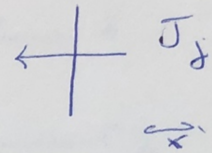
2/10/06

Fick's Laws

#1



$$J_j\ (\text{mol s}^{-1}\,\text{cm}^{-2}) = -D_j \frac{\partial C_j}{\partial x}$$

D_j is the diffusion constant $(\text{cm}^2\,\text{s}^{-1})$

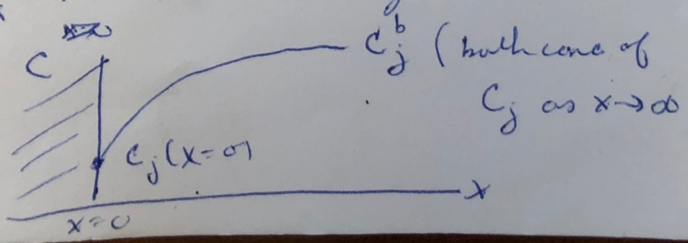
C_j = Conc. of species j.

If the surface e^- transfer rxn is very fast, then the current is just related to the flux of electroactive species across the surface of the electrode:

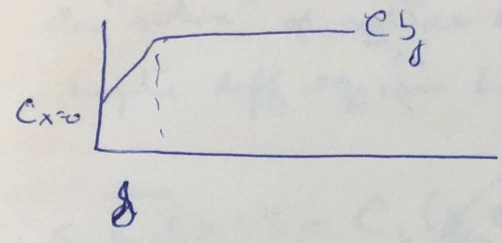
$$i(t) = -nFA\, J_j(x=0)$$

$$= nFA\, D_j \frac{\partial C_j}{\partial x}\bigg|_{x=0}$$

$\frac{\partial C}{\partial x}$ is the concentration gradient



If we assume the conc gradient is linear, we can define a depletion layer distance δ



$$\left.\frac{dC_j}{dx}\right|_{x=0} = \frac{C_j^b - C_j(x=0)}{\delta}$$

$$i = nFAD_j \frac{(C_j^b - C_j(x=0))}{\delta}$$

if $C_j(x=0)$, that's the max. gradient & ∴ maximum current observable — "diffusion limited current":

$$i_l = \frac{nFAD_j C_j^b}{\delta} = nFAm_j C_j^b$$

$m_j = D_j/\delta$. mass transfer coefficient

#2

$$= -\frac{\partial J_j}{\partial x}$$

$$\frac{\partial C_j(x,t)}{\partial t} = D_j \frac{\partial^2 C_j(x,t)}{\partial x^2}$$

Can "solve" or reduce this to a simple diff eq. w/ L.T. in time.

$$s\,\overline{C_j}(x,s) - C_j(\cancel{x}, t=0) \xrightarrow{} C_j^b \text{ for all } x.$$

$$= D_j \frac{\partial^2 \overline{C_j}(x,s)}{\partial x^2}$$

$$\boxed{\frac{\partial^2 \overline{C}_j}{\partial x^2} - \frac{s}{D_j}\overline{C}_j + \frac{C_j^b}{D_j} = 0}$$

Solution of this eqn for diff. limited case. potl step.

$$\overline{C}_j(x,s) = \frac{C_j^b}{s} - \frac{C_j^b}{s}\exp\left(-\sqrt{\frac{s}{D_j}}\,x\right)$$

In general

$$\overline{C}_j(x,s) = \frac{C_j^b}{s} + A(s)\, e^{-\sqrt{\frac{s}{D}}\,x}$$

The current can be obtained in LaPlace space & then inverse transformed:

$$\lim_{x\to\infty} \bar{C}_j = \frac{C_j^b}{s}$$

$$\bar{C}_j(0,s) = 0 \quad s \neq 0$$

$$i(s) = nFAD_j \left. \frac{\partial \bar{C}}{\partial x} \right|_{x=0}$$

$$i(s) = -\frac{A(s)\cdot\sqrt{s}}{\sqrt{D_j}} \cdot nFAD_j$$

If $A(s) = \dfrac{-C_j^b}{s}$,

$$i(s) = \frac{C_j^b \cdot nFAD_j^{1/2}}{\sqrt{s}}$$

$\downarrow LT^{-1}$

$$i_d(t) \propto \frac{1}{\pi t^{1/2}} \quad \text{Cottrell Eqn.}$$

Nernstian Behavior $\quad O + ne \rightleftarrows R$

$$\Theta = \exp\left(nF(E - E^{0\prime})/RT\right)$$

$$i(t) = \frac{i_d(t)}{1 + \xi\Theta} \qquad \xi = \sqrt{\frac{D_O}{D_R}}$$

$$A(s) = \frac{-C_O^b}{s(1+\xi\Theta)}$$

B-V potl step

$$A(s) = \frac{-k_f}{\sqrt{D_O}} \frac{C_O^b}{s(s^{1/2}+H)}$$

$$H = \frac{k_f}{\sqrt{D_O}} + \frac{k_b}{\sqrt{D_R}}$$

$$i(s) = \frac{nFA\, k_f\, C_O^b}{s^{1/2}(H + s^{1/2})}$$

$$i(t) = nFA\, k_f\, C_O^b \exp(H^2 t)\, \cancel{\mathrm{erfc}\,(Ht^{1/2})}$$

$i(t=0)$

$= nFA\, k_f\, C_O^b$