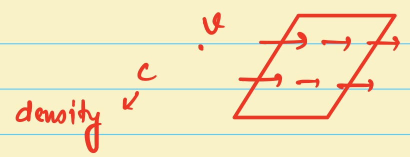
PARTIAL NON-LINEAR INTEGRO DIFFERENTIAL EQUATION

Electrochemical Cell :-

Flux = velocity × density ———— ①



How many particles will pass through the frame in 1s?
In 1s, particles that are v m away, will pass through the plane.
Total volume that passes ⇒ $v \times 1 m^2 = v\ m^3$
Total amount = cv

Force = (-)ve gradient of potential ———— ②

→ $D_i = \frac{RT}{6\pi\mu R_s}$ ———— ③

$\mu_i = \mu_i^\circ + RT \ln c_i$

Electric Potential = ϕ
Force = $-z_i \frac{d\phi}{dx} F$

charge

Faraday's constant (to convert it into mole terms).

Now the force = drag force

→ $-z_i F \frac{d\phi}{dx} = 6\pi R_s \mu . v$ → migration velocity

Flux = Diffusive Flux + Migration Flux

$\rightarrow$ $$u = \frac{-z_i F \frac{d\phi}{dx}}{6\pi R_s \mu}$$

substituting from eq'n 3

$$u = \frac{-z_i F (d\phi/dx) \cdot D_i}{RT}$$

Migration Flux : $v \cdot C_i = \frac{-z_i F \; d\phi/dx \cdot C_i \cdot D_i}{RT}$

Total Flux : $\frac{-z_i F C_i D_i}{RT} \frac{d\phi}{dx} - D_i \frac{dc_i}{dx}$

Note: In electrical cell, we can use c_i for density as well.

Diffusion - Migration Transport in a System

we have:

1) Steady 1D system.
2) Potentiostatic Electrolysis.
3) Three ionic species.
4) Species 1 & 2 are cations and 3 is an anion.
5) Only species 1 reacts at the electrode.

c_1 c_2 c_3 - species

Hence for non-reactive species, $N_i = 0$ at SS

At $N_i = 0$

$$-D_i \frac{dc_i}{dx} - \frac{z_i C_0 D_i F}{RT} \frac{d\phi}{dx} = 0 \qquad i = 2,3$$

Now,

Galvanostatic Condition $\rightarrow$ constant current

i : current density (Amp/m²).

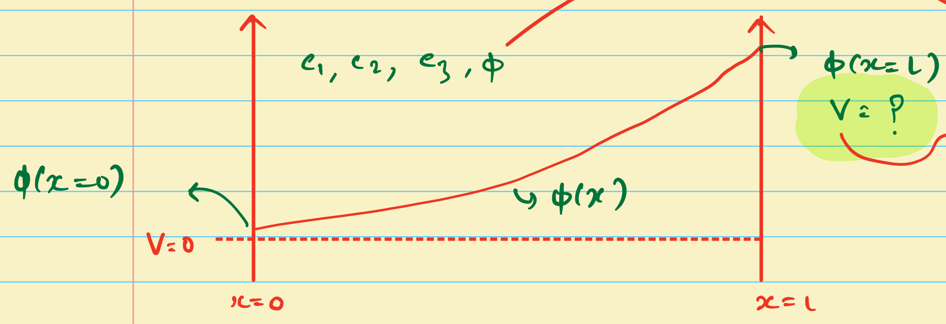
$$\underbrace{\left(-D_1 \frac{dc_1}{dx} - \frac{z_1 c_1 D_i F}{RT} \frac{d\phi}{dx}\right)}_{\text{Molar Flux}} F z = i$$

Now, local neutrality

↳ Approximate law of Physics.

$$\sum z_i c_i = 0$$

→ Now, to keep the cell at constant current, you don't know the voltage



electrochemical potential of the electrolyte

This voltage is different from ϕ. This voltage is the potential difference that drives the rxn.

