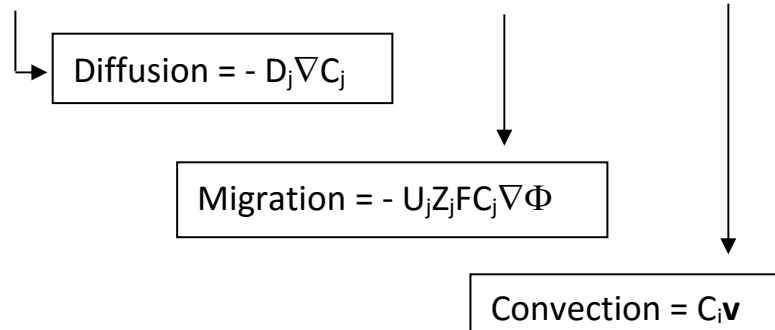


## Chapter 3: IONIC TRANSPORT

1. Ionic flux and current density
2. Validity of Ohm's law in electrochemical Cells
3. Transport number and concentration gradients
4. Supporting electrolyte
5. Concentration gradients at electrodes and their dependence on the current density
6. The limiting current

# IONIC TRANSPORT

Ionic flux is due to: **Diffusion + Electric Migration + Convection +...**



$$\mathbf{N}_j = - D_j \nabla C_j - U_j z_j F C_j \nabla \Phi + C_j \mathbf{v} + \dots \quad [\text{moles/sec cm}^2]$$

Current density is due to flux of all charge carrying species:

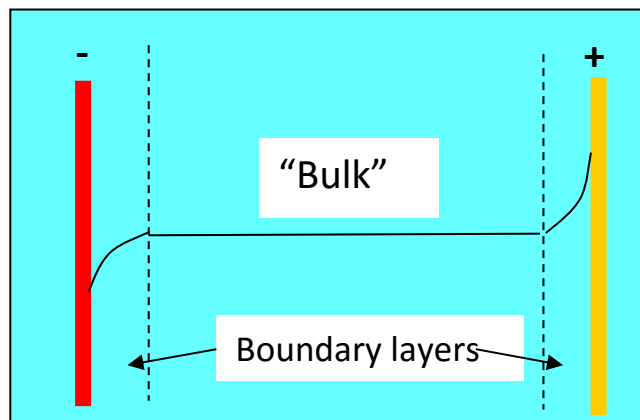
$$i = \sum z_j F N_j$$

$$= - F \sum z_j D_j \nabla C_j - F^2 \sum U_j z_j^2 C_j \nabla \Phi + F \sum z_j C_j \mathbf{v}$$

However, because of electroneutrality,  $\sum z_j C_j = 0$ ,  $\rightarrow$  the last term is identically zero,

$$i = - F \sum z_j D_j \nabla C_j - \kappa \nabla \Phi$$

Compare with (the differential form of) Ohm's law:  $i = - \kappa \nabla \Phi$



## Ionic flux and the current density:

The current flow in electrochemical cells is related to the ionic flux  $N_j$ . The latter is typically described in terms of three major modes of transport: migration of charged ions down the electric field, diffusion of ions across a concentration gradient and transport of ions due to bulk electrolyte convection. Consequently, the flux of an ionic species  $[i]$  is given by

$$N_j = -D_j \nabla C_j - U_j F Z_j C_j \nabla \Phi + C_j v \quad [\text{M sec}^{-1} \text{cm}^{-2}] \quad [1]$$

Electroneutrality is present throughout the cell and is described by

$$\sum z_i C_i = 0 \quad [(\text{eq./M}) (\text{M/cm}^3) = \text{eq/cm}^3] \quad [2]$$

The total current density is determined by multiplying the flux of each species by its charge  $FZ$ ; and summing over all ionic species:

$$i = F \sum z_i N_i \quad [\text{A/cm}^2] \quad [3]$$

Substituting Eqs. [1] into Eq. [3] yields

$$i = -F^2 \left( \sum z_i^2 u_i c_i \right) \nabla \phi - F \sum z_i D_i \nabla c_i + F \left( \sum z_i C_i \right) v \quad [4]$$

Because of electroneutrality (Eq. [2]), the last term on the right is identically zero and cancels, giving the expression for the total current density in terms of the concentration and potential fields in the cell:

$$i = -F^2 \left( \sum z_i^2 u_i c_i \right) \nabla \phi - F \sum z_i D_i \nabla c_i \quad [5]$$

It becomes apparent that the current density is determined by both the potential and concentration gradients. The velocity term is absent in Eq. [5] due to electroneutrality, however, convection still affects transport by controlling the concentration field.

To solve for the current density, one has to know the potential distribution in the cell,  $\Phi$ , and the concentration distribution of all species present,  $c_j$ . The latter are affected by the flow. However, as we shall subsequently see, some simplifications are often possible. In any event, Eq. [5], while giving the current density as a function of the potential and concentration distributions, does *not* provide the necessary relationships required for solving the latter. These come from the constitutive relationships described below.

## The Transport Parameters U and D:

Two transport parameters were introduced in the derivation: U and D.

