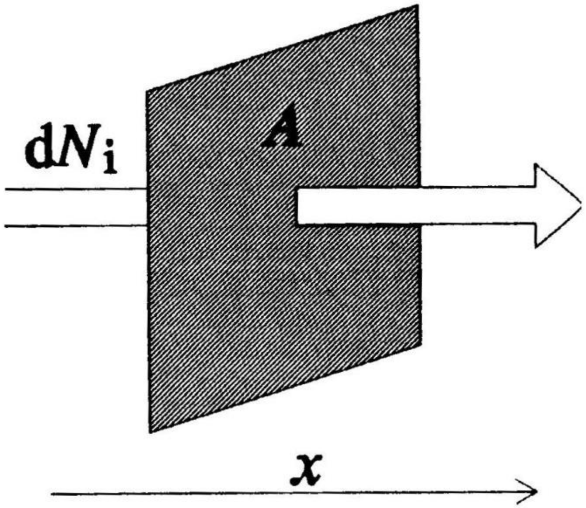
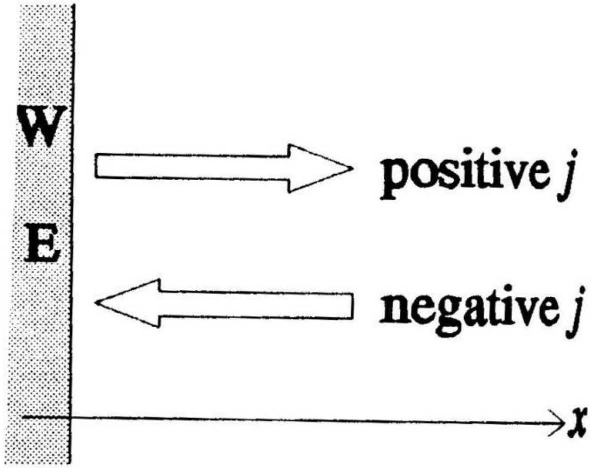
Electrochemical Engineering
Chapter 5: Mass Transport

黃 炳 照 (Bing Joe Hwang)
bjh@mail.ntust.edu.tw
NTUST

Flux density





Total flux of solute i, J_i

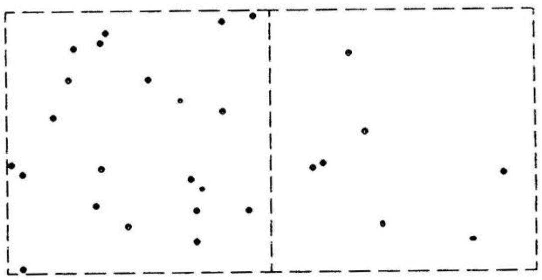
$$J_i = dN_i/dt$$

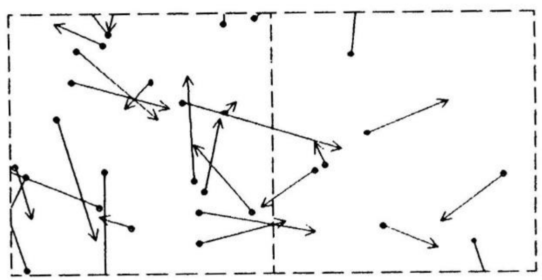
Flux density of solute i, j_i

$$j_i = (1/A)dN_i/dt$$

Transport mechanisms

Transport	Occurs in response to
migration	a gradient of electrical potential
diffusion	a gradient of activity or concentration
convection	a gradient of pressure





Migration ~ $\nabla\Phi$

Diffusion ~ ∇C

Convection ~ ∇P

Brownian motion,

$$\Delta G = \Delta H - T\Delta S$$

Electrochemical potential

$$\mu_i = RT\ln a_i + z_i F\Phi$$

Flux equations

The flux density equation,

$$j_i = -(C_iD_i/RT)\nabla\mu_i + C_iv$$

$$= -(C_iD_i/RT)(RT\nabla(\ln a_i) + z_iF\nabla\Phi) + C_iv$$

Nernst-Planck equation, (assume $a_i \sim C_i$)

$$j_i = -(C_iD_i/RT)(RT\nabla\ln C_i + z_iF\nabla\Phi) + C_iv$$

$$= -D_i\nabla C_i - (z_iFD_iC_i/RT)\nabla\Phi + C_iv$$

$$= -D_i\nabla C_i - (z_iu_iC_i/|z_i|)\nabla\Phi + C_iv$$

General Mass Transfer Equation

$$J_j = -D_j \nabla C_j - \frac{z_j F}{RT} D_j C_j \nabla \phi + C_j \cdot v$$

Diffusion Migration Convection

No mixing (flow)

$$J_j = -D_j \nabla C_j - \frac{z_j F}{RT} D_j C_j \nabla \phi$$

solution : electroactive species

electrolyte

Migration

$$u_j = \frac{|z_j| F D_j}{RT}$$

One-dimension eq.

