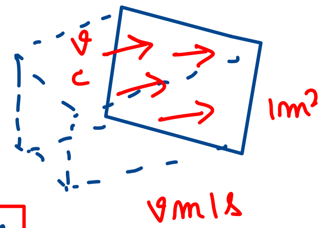
CAPE JC SIR

Partial Non linear integro differential Equation

$\boxed{\text{Flux} = \text{Velocity} \times \text{Density}}$



$\boxed{\text{Force} = -\text{ve gradient of potential}}$

$$\boxed{D_i = \frac{RT}{6\pi\mu R_s}}$$

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

↳ this is per mole
for per molecule
↳ R ⇒ k
↓
boltzmann's constant

Electric potential = ϕ

$$-z_i F \frac{d\phi}{dx} \rightarrow \text{Force}$$

↳ charge in 1 mole i.e. $N_A \times e$

$z_i \rightarrow$ valency of i^{th} ion

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

(u ↳ migration velocity)

We are considering two superimposed flux i.e. diffusive flux and flux due to electric potential difference

Flux = velocity × density

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

$$c_i u = -z_i c_i D_i \frac{F}{RT} \frac{d\phi}{dx} \rightarrow \text{migration flux}$$

$$\boxed{N_i = -D\frac{dc_i}{dx} - \frac{z_i c_i D_i F}{RT}\frac{d\phi}{dx}}$$

→ Total flux (superimposition)

Diffusion migration transport in a system . . . . .

Artjom V. Sokirko and Fritz H Bark BLAH...BLAH....

Assumptions

1) Steady 1D system
2) Potentiostatic electrolysis
3) Three ionic species
4) Species 1 and 2 are cations and 3 are anion
5) Only species 1 reacts at the electrode

1/11/22

generally we consider only diffusive flux but here since it is a electrical system we consider diffusive + migrating flux.

so,

$$N_i = -D_i \frac{dc_i}{dx} - z_i c_i \frac{D_i F}{RT} \frac{d\phi}{dx}$$

galvanostatic condition → constant current

i: current density C/m^2

Three species

c_1	c_2	c_3
+	+	−

(Reacting species: c_1)

[$z_1 z_2 z_3$ valences]

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

[Under steady state Net flux of 2,3 will be zero as they are not reacting]

↓

going to electrode, reacting and then gone

$$\left(-D_1 \frac{dc_1}{dx} - z_1 c_1 \frac{D_1 F}{RT} \frac{d\phi}{dx}\right) F z_1 = i$$

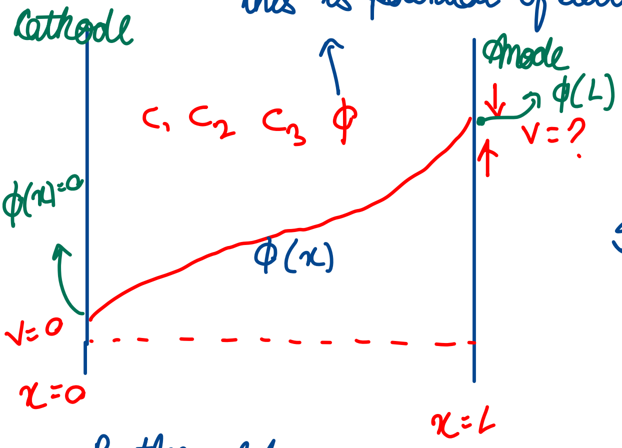
Local electron neutrality

$$\sum z_i c_i = 0$$

4 unknowns − c_1, c_2, c_3, ϕ

3 eqns, so we use local electron neutrality to get 1 more eqn

this is potential of electrolyte, but reaction is driven by the potential difference ($V=?$ & $V=0$)



If we change the voltage, reaction may change

Butler Volumer Kinetics

$\phi(0)$

$$i = i_0 \left\{ \exp\left(-\frac{\alpha z_1 F}{RT}\phi(0)\right) - \frac{c_1(0)}{c_1^0} \exp\left(\frac{(1-\alpha) z_1 F}{RT}\phi(0)\right) \right\} \quad \text{. Cathode}$$

conc. of c_1 at $x=0$

↳ reference conc.