They both express the ability of an ion to move under the influence of an applied force, hence we can expect them to be related.

U is the 'mobility', i.e., the velocity of an ion due to an applied electric field.

D is the 'diffusivity' or the velocity of the ion associated with intermolecular collisions.

Both parameters are expected to relate (be inversely proportional) to the size of the molecule being translated, and be affected also by the nature of the medium (solvent) which typically (but not always) is water. Accordingly, we should be considering  $U_{i,j}$  and  $D_{i,j}$  where i refers to the given ion and j represents the other species in the medium.

Stokes Einstein law relates both parameters:

$$D_i = RTU_i \quad [6]$$

where the index j representing the solvent (water) has been omitted.

We also noted before that the equivalent ionic conductivity was related to the mobility through:

$$\lambda_i = F^2 Z_i U_i \quad [7]$$

Since  $\lambda_i$  was about constant for most ions ( $\lambda_i \sim 50-70$ ) due to their about uniform hydrated shell, except for protons ( $\lambda_i$  350) and hydroxyl ions ( $\lambda_i$  200), we expect the diffusivity for most ions to be about the same. We indeed find:

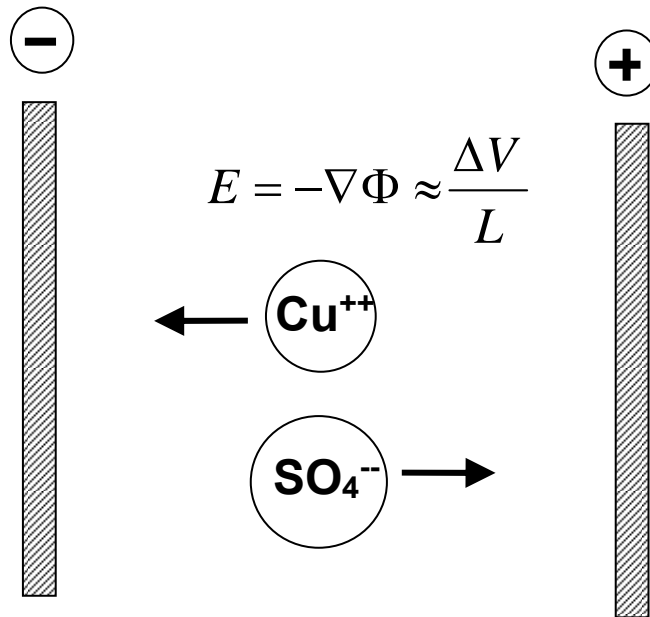
$$D \sim 10^{-5} \text{ cm}^2/\text{s} \quad [8]$$

for most ions except for protons and hydroxyl ions. This equivalency, coupled with the small magnitude of D was first recognized by Venjamin Levich and enabled him to characterize the Rotating Disk Electrode ('RDE') as a useful and fairly universal tool for characterizing electrolytic solutions.

## A few questions:

- How come that the electrolyte velocity appears not to affect the current density? Does this make sense or correlate with Experimental evidence?
- Can we measure electrolyte conductivity using an ohmmeter?
- **Why do we have concentration gradients at the electrodes?**
- How significant are the concentration gradients and what do these depend on?
- Which term is more important:  $F\sum z_j D_j \nabla C_j$  or  $\kappa \nabla \Phi$  ?
- Can there be a functioning electrochemical cell ( $i>0$ ) with no concentration gradients?
- When are the concentration gradients established?
- How long does it take them to be established or to decay?
- How far do the concentration gradients extend into the solution?
- Are the concentration gradients harmful, or these beneficial?
- Can these be minimized? How?
- How do we plate from anions?

# The Transport Number



Current is carried by *all ions* that are moving under the applied electrical field

Define:

The transport number of ionic species  $j$  =

*The fraction of the current that is carried by ionic species  $j$  in the absence of concentration gradient*

(i.e., migration current in the well-mixed bulk).

$$t_j = \frac{i_j^M}{i^M} = \frac{\lambda_j Z_j C_j \nabla\Phi}{\sum_{j=1}^{j=n} \lambda_j Z_j C_j \nabla\Phi} = \frac{\kappa_j}{\kappa}$$

$$\sum_1^{j=n} t_j = 1 \quad (\text{always})$$

$$t_+ \sim t_- \sim 0.5 \quad \text{Binary electrolyte}$$

$$t_R \sim 0 \quad \text{Well-supported electrolytes}$$

## TRANSPORT NUMBER (Transference)

$t_j \equiv$  fraction of current carried by species  $j$  in the absence of concentration gradients.

$$t_j = \frac{i_j^{\text{mig}}}{i^{\text{mig}}} = \frac{-F^2 \sum_j Z_j^2 U_j C_j \nabla \phi}{-F^2 (\sum_j Z_j^2 U_j C_j) \nabla \phi} = \frac{\sum_j Z_j^2 U_j C_j}{\sum_j Z_j^2 U_j C_j} = \frac{\sum_j Z_j \lambda_j C_j}{\sum_j Z_j \lambda_j C_j}$$

$$\sum t_j = 1$$

Example: 0.1M  $\text{CuSO}_4$ :

$$t_{\text{Cu}^{++}} = \frac{2 \times 54 \times 0.1 \times 10^{-3}}{2 \times 54 \times 0.1 \times 10^{-3} + 2 \times 80 \times 0.1 \times 10^{-3}} = 0.4$$

$$t_{\text{SO}_4^{--}} = \frac{2 \times 80 \times 0.1 \times 10^{-3}}{2 \times 54 \times 0.1 \times 10^{-3} + 2 \times 80 \times 0.1 \times 10^{-3}} = 0.6$$

## SUPPORTING ELECTROLYTE

Electrolyte that does not participate in the electrode reactions.