flux

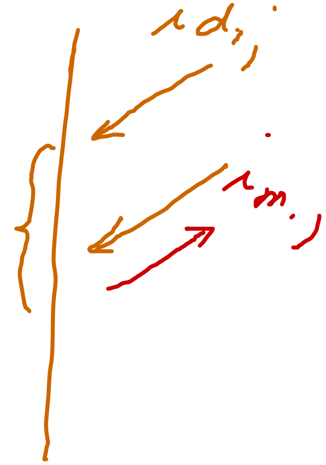
$$J_j(x) = -D_j \left(\frac{\partial C_j(x)}{\partial x} \right) - \frac{z_j F}{RT} D_j C_j \frac{\partial \phi(x)}{\partial x}$$

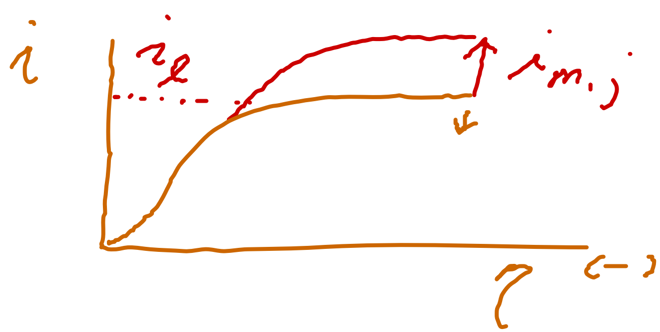
↓

Current

$$\frac{i_j}{z_j F A} = \frac{i_{d,j}}{z_j F A} + \frac{i_{m,j}}{z_j F A}$$

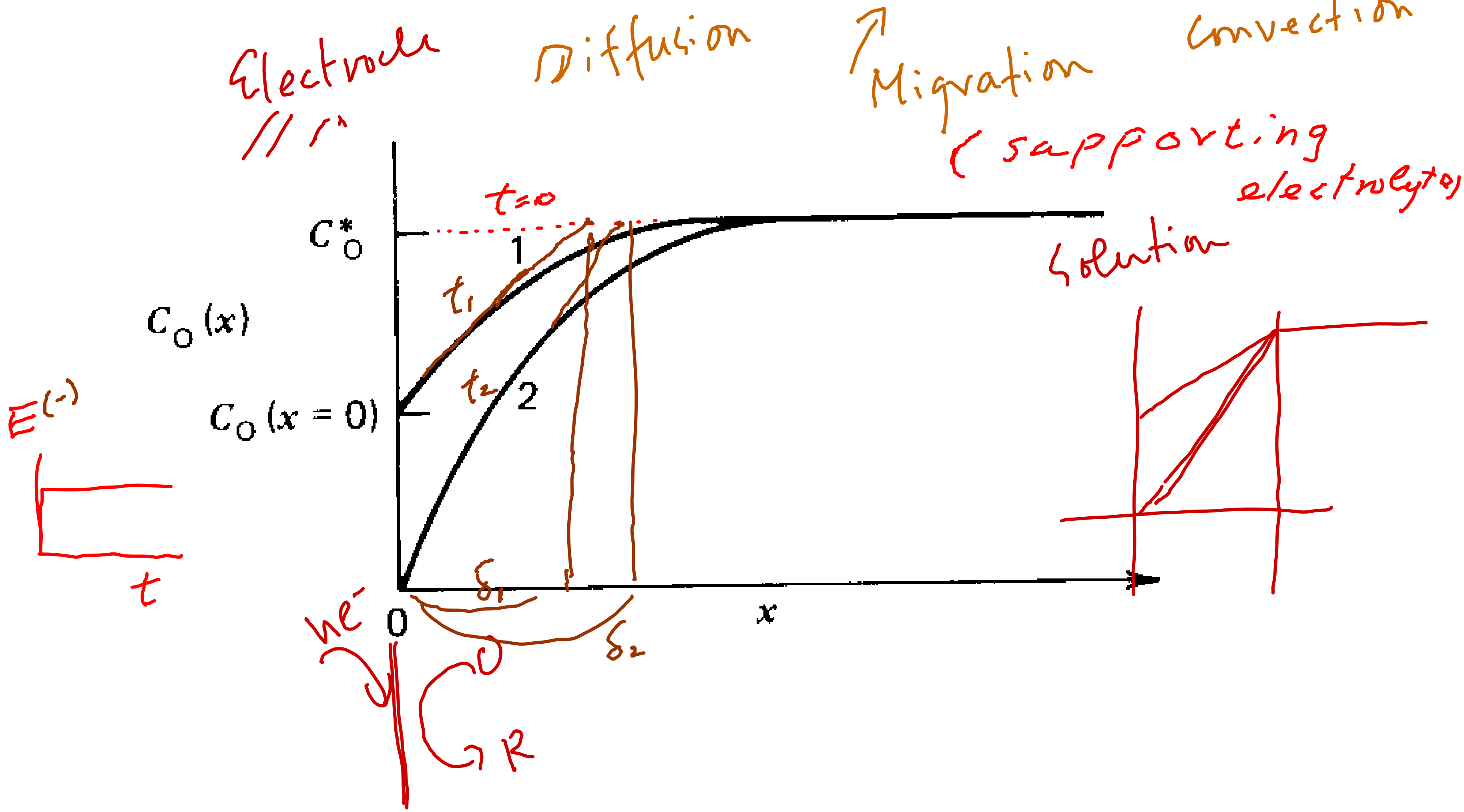
$$i_j = i_{d,j} + i_{m,j}$$

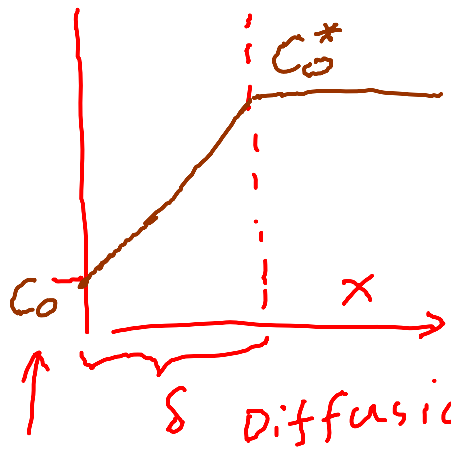




Concentration profiles

$$j_i(x) = -D \frac{\partial C_i}{\partial x} - \frac{z_i F}{RT} D_i \frac{\partial \phi}{\partial x} + C_i v(x)$$





Diffusion layer thickness

$C_o(x=0)$

$$\frac{mol}{cm^2 \cdot s} \quad j_o = +D_o \frac{C_o^* - C_o}{\delta_o}$$

$$= m_o (C_o^* - C_o)$$

↑ mass transfer coeff.