The kinetics of this reaction is governed by the Butler-Volmer kinetics

$$i = i_0 \left\{ \exp\left(-\overset{0.5 \text{ in our case}}{\alpha}\, z_1 \frac{F}{RT} \underset{\phi \text{ at } x=0}{\phi(0)}\right) - \frac{\overset{c_1(x=0)}{c_1(0)}}{\underset{\text{reference conc'n}}{c_1^{\circ}}} \exp\left((1-\alpha) z_1 \frac{F}{RT} \phi(0)\right) \right\}$$

CATHODE

$$i = i_0 \left\{ \frac{c_1(L)}{c_1^{\circ}} \exp\left((1-\alpha) z_1 \frac{F}{RT} (\phi(L) - V)\right) - \exp\left(\alpha z_1 \frac{F}{RT} (V - \phi(L))\right) \right.$$

ANODE

(These are differences of forward and backward reactions).

Reactions:

−ve electrode:

$$Pb^{2+} + 2e^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} Pb$$

+ve electrode:

$$Pb^{+2} + 2H_2O \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} PbO_2 + 4H^+ + 2e^-$$

Pb^{+2}, H^+, $CH_3SO_3^-$

Unsteady Mass balance eq'n for i^{th} species:

$$\frac{\partial c_i}{\partial t} = \frac{-\partial N_i}{\partial x}$$

$$\frac{\partial c_i}{\partial t} = D_i \frac{\partial^2 c_i}{\partial x^2} + \frac{z_i F D_i}{RT} \frac{\partial \phi}{\partial x} \frac{\partial c_i}{\partial x} + \frac{z_i D_i F c_i}{RT} \frac{\partial^2 \phi}{\partial x^2}$$

$\downarrow$ $i = 1, 2, 3$

$$\sum z_i c_i = 0$$

- Now, for making calculations simpler, we combine equations and add a $\sum z_i$.

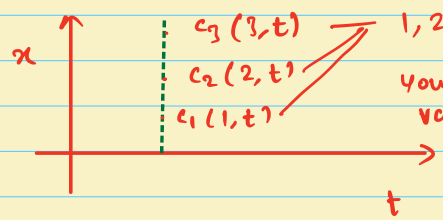
$$\sum z_i \left[\left(\frac{\partial c_i}{\partial t} = D_i \frac{\partial^2 c_i}{\partial x^2} + \frac{z_i F D_i}{RT} \left(\frac{\partial c_i}{\partial x} \frac{\partial \phi}{\partial x} + c_i \frac{\partial^2 \phi}{\partial x^2} \right) \right) \right]$$

$$\cancel{\frac{\partial}{\partial t} (z_1 c_1 + z_2 c_2 + z_3 c_3)} \rightarrow 0$$

$$0 = \sum z_i D_i \frac{\partial^2 c_i}{\partial x^2} + \sum \left[\frac{z_i^2 F D_i}{RT} \frac{\partial c_i}{\partial x} \right] \frac{\partial \phi}{\partial x} + \sum \left[z_i^2 c_i \right] \frac{\partial^2 \phi}{\partial x^2}$$

$$0 = \left[\sum z_i D_i \frac{\partial^2 c_i}{\partial x^2} \right] + \left[\sum z_i^2 \frac{F D_i}{RT} \frac{\partial c_i}{\partial x} \right] \frac{\partial \phi}{\partial x} + \left[\sum \frac{z_i^2 F D_i c_i}{RT} \right] \frac{\partial^2 \phi}{\partial x^2}$$

Now, we use - Method of line



1, 2, 3 $\rightarrow$ nodes

You fix one variable and solve for the other variable, and then you move ahead.