Examples:  $\text{H}_2\text{SO}_4$  in copper plating from  $\text{CuSO}_4$   
 $\text{KOH}$  in Alkaline ( $\text{Zn}/\text{MnO}_2$ ) batteries.

Why:

1. Increased conductivity
2. Enhance reactant solubility
3. pH adjustment
4. Chemical or catalytic effects (e.g. complexation, adsorption...)

Note:  $\lambda_{\text{H}^+} = 350$  ,  $\lambda_{\text{OH}^-} = 200$  ,  $\lambda_{\text{X}} \equiv 70$

Effect on transport number:

Example:  $0.1\text{M CuSO}_4 + 1\text{M H}_2\text{SO}_4$

$\text{Cu}^{++}$ :  $C = 0.1\text{ M}$      $Z = +2$      $\lambda = 54$

$\text{H}^+$ :  $C = 2\text{ M}$      $Z = 1$      $\lambda = 350$

$\text{SO}_4^{--}$ :  $C = 1.1\text{ M}$      $Z = 2$      $\lambda = 80$

$$t_{\text{Cu}^{++}} = \frac{0.1 \times 2 \times 54}{0.1 \times 2 \times 54 + 2 \times 1 \times 350 + 1.1 \times 2 \times 80} = \frac{108}{8868} = 0.01$$

$$t_{\text{H}^+} = \frac{2 \times 1 \times 350}{0.1 \times 2 \times 54 + 2 \times 1 \times 350 + 1.1 \times 2 \times 80} = \frac{700}{8868} = 0.79$$

$$t_{\text{SO}_4} = \frac{1.1 \times 2 \times 80}{0.1 \times 2 \times 54 + 2 \times 1 \times 350 + 1.1 \times 2 \times 80} = \frac{176}{8868} = 0.2$$

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## Current and Concentration Gradients

The current associated with species j is due to diffusion and migration:

$$i_j = i_j^D + i_j^M \quad [3-1a]$$

We can write down the diffusion and migration components explicitly

$$i_j = -z_j D_j F \nabla C_j - F^2 z_j^2 U_j C_j \nabla \Phi \quad [3-2a]$$

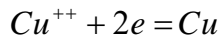
We can make use of the transport number to express ( only approximately) the migration current

$$t_j = \frac{i_j^M}{i} = \frac{F^2 z_j^2 U_j C_j \nabla \Phi}{i} \quad [3-3a]$$

Substituting the last term in eq. 3-2a in terms of the transport number,

$$i_j = -z_j D_j F \nabla C_j + t_j i \quad [3-4a]$$

We recognize that if we only have a single reaction at the electrode, e.g.,



Or, in a more general way, recognizing that there may be **a stoichiometric coefficient,  $s_R$**  for the reactant,

$$s_R M^{z+} + ne = s_R M^{z-n/s} \quad [3-5a]$$

We assign species j as the reactant, recognizing that if only one reaction takes place, the entire current is associated with it:

$$i_R = i_j = i \quad [3-6a]$$

Substituting in 3-4a:

$$i = -z_R D_R F \nabla C_R + t_R i \quad [3-7a]$$

Solving for i,

$$i = -\frac{z_R D_R F \nabla C_R}{1 - t_R} \sim -\frac{z_R D_R F (C^B - C^E)}{(1 - t_R) \delta_{N,R}} \quad [3-8a]$$

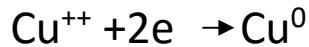
The negative sign in Eq. 3-8 indicates that the direction of the current is down the concentration gradient. By convention, we assign cathodic currents (and overpotentials) as negative and anodic currents (and overpotentials) as positive.

Clearly, as the current increases (due to larger potential driving force for the electrode reaction), the concentration gradient must increase. Since the boundary layer thickness is typically determined by the convective flow, this implies that the concentration of the reactant near the cathode drops (and near the anode increases).