$$m_o = \frac{D_o}{\delta_o}$$

$$O + ne = R$$

Current i

Amp

Current density

i/A

$$(C/s) \quad i = j_o \cdot nF \cdot A$$

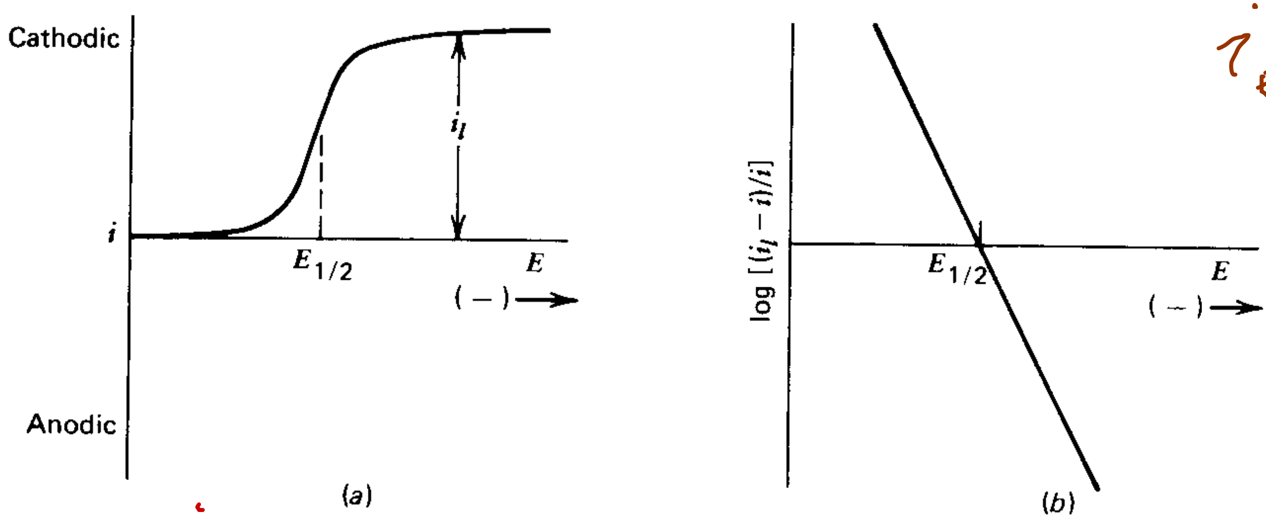
$$\frac{i}{nFA} = j_o$$

Current density

$$\frac{i}{A}$$

Amp/cm^2

Current-potential curve for a nernstian reaction involving two soluble species with only oxidant present initially



i_l : limiting current

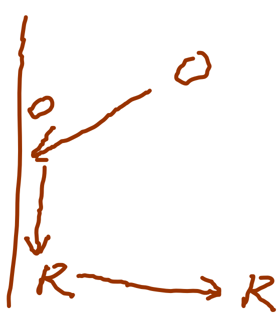
$i\ (+)$: cathodic current

Reduction

$(-)$ Anodic current

$$\frac{i}{nFA} = m_O\left(C_O^* - C_O\right)$$

$$\frac{i}{nFA} = m_R\left(C_R - C_R^*\right)$$



if $C_O \to 0$

r.d.s mass transfer

$$\frac{i_l}{nFA} = m_O C_O^*$$

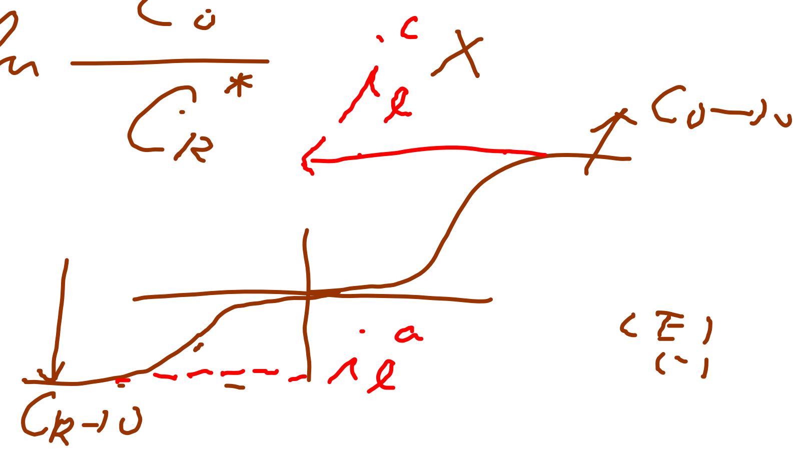
$$i_l^c = nFm_OC_O^* \quad (C_O \to 0)$$

$$i_l^a = -nFm_RC_R^* \quad (C_R \to 0)$$

Nernstian reaction $\quad O + ne \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R$

$$E = E^{0'} + \frac{RT}{nF}\ln\frac{C_O(x=0)}{C_R(x=0)}$$

$$E = E^{0'} + \frac{RT}{nF}\ln\frac{C_O^*}{C_R^*}$$



$$i = nFA\, m_O \left(C_O^* - C_O \right)$$

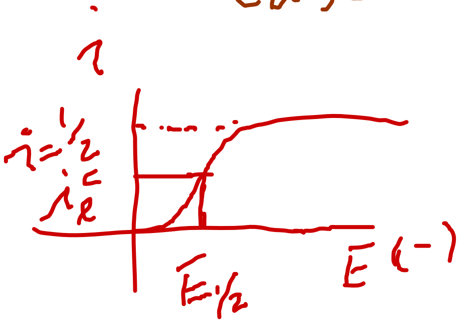
$$i_l^c = nFA\, m_O\, C_O^* \Rightarrow C_O^* = \frac{i_l^c}{nFA\, m_O}$$