For an i^{th} space node,

$$\frac{\partial c_i}{\partial t} = D_i \left(\frac{c_{k+1} + c_{k-1} - 2c_k}{\Delta x^2} \right) + z_i \frac{F D_i}{RT} \left(\frac{c_{k+1} - c_{k-1}}{2\Delta x} \right) \left(\frac{\phi_{k+1} - \phi_{k-1}}{2\Delta x} \right)$$

$$+ z_i \frac{F D_i}{RT} c_k \times \left(\frac{\phi_{k+1} - \phi_{k-1} - 2\phi_k}{\Delta x^2} \right)$$

$c_k = c_{i,k}$

i: species
k: node for iteration

Now discretizing the last eq'n

$$0 = \sum z_i D_i \left(\frac{c_{i,k+1} + c_{i,k-1} - 2c_{i,k}}{\Delta x^2} \right)$$

$$+ \left[\sum \frac{z_i^2 F D_i}{RT} \left(\frac{c_{i,k+1} - c_{i,k-1}}{2\Delta x} \right) \right] \left(\frac{\phi_{i,k+1} - \phi_{i,k-1}}{2\Delta x} \right)$$

$$+ \left[\sum \frac{z_i^2 F D_i}{RT} c_{i,k} \right] \left(\frac{\phi_{i,k+1} + \phi_{i,k-1} - 2\phi_{i,k}}{\Delta x^2} \right)$$

Now, we use a DAE solver to solve these equations

At $t=0$, let all concentrations be 0.
↓
zero-time sol'n.

Through zero-time sol'n, we get initial conditions.
Then we solve these on code.

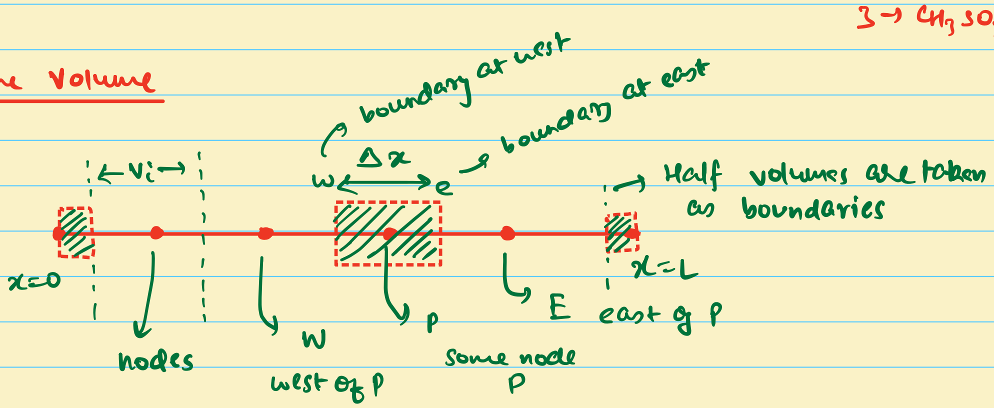
FINITE VOLUME TECHNIQUE FOR DISCRETIZATION OF PARTIAL DIFFERENTIAL EQUATION

$$\frac{\partial c_i}{\partial t} = D_i \frac{\partial^2 c_i}{\partial x^2} + \frac{z_i F D_i}{RT} \left[\frac{\partial c_i}{\partial x} \frac{\partial \phi}{\partial x} + c_i \frac{\partial^2 \phi}{\partial x^2} \right]$$

$$= D_i \frac{\partial^2 c_i}{\partial x^2} + \frac{\partial}{\partial x} \left[\frac{z_i F c_i D_i}{RT} \frac{\partial \phi}{\partial x} \right]$$

$1 \rightarrow Pb^{+2}$
$2 \rightarrow H^+$
$3 \rightarrow CH_3SO_3^-$

Finite Volume



$$\int_w^e \frac{\partial c_i}{\partial t}\,dx = \int_w^e D_i \frac{\partial^2 c_i}{\partial x^2}\,dx + \int_w^e \frac{\partial}{\partial x}\left[\frac{z_i c_i D_i}{RT}\frac{\partial \phi}{\partial x}\right]dx$$