Remember also that for well-supported electrolytes,  $t_R \sim 0$ , (while for binary electrolytes  $t_R \sim 0.5$ )

# CURRENT DENSITY AT ELECTRODES

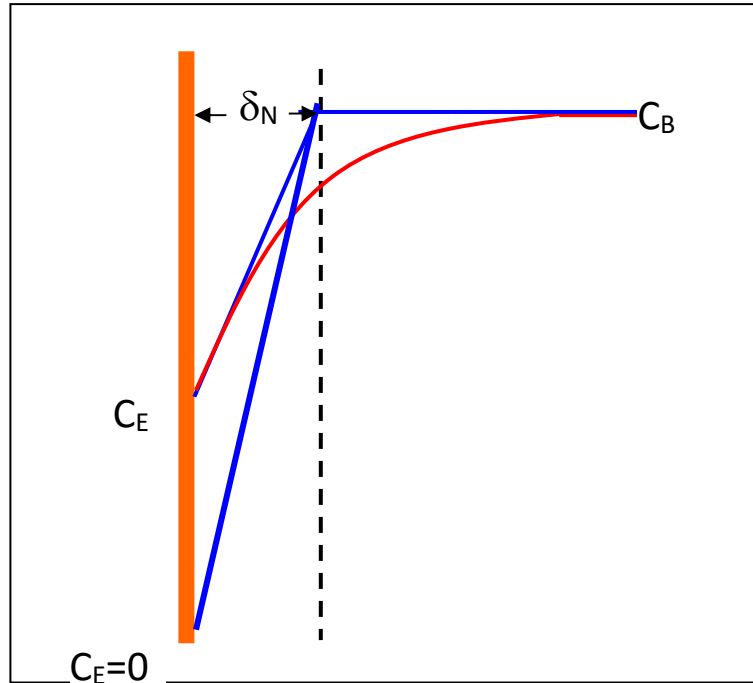
$$\mathbf{i} = -F \sum Z_j D_j \nabla C_j - \kappa \nabla \Phi$$



$$i = \frac{nFD \nabla C_R}{s_R (1 - t_R)}$$

Define the equivalent Nernst boundary layer,  $\delta_N$ :

$$i = \frac{-nFD(C_B - C_E)}{s_R (1 - t_R) \delta_N}$$



Note: By convention, cathodic current is negative, anodic is positive

The higher the current, the lower is the interfacial concentration.

$C_E = 0$  defines the maximum current density:

The limiting current:

$$i_L = \frac{-n F D C_B}{s_R (1 - t_R) \delta_N}$$

The limiting current is the maximal current that can be passed for a given reaction, irrespective of the voltage. It can be exceeded only when secondary, typically parasitic reactions start taking place.

$\delta_N = f(\text{velocity, geometry, fluid properties})$

$t_R = 0$  in well supported electrolyte (e.g.; acid)

$t_R = 0.5$  in binary electrolyte (e.g.;  $\text{CuSO}_4$  only)

## Increasing the Limiting Current:

The limiting current has a major process design implication since no electrochemical reaction can proceed at a rate exceeding it, irrespective of the applied voltage. The only way the limiting current can be exceeded is that once it is reached, the voltage will swing to a higher value, eventually kicking off a secondary, typically parasitic reaction, e.g., hydrogen evolution, resulting in a diminished current efficiency.

As noted, the limiting current can be increased by increasing the bulk reactant concentration, however, we are limited by the solubility to about 1 M ( $\approx 10^{-3}$  M/cc). We have little control over the diffusivity (typically increases slightly with temperature), and no control over  $n$ ,  $F$ , and  $s$ . We can, however, affect significantly  $\delta$ , by enhancing the convective velocity past the electrode.  $\delta$  depends mostly on the velocity, and also is a function of the geometry (shape of the electrode, and position along it), and electrolyte properties ( $\mu$ ,  $\rho$ , and  $D$ ). Being inversely proportional to the velocity, it becomes smaller with enhanced flow. At lower, laminar flow rates,  $\delta$  is inversely proportional to  $v^{0.33}$ , however, at higher, turbulent flow rates,  $\delta$  becomes inversely proportional to approximately  $v^{0.9}$ .

If no convective velocity is present,  $\delta_N$  increases rapidly with time (we shall quantify this later), and after a relatively short time (few minutes) will shut the process down due to  $\delta_N$  becoming very large and  $i_L$  going to zero. However, most electrochemical systems, will have some free convection, that will kick in due to density variations within the electrolyte, and prevent  $\delta_N$  from decaying to zero.

## The effect of supporting electrolyte on the limiting current:

With well supported electrolytes, i.e., in the presence of an acid, base, or salt,  $t \sim 0$  and we have:

$$i_{L, \text{well supported}} = \frac{nFDC_B}{s_r \delta_N}$$

However, when we remove the supporting electrolyte we have  $t \sim 0.5$ , giving:

$$i_{L, \text{binary}} = \frac{nFDC_B}{s_r (0.5) \delta_N} = 2i_{L, \text{well supported}}$$

Accordingly, by removing the supporting electrolyte we double our maximal transport rates or half the mass transport resistance. Why then do we typically add supporting electrolyte?

The answer is related to the fact that by adding supporting electrolyte we increase significantly the electrolyte conductivity, lowering the ohmic drop and improving, as we shall see later, the current distribution. Furthermore, most electrochemical processes, particularly those involving

the deposition of a solid phase, do not operate close to the mass transport limit (to prevent dendritic deposition), hence improving mass transport is not very relevant. Also, enhancing agitation and increasing the reactant concentration are two other means of improving mass transport. Nonetheless, there are situations when improving 'chemically' the mass transport by removing the supporting electrolyte is useful.