$$\frac{i}{i_l^c} = 1 - \frac{C_O}{C_O^*} \Rightarrow C_O = C_O^* \left(1 - \frac{i}{i_l^c} \right)$$

$$\left. \begin{aligned} i &= +nFA\, m_R \left(C_R - C_R^* \right) \\ i_l^a &= -nFA\, m_R\, C_R^* \end{aligned} \right\} C_R = C_R^* \left(1 - \frac{i}{i_l^a} \right)$$

$$\frac{i}{i_l^a} = 1 - \frac{C_R}{C_R^*}$$

Case a: $C_R^* = 0 \qquad C_O^*$



$$i = nFA\, m_R (C_R - 0) = nFA\, m_R C_R$$

$$E = E^{0'} + \frac{RT}{nF} \ln \frac{C_O}{C_R}$$

$$= E^{0'} + \frac{RT}{nF} \ln \frac{C_O^* \left(1 - \frac{i}{i_l^c}\right)}{\frac{i}{nFAm_R}}$$

formal potential

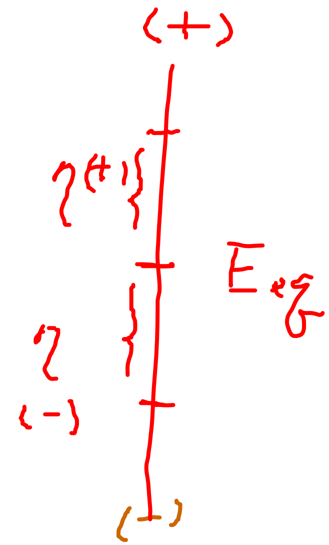
$$= \left(E^{0'} + \frac{RT}{nF} \ln \frac{m_R}{m_O} \right) + \frac{RT}{nF} \ln \frac{i_l^c - i}{i}$$