↳ based on reversible rxn, combination of forward + backward reaction

$$i = i_0 \left\{ \frac{c_1(L)}{c_1^0} \exp\left(\frac{(1-\alpha) z_1 F}{RT}(\phi(L) - V)\right) - \exp\left(\frac{\alpha z_1 F}{RT}(V - \phi(L))\right) \right\} \quad \text{.. Anode.}$$

↳ At equilibrium, combination of forward + backward

→ Depends on potential difference

→ Valencies

Now we are considering lead-acid battery at unsteady state

↳ conc. will change wrt x & t

Reactions

-ve electrode

$$Pb^{+2} + 2e \underset{Disc.}{\overset{Ch}{\rightleftharpoons}} Pb$$

+ve electrode

$$Pb^{+2} + 2H_2O \underset{Disc.}{\overset{Ch}{\rightleftharpoons}} PbO_2 + 4H^+ + 2e$$

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

$$\frac{\partial C_i(x,t)}{\partial t} = -\frac{\partial N_i(x,t)}{\partial x} \rightarrow \text{Fick's second law}$$

Put

$$N_i = -D_i \frac{dc_i}{dx} - z_i c_i \frac{D_i F}{RT} \frac{d\phi}{dx} \rightarrow \text{From above}$$

$$\frac{\partial c_i}{\partial t} = D_i \frac{\partial^2 c_i}{\partial x^2} + \frac{z_i F D_i}{RT} \left(\frac{\partial c_i}{\partial x} \frac{\partial \phi}{\partial x} + c_i \frac{\partial^2 \phi}{\partial x^2} \right) \quad -①$$

$$\downarrow$$

$\Sigma z_i c_i = 0$

To get c_1 & c_2

Now to ϕ, we will multiply ① with z_i and sum

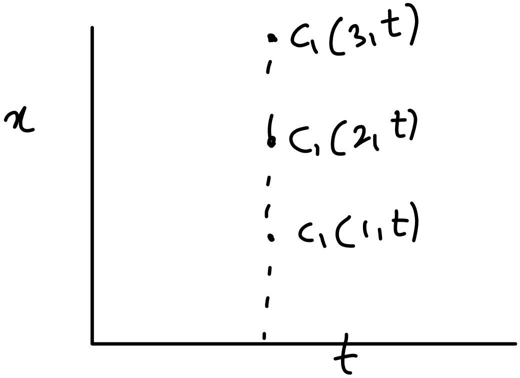
i.e.

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

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

↳ we have removed the transient term

Method of line



$$\frac{\partial c_1}{\partial t} = D_1 \frac{\partial^2 c_1}{\partial x^2} + \frac{z_1 F D_1}{RT}\left(\frac{\partial c_1}{\partial x} \frac{\partial \phi}{\partial x} + c_1 \frac{\partial^2 \phi}{\partial x^2} \right)$$

→ discretization for i^{th} space note

→ use central difference formula.

$$\frac{dc_{1,k}(t)}{dt}$$

↳ c_1 on k^{th} note

$$\frac{dc_{1,k}(t)}{dt} = D_1\left[\frac{c_{1,k+1} - 2c_{1,k} + c_{1,k-1}}{(\Delta x)^2}\right] + \frac{z_1 F D_1}{RT}\left[\frac{c_{1,k+1} - c_{1,k-1}}{2\Delta x} \times \frac{\phi_{k+1} - \phi_{k-1}}{2\Delta x} + c_{1,k}\cdot\frac{\phi_{k+1} - 2\phi_k + \phi_{k-1}}{(\Delta x)^2}\right]$$

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

↳ Now we need to discretize this involving ϕ

we get

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

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

→ once recheck not correct

we will get zero time solution. with $c_1 = c_2 = 0$, that potential we will get will be electrolytic potential (of electrolyte), now to get potentials of rods we will use Buttler Volmer Kinetics and use i wala equation, bcz in our problem statement we been given i ↳ to get $V(x)$

→ Basic laws

→ Discretization scheme for PDE → Fick's 1st law, 2nd law

→ Look at set of equations → Finite difference method

→ Accuracy

For exams → discretization scheme for closed system