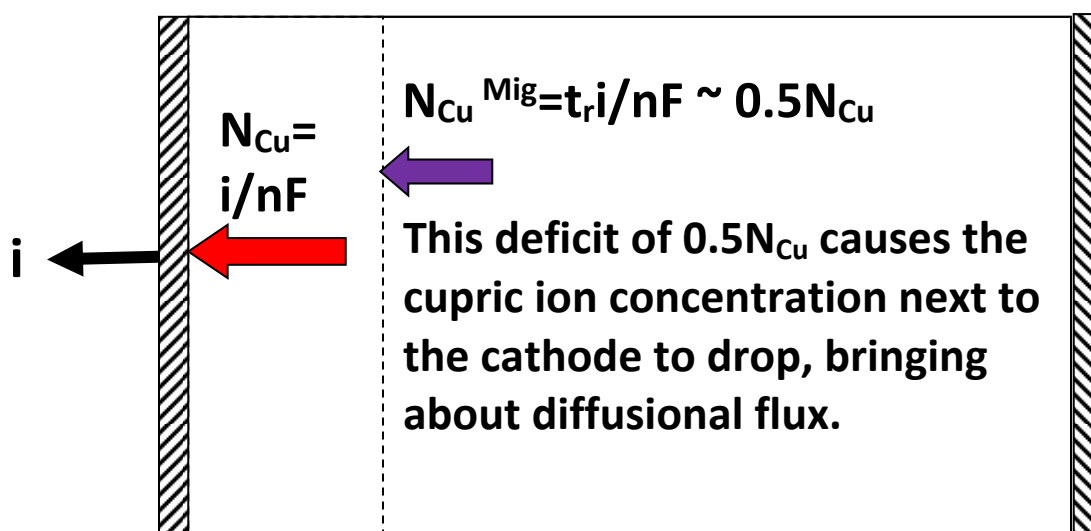
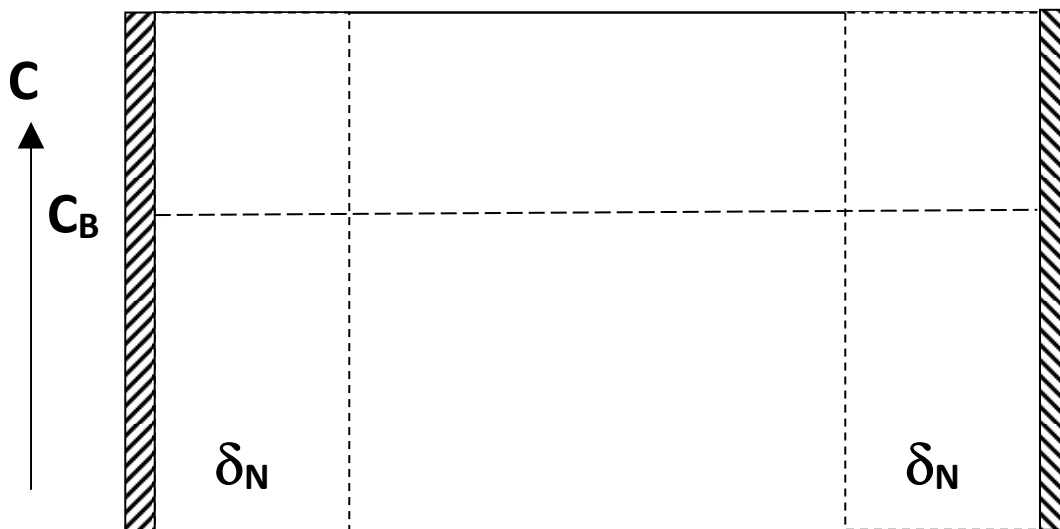
The reason for the diminished mass transport in the presence of supporting electrolyte is that due to the reduced migration in the presence of a weak electric field, hence essentially all the reactant must be brought to the electrode by transport (convection and diffusion) and virtually none arrive via migration.

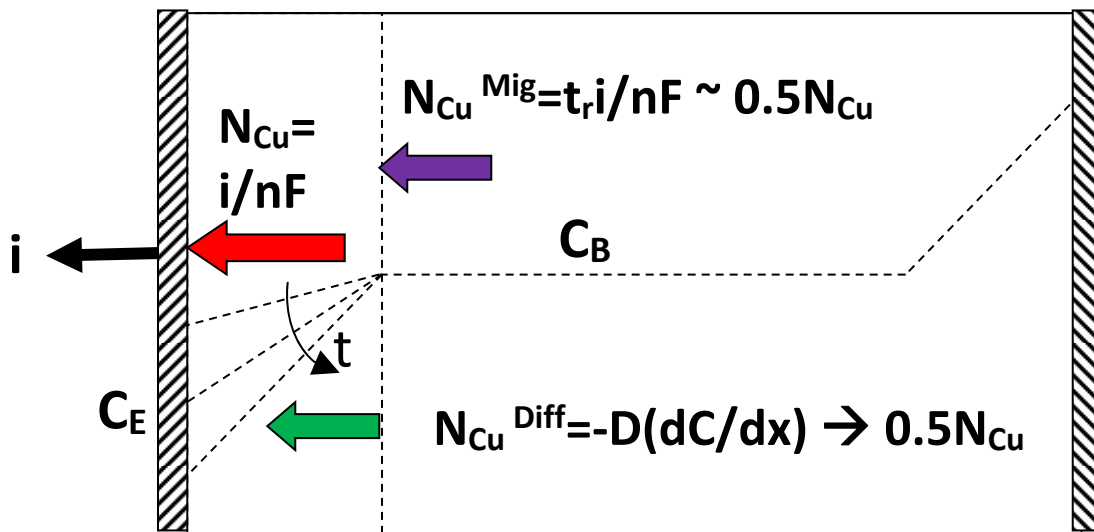
There is a great sensitivity to the supporting electrolyte, and even a relatively small amount, will reduce transport (and increase conductivity).