if $i = \frac{1}{2} i_l^c \Rightarrow E_{1/2}$

Driving force

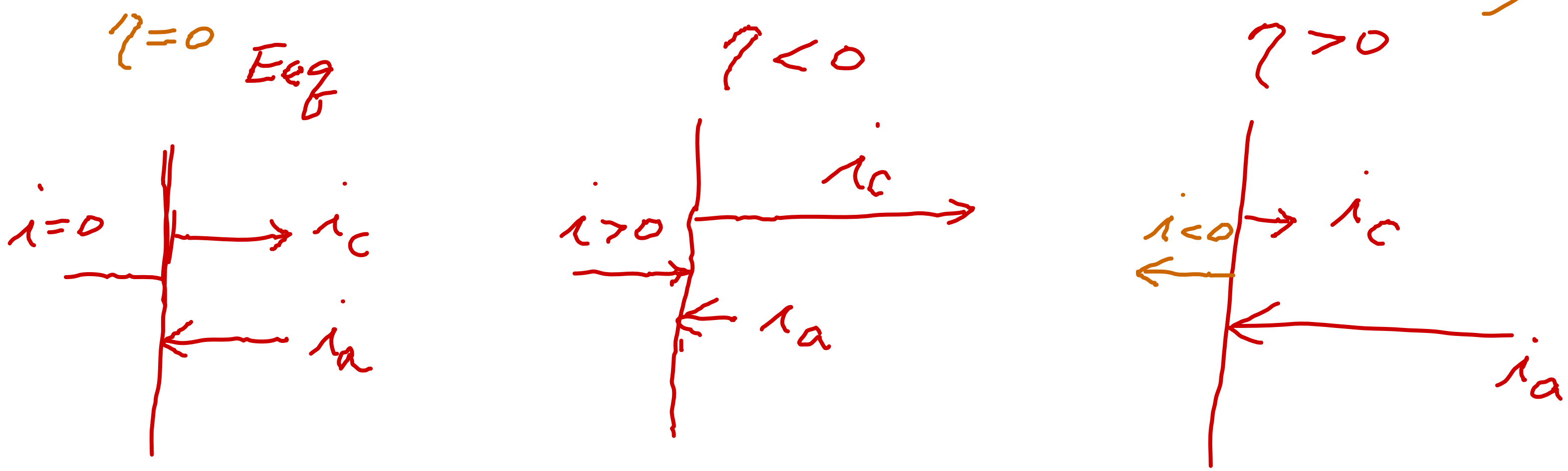
$$\eta = E - E_{eq}$$

overpotential



i-E curve

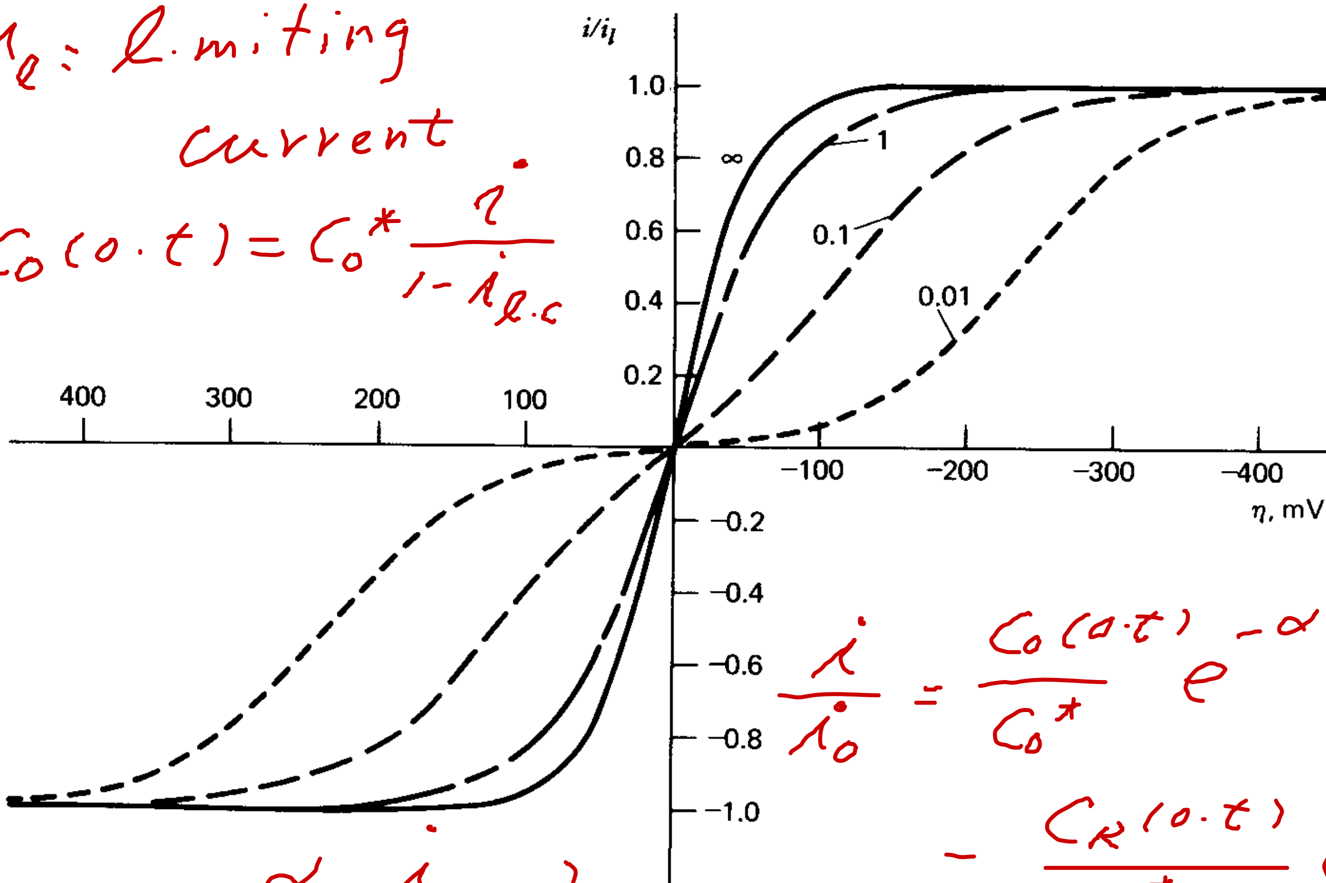
$$i = i_0 \left[\frac{C_O(0,t)}{C_O^*} e^{-\alpha f \eta} - \frac{C_R(0,t)}{C_R^*} e^{(1-\alpha) f \eta} \right]$$