Assuming c_i remain constant from $w \to e$ $= c_{i,p}$

$$\frac{\partial}{\partial t}\int_w^e c_i\,dx = \left[\frac{d}{dt} c_{i,p}\right]\Delta x \quad , \quad D_i\int_w^e \frac{\partial^2 c_i}{\partial x^2}\,dx = D_i\left[\frac{\partial c}{\partial x}\Big|_e - \frac{\partial c}{\partial x}\Big|_w\right]$$

$$\frac{z_i D_i c_i F}{RT}\int_w^e \frac{\partial \phi}{\partial x}\,dx = \frac{z_i D_i c_i F}{RT}\frac{\partial \phi}{\partial x}\Big|_e - \frac{z_i D_i c_i F}{RT}\frac{\partial \phi}{\partial x}\Big|_w$$

Hence,

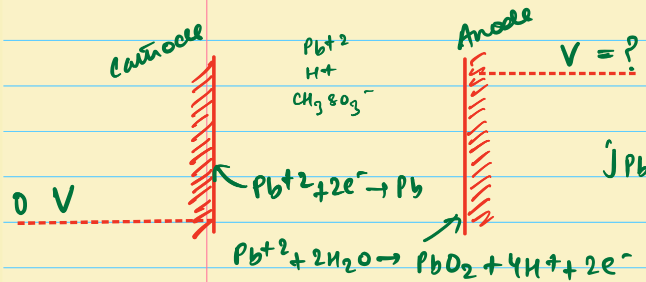
$\left[\frac{d}{dt} c_{ip}\right]\Delta x =$ Assuming all nodes are equally spaced.

$$\frac{\partial c_i}{\partial x}\Big|_e = \frac{c_{i,E} - c_{i,p}}{\Delta x} \qquad \frac{\partial c_i}{\partial x}\Big|_w = \frac{c_{i,p} - c_{i,w}}{\Delta x}$$

$$\frac{\partial \phi}{\partial x}\Big|_e = \frac{\phi_{i,E} - \phi_{i,p}}{\Delta x} \qquad \frac{\partial \phi}{\partial x}\Big|_w = \frac{\phi_{i,p} - \phi_{i,w}}{\Delta x}$$

Let, $c_{i,e} = \frac{c_{i,p} + c_{i,e}}{2}$, then for consistency, $c_{i,w} = \frac{c_{iw} + c_{i,p}}{2}$

For Boundary nodes, we review BC.



Reaction flux

$$j_{Pb} = 2F k_{Pb}\left(\frac{c_i}{c_i^\circ}\right)\left[\exp\left(\frac{F z_c}{2RT}\right) - \exp\left(-\frac{F z_c}{2RT}\right)\right]$$

$$j_{PbO_2} = 2F k_{PbO_2}\left(\frac{c_i}{c_0}\right)\left(\frac{c_2}{c_2^\circ}\right)\left[\exp\left(\frac{F z_a}{2RT}\right) - \exp\left(\frac{-F z_a}{2RT}\right)\right]$$

$$z_c = V_c - \phi - E_c$$
$$z_a = V_a - \phi - E_a$$

Now, we can write

$$-D_1 \frac{\partial c_1}{\partial x}\bigg|_p - \frac{z_1 c_1 D_1 F}{RT}\frac{\partial \phi}{\partial x}\bigg|_p = -\frac{j_{Pb}}{2F} \qquad \boxed{@\, x=0}$$

Pb is the boundary

$Pb \rightarrow Pb^{+2}$

Hence for B.C.

$$\left[\frac{d}{dt} c_{1,p}\right]\frac{\Delta x}{2} = D_1 \frac{\partial c}{\partial x}\bigg|_e + \frac{z_1 c_1 D_1}{RT}\frac{\partial \phi}{\partial x}\bigg|_e - D_1 \frac{\partial c}{\partial x}\bigg|_p$$

$$\frac{-j_{Pb}}{2F} \Leftarrow -\frac{z_1 c_1 D_1 F}{RT}$$