## The establishment of concentration gradients in an electrochemical cell:

Consider first a binary electrolyte ( $\text{CuSO}_4$ ) in a simple cell consisting of two parallel, infinite electrodes. Assume a mixed bulk with a boundary layer thickness  $\delta_N$ . Furthermore, assume linear concentration gradient within the thin boundary layer.

### Before applying current:





While we apply a current density  $i$  to the cathode, the corresponding flux of copper removal by plating is:

$$N_{\text{Cu}}^{\text{Total}} = i/nF$$

Since migration flux, in the binary electrolyte brings only

$$N_{\text{Cu}}^{\text{Mig}} = t_r i/nF \sim 0.5 i/nF \sim 0.5 N_{\text{Cu}} \quad \leftarrow$$

The removal rate of cupric ions from the electrolyte next to the cathode exceeds the rate of replenishment by migration, leading to a deficit and to lower concentration near the cathode. This lowered concentration brings about diffusional flux towards the cathode:

$$N_{\text{Cu}}^{\text{Dif}} = -D(dC/dx)|_e \sim -D(C_E - C_B)/\delta_N \sim 0.5 N_{\text{Cu}}^{\text{Total}} = 0.5 i/nF \quad \rightarrow$$

Initially this diffusional flux is zero (initially no conc. gradients), however, as time passes and the deficit increases, the concentration gradients build up and the diffusional flux increases.

Once the diffusional flux provides the entire deficit,

$$\sim 0.5 N_{\text{Cu}} = 0.5 i/nF \text{ for the binary electrolyte,}$$

The concentration gradient stabilizes. This establishes the concentration near the cathode,  $C_E$ .

$$C_E = C_B + \frac{s_R i \delta_N}{nFD(1-t_R)} \quad [by\ convention : i_{cathodic} < 0]$$

$$C_E = C_B - \frac{s_R |i| \delta_N}{nFD(1-t_R)}$$

For the **well supported electrolyte**, the process is similar, except, that  $t_R$  is about zero. Accordingly, the migration flux of copper,

$$N_{Cu}^{Mig} = t_R i / nF \sim 0$$

is vanishingly small. Therefore, since the cupric ions are still removed at a flux of

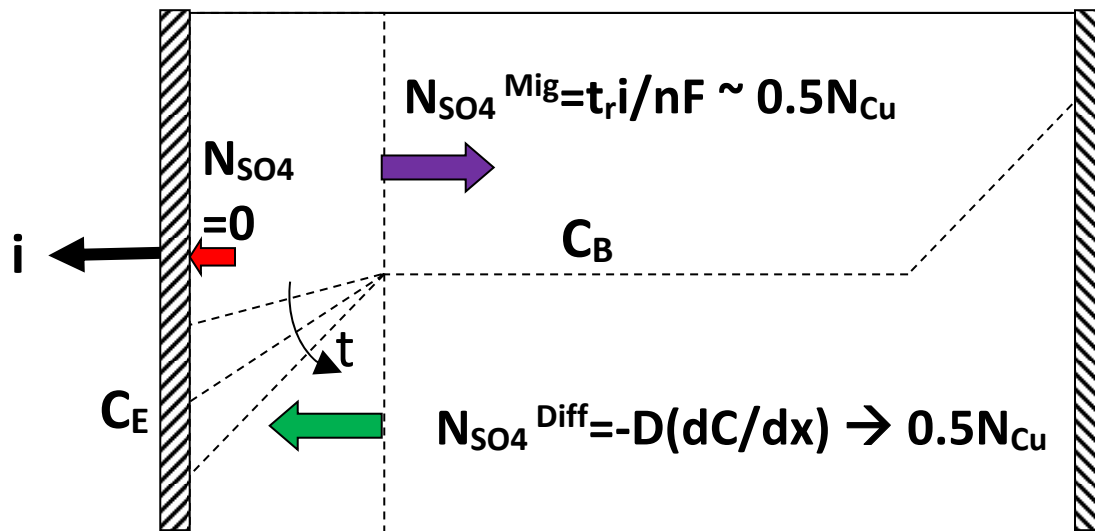
$$N_{Cu} = i / nF$$

and no copper arrives to the region next to the cathode by migration, the deficit builds up much faster. The diffusional flux builds up faster, since it must provide all the cupric ions that are removed by plating. The diffusional flux will be double that for the binary electrolyte, and the concentration at the cathode will be twice lower. We have now:

$$N_{Cu}^{Dif} = -D(dC/dx)|_e \sim -D(C_B - C_E)/\delta_N = N_{Cu}^{Total} = i / nF$$

The processes at the anode, are analogous. Here the amount of copper dissolved can't be carried out just by migration. Therefore the concentration builds up next to the anode, building up a diffusional flux away from the anode region.

