1 at the cathode

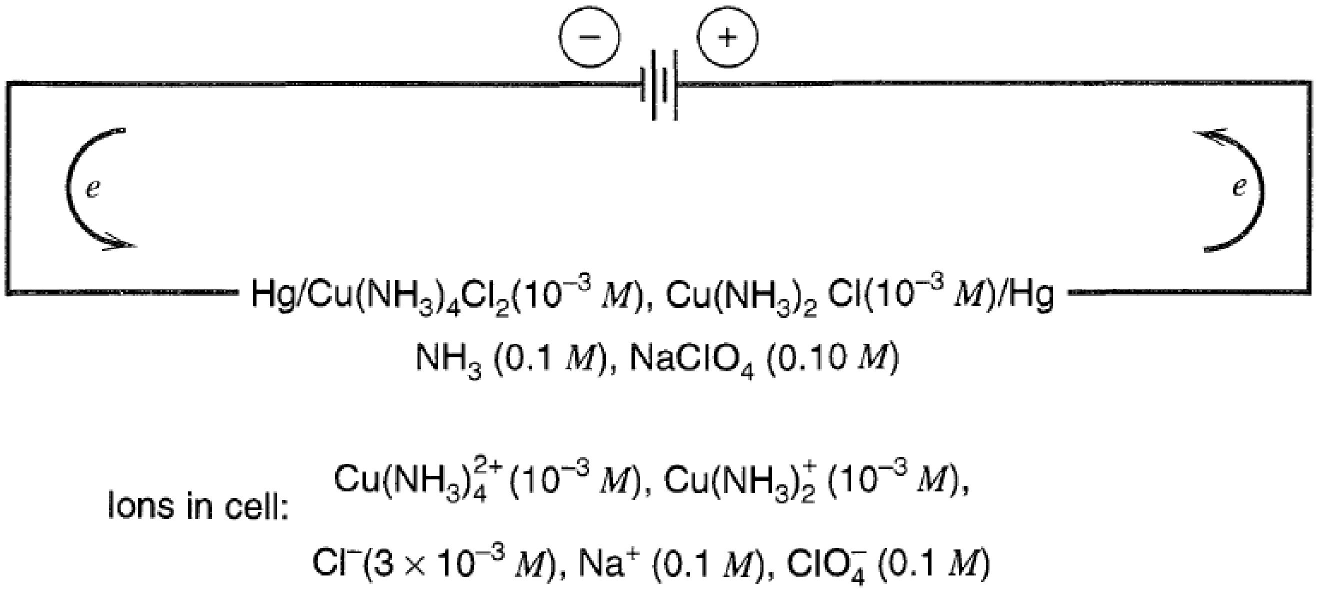
→ Cu(I): i_d = 7, i_m = -1 at the anode

4.3.1 Balance Sheets for Mass Transfer During Electrolysis

Example 4.3

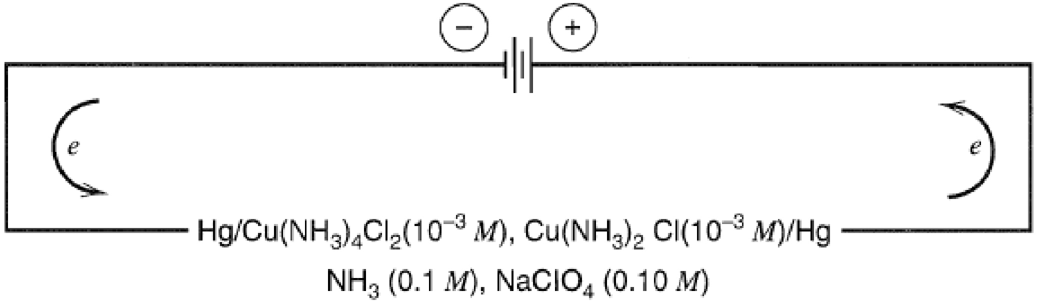
- Let us consider the same cell as in Example 4.2, except with the solution containing

0.10 *M* $NaClO_4$ as an excess electrolyte



(*a*)

