15. Potential step

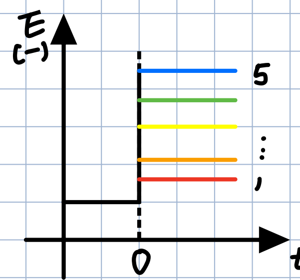
① Review

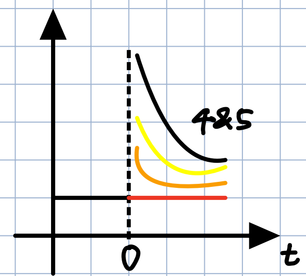
→ $J_i(x) = -D_i \frac{dC_i(x)}{dx} - \frac{z_i F}{RT} D_i C_i \frac{d\phi(x)}{dx}$ → In bulk solution & near the electrode

→ balance sheet problem

② Potential step 1: Faradaic current

→ electrochemical techniques
- potentiostat : potential control & current measure
  → ex) potential step ("chronoamperometry" & "chronocoulometry")
- galvanostat : current control & potential measure

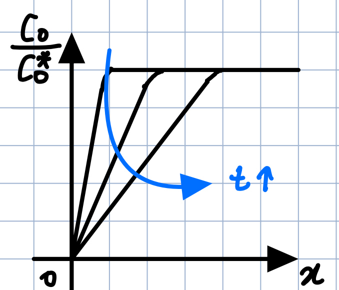
→ 



→ ① : O가 reduction하기에 부족한 potential

② & ③ : { surface concentration $\neq 0$; diffusion이 ④&⑤보다 적고, ∴ Faradaic current ↓ }

④ & ⑤ : { surface concentration $= 0$; mass transfer limiting (diffusion) }



→ 기울기 : diffusion에 비례 & 감소

→ Assumptions : ① C_O^* & C_R^* constant
② only diffusion (migration & convection ✗)
③ planar electrode (1D)

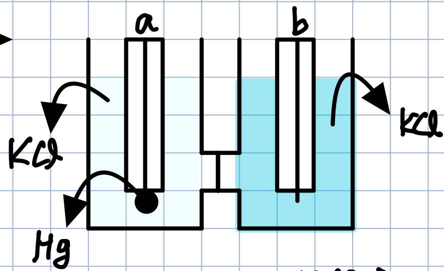
↳ from $\frac{\partial C_O}{\partial t} = D_O \nabla^2 C_O$, using Laplacian operator, PDE, boundary condition ($C_O(x,0) = C_O^*$ & $\lim_{x\to\infty} C_O(x,t) = C_O^*$ & $C_O(0,t) = 0$ $(t>0)$)

↳ Cottrell equation (i vs. t) : $i(t) = i_d(t) = \frac{nFAD_O^{1/2}C_O^*}{\pi^{1/2}t^{1/2}}$ & $Q(t) = \frac{2nFAD_O^{1/2}C_O^* t^{1/2}}{\pi^{1/2}}$

↳ Concentration vs. t : $C_O(x,t) = C_O^* \, \mathrm{erf}\left[\frac{x}{2(D_O t)^{1/2}}\right]$

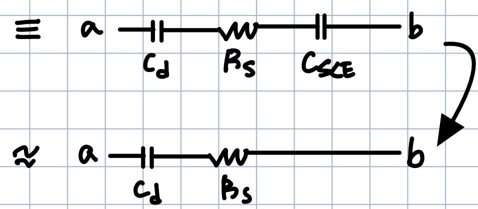
3 Potential step 2: non-Faradaic current

→ non-Faradaic current : "Electric double layer current"

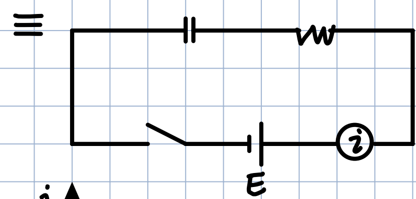
→ 

ideal polarized mercury drop electrode
(C로 가정)

SCE (RE)
($R_{ct}=0$)



$$C_T = \frac{C_d C_{SCE}}{\cancel{C_d}+C_{SCE}} \approx C_d \quad (\because C_{SCE} \gg C_d)$$

≡ 

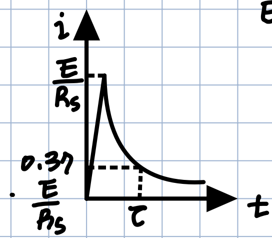
$$E = E_R + E_c = iR + \frac{q}{C_d}$$

$$\frac{dq}{dt}R + \frac{q}{C_d} = E$$

$$\therefore \frac{dq}{dt} = -\frac{q}{RC_d} + \frac{E}{R}$$

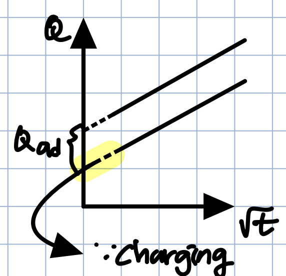
→ $q = EC_d(1-e^{-t/RC_d})$

$i_c = \frac{E}{R}e^{-t/RC_d} \quad (\tau = RC_d)$



4 Anson plot

→ $$Q_t = \int_0^t i_f\,dt + \int_0^t i_c\,dt = \frac{2nFAD_0^{1/2}C_0^*}{\pi^{1/2}}\sqrt{t} + Q_{dl}$$



: 만약 species가 electrode에 흡착되면, two Faradaic current flow

$$Q_t = \frac{2nFAD_0^{1/2}C_0^*}{\pi^{1/2}}\sqrt{t} + Q_{dl} + Q_{ad}$$