### What about the Sulfate concentration?



Consider first the cathode region. Clearly, sulfate is not removed or generated by the electrode reaction, hence

$$N_{SO_4}^{Total} = 0$$

Sulfate is carried **away** from the cathode by migration (due to the electric field), since, unlike the cupric ion it is negatively charged.

$$N_{SO_4}^{Mig} = t_r i / nF \sim 0.5 i / nF \quad \rightarrow$$

As a consequence, a deficit of sulfate will be generated next to the cathode. This will lower the sulfate concentration next to the cathode, resulting in diffusional flux of sulfate towards the cathode.

$$N_{SO_4}^{Dif} = -D(dC/dx)|_e \sim -D(C_B - C_E)/\delta_N \sim 0.5 i / nF \quad \leftarrow$$

Since the net flux of sulfate is zero, these two fluxes must be of opposite direction and equal in magnitude.

$$N_{SO_4}^{Dif} = - N_{SO_4}^{Mig} \quad \rightarrow \leftarrow$$



The sulfate interfacial concentration is identical to this of the cupric ions and given by:

$$C_E = C_B + \frac{s_R i \delta_N}{nFD(1-t_R)} = C_B - \frac{s_R |i| \delta_N}{nFD(1-t_R)}$$

We find that the sulfate concentration profile is identical to this of the cupric ions. This was actually expected, because due to electroneutrality:

$$\sum_j z_j C_j = 0 \rightarrow z_{Cu} C_{Cu} + z_{SO_4} C_{SO_4} = 0$$

$$C_{SO_4} = -\frac{z_{Cu}}{z_{SO_4}} C_{Cu} = -\frac{2}{-2} C_{Cu} = C_{Cu}$$

## Sulfate and Proton concentrations in the non-binary (supported) electrolyte:

For the sulfate ion:

$$N_{SO_4} = 0 = -D_{SO_4} \frac{(C_{SO_4}^E - C_{SO_4}^B)}{\delta_{SO_4}} - U_{SO_4} z_{SO_4} F C_{SO_4} \nabla \Phi = 0$$

$$N_{SO_4} = -D_{SO_4} \frac{(C_{SO_4}^E - C_{SO_4}^B)}{\delta_{SO_4}} + t_{SO_4} \frac{i}{nF} = 0$$

$$C_{SO_4}^E = C_{SO_4}^B + t_{SO_4} \frac{i \delta_{SO_4}}{nFD_{SO_4}} \quad [i_{cathodic} < 0]$$

$$C_{SO_4}^E = C_{SO_4}^B - t_{SO_4} \frac{|i| \delta_{SO_4}}{nFD_{SO_4}}$$

Since  $t_{SO_4}$  is not equal to that of  $t_{Cu}$  in the well supported electrolyte, the concentration profile of the sulfate will no longer follow that of copper. Electroneutrality is maintained through the proton concentration.

By analogous derivation we find that the proton concentration increases near the cathode:

$$N_H = \frac{i_H}{F} = -D_H \frac{(C_H^E - C_H^B)}{\delta_H} - U_H z_H F C_H \nabla \Phi$$

$$N_H = \frac{i_H}{F} = -D_H \frac{(C_{SO_4}^E - C_{SO_4}^B)}{\delta_H} + t_H \frac{i_{Cu}}{nF}$$

$$C_H^E = C_H^B + \frac{i_H \delta_H}{FD_H} - t_H \frac{i_{Cu} \delta_H}{nFD_H}$$

$$C_H^E = C_H^B + \frac{\delta_H}{FD_H} \left[ i_H - t_H \frac{i_{Cu}}{n} \right] = C_H^B - \frac{\delta_H}{FD_H} \left[ |i_H| - t_H \frac{|i_{Cu}|}{n} \right] \quad [i_{cathodic} < 0]$$