4.3.1 Balance Sheets for Mass Transfer During Electrolysis



Hg/$Cu(NH_3)_4Cl_2$(10^{-3} *M*), $Cu(NH_3)_2$ Cl(10^{-3} *M*)/Hg
NH_3 (0.1 *M*), $NaClO_4$ (0.10 *M*)

Ions in cell: $Cu(NH_3)_4^{2+}$ (10^{-3} *M*), $Cu(NH_3)_2^{+}$ (10^{-3} *M*),
Cl^-(3×10^{-3} *M*), Na^+ (0.1 *M*), ClO_4^- (0.1 *M*)

- Assuming the limiting equivalent conductances of all ions are equal, that is,

$$\lambda_{\mathrm{Cu^{2+}}} = \lambda_{\mathrm{Cu^{+}}} = \lambda_{\mathrm{Cl^{-}}} = \lambda_{\mathrm{Na^{+}}} = \lambda_{\mathrm{ClO_4^{-}}}$$

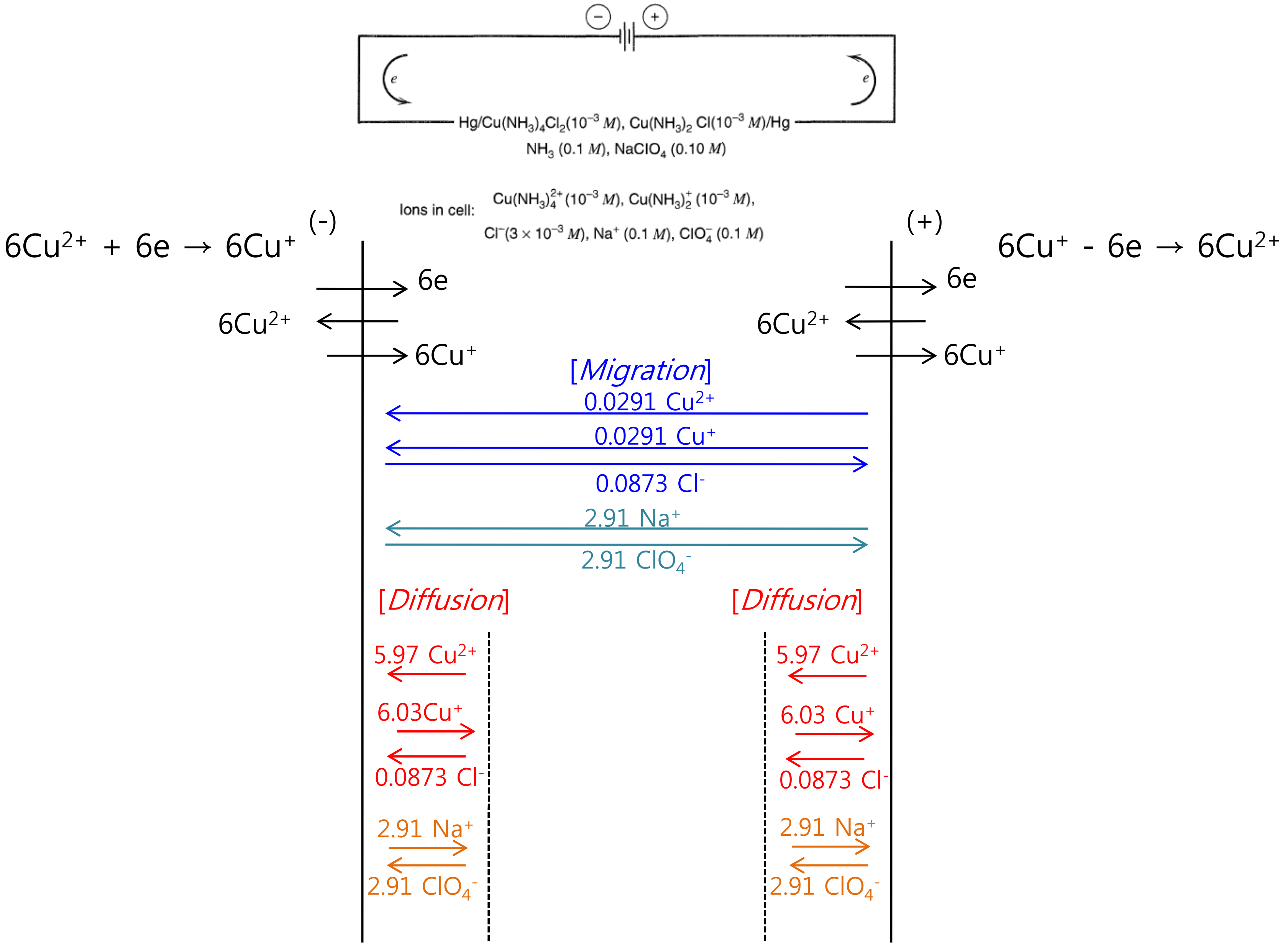
$$\boxed{t_j = \frac{i_j}{i} = \frac{|z_j| u_j C_j}{\sum_k |z_k| u_k C_k} = \frac{|z_j|\, C_j \lambda_j}{\sum_k |z_k|\, C_k \lambda_k}}$$

$$t_{\mathrm{Cu^{2+}}} = \frac{|z_{\mathrm{Cu^{2+}}}| c_{\mathrm{Cu^{2+}}}}{|z_{\mathrm{Cu^{2+}}}| c_{\mathrm{Cu^{2+}}} + |z_{\mathrm{Cu^{+}}}| c_{\mathrm{Cu^{+}}} + |z_{\mathrm{Cl^{-}}}| c_{\mathrm{Cl^{-}}} + |z_{\mathrm{Na^{+}}}| c_{\mathrm{Na^{+}}} + |z_{\mathrm{ClO_4^{-}}}| c_{\mathrm{ClO_4^{-}}}}$$

$$= \frac{2\times10^{-3}}{(2\times10^{-3}) + (1\times10^{-3}) + (3\times1\times10^{-3}) + (1\times10^{-1}) + (1\times10^{-1})} = 0.0097$$

$$t_{\mathrm{Cu^{+}}} = 0.00485$$
$$t_{\mathrm{Cl^{-}}} = 0.0146$$
$$t_{\mathrm{Na^{+}}} = 0.485$$
$$t_{\mathrm{ClO_4^{-}}} = 0.485$$

4.3.1 Balance Sheets for Mass Transfer During Electrolysis



Hg/Cu(NH$_3$)$_4$Cl$_2$(10^{-3} M), Cu(NH$_3$)$_2$Cl(10^{-3} M)/Hg

NH$_3$ (0.1 M), NaClO$_4$ (0.10 M)

Ions in cell: Cu(NH$_3$)$_4^{2+}$ (10^{-3} M), Cu(NH$_3$)$_2^{+}$ (10^{-3} M), Cl$^-$ (3×10^{-3} M), Na$^+$ (0.1 M), ClO$_4^-$ (0.1 M)

(-) $6Cu^{2+} + 6e \rightarrow 6Cu^{+}$

(+) $6Cu^{+} - 6e \rightarrow 6Cu^{2+}$

[*Migration*]

0.0291 Cu^{2+}

0.0291 Cu^{+}

0.0873 Cl^-

2.91 Na^+

2.91 ClO_4^-

[*Diffusion*]

5.97 Cu^{2+}

6.03 Cu^{+}

0.0873 Cl^-

2.91 Na^+

2.91 ClO_4^-

4.3.1 Balance Sheets for Mass Transfer During Electrolysis

- Thus, when the solution contains additional 0.10 *M* $NaClO_4$ as an excess electrolyte (supporting electrolyte)

→ $i = 6$

→ Cu(II): $i_d = 5.97$, $i_m = 0.03$ at the cathode

→ Cu(I): $i_d = 6.03$, $i_m = -0.03$ at the anode

- Note that, when the solution contains no supporting electrolyte,

→ $i = 6$

→ Cu(II): $i_d = 5$, $i_m = 1$ at the cathode

→ Cu(I): $i_d = 7$, $i_m = -1$ at the anode

➔ Thus, the addition of an excess of nonelectroactive ions (a supporting electrolyte) nearly eliminates the contribution of migration to the mass transfer of the electroactive species.