## How Long does it take to establish the Concentration Gradients?

We shall later see that the time constant for the transient process is given by

$$t \sim \frac{\delta_N^2}{D}$$

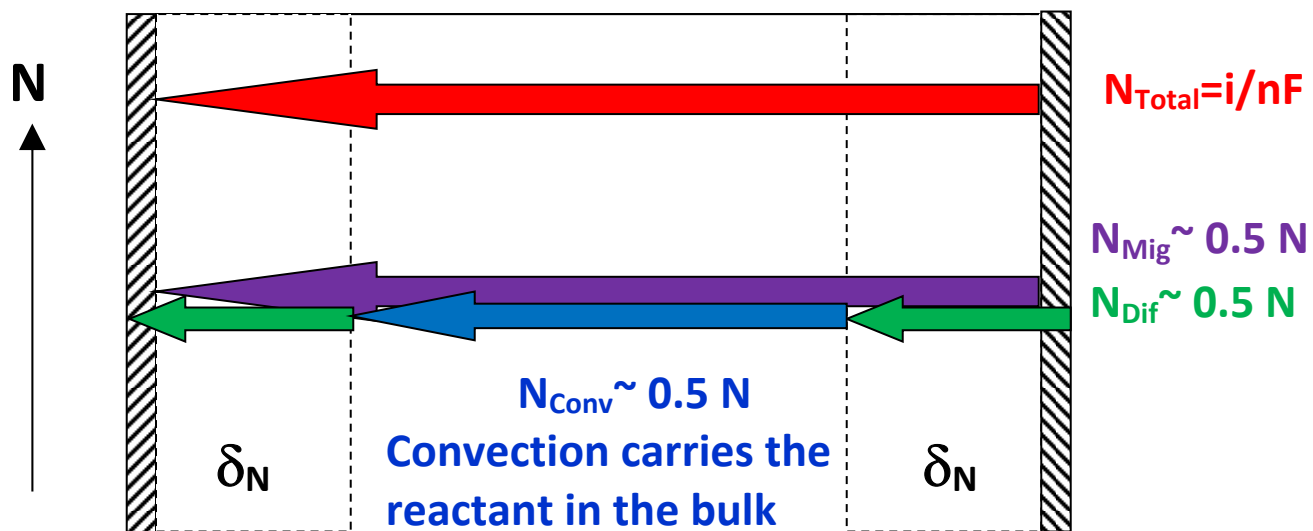
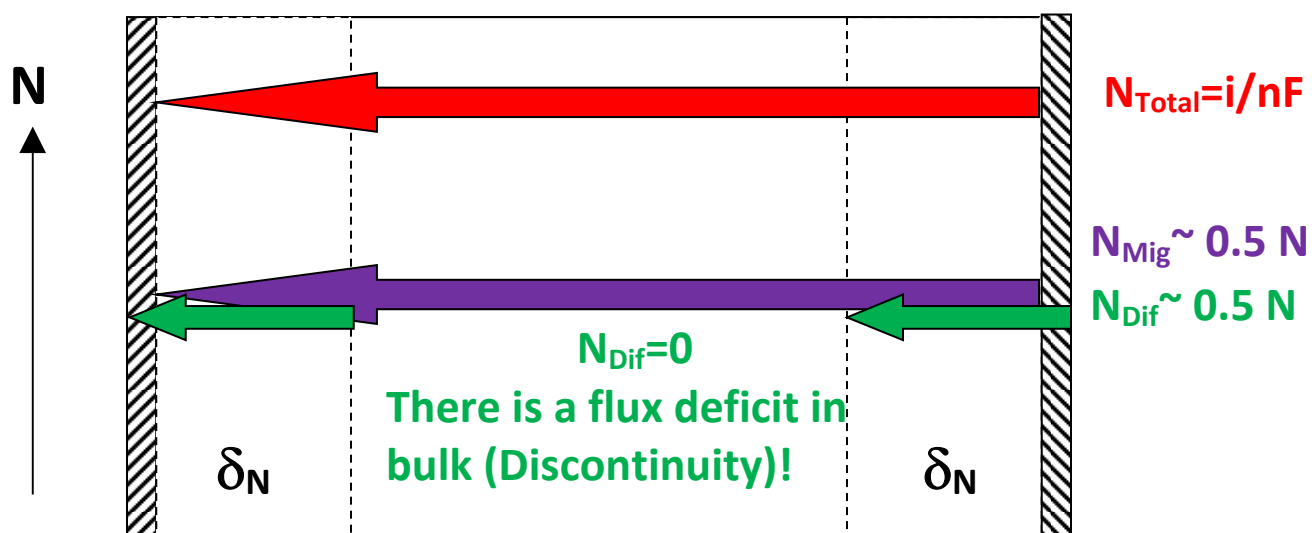
$$D \sim 10^{-5} [cm^2 / s]$$

$\delta_N$ [cm]	$10^{-2}$	$10^{-3}$	$10^{-4}$
t [s]	10	0.1	$10^{-3}$

## Fluxes across the cell.

Assume a binary electrolyte,  $\text{CuSO}_4$ :

$\text{Cu}^{++}$



## Review questions:

- **Why do we have concentration gradients at the electrodes?**
- How significant are the concentration gradients and what do they depend on?
- Which term is more important:  $F\sum z_j D_j \nabla C_j$  or  $\kappa \nabla \Phi$  ?
- **Can there be a functioning electrochemical cell ( $i > 0$ ) with no concentration gradients?**
- **When are the concentration gradients established?**
- **How long does it take them to be established or to decay?**
- How far do the concentration gradients extend into the solution?
- Are the concentration gradients harmful, or do they help us?
- Can they be minimized? How?
- Can we draw the different fluxes across the cell?
- **Which species actually moves inside the cell?**
- How do we plate from anions? (plating of gold from  $\text{KAu}(\text{CN})_2$ )