Effect of mass transfer

i_l: limiting current

$$C_O(0,t) = C_O^* \frac{i}{1 - i_{l,c}}$$



$$\frac{i}{i_0} = \frac{C_O(0,t)}{C_O^*} e^{-\alpha f \eta} - \frac{C_R(0,t)}{C_R^*} e^{(1-\alpha) f \eta}$$

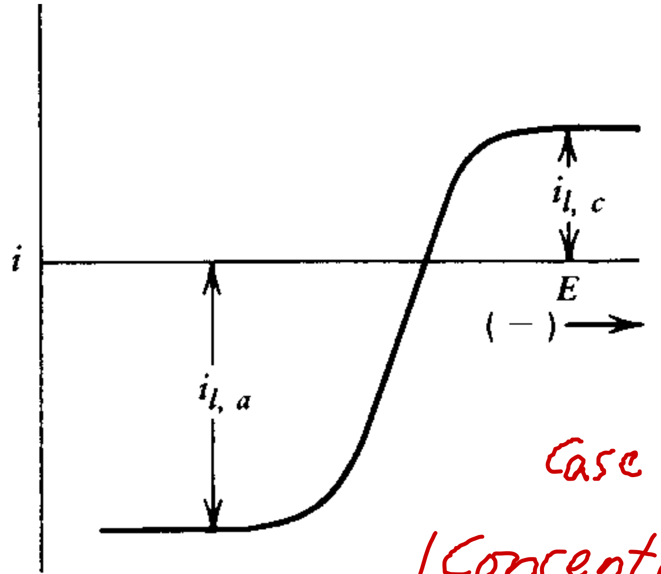
α, i_0

$i_{l,c}$ $i_{l,a}$

δ ← ↓ m_O ↓ m_R

$$\frac{i}{i_0} = \left(1 - \frac{i}{i_{l,c}}\right) e^{-\alpha f \eta} - \left(1 - \frac{i}{i_{l,a}}\right) e^{(1-\alpha) f \eta}$$

Current-potential curve for a nernstian reaction involving two soluble species with both forms initially present



Overpotential

$\eta(i) = E - E_{eq}$

Case (c) R insoluble

η_{conc} η_{mt} (Concentration overpotential) $Cu^{+} + ze = Cu$

$O + ze = R$ $a_R = 1$

$E_{eq} = E^{0'} + \frac{RT}{nF} \ln C_O^*$ Nernstian eq

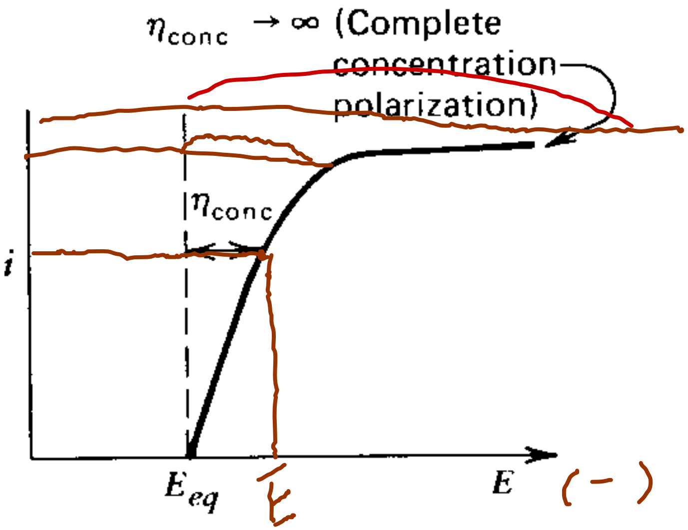
$E = E^{0'} + \frac{RT}{nF} \ln C_O$

$\frac{RT}{RT} \ln \frac{i_l^c - i}{i_l^c}$

$= E^{0'} + \frac{RT}{nF} C_O^* + \frac{RT}{nF} \ln\left(1 - \frac{i}{i_l^c}\right)$

$\eta = E - E_{eq} =$

Current-potential curve for a nernstian system where the reduced form is insoluble



$$\eta_{conc} = \frac{RT}{nF} \ln \frac{i_l^c - i}{i_l^c}$$

η small ↓

$$1 - \frac{i}{i_l^c} = \exp\left(\frac{nF}{RT}\eta_{conc}\right)$$

$$\eta_{conc} = -\frac{RT i}{nF i_l^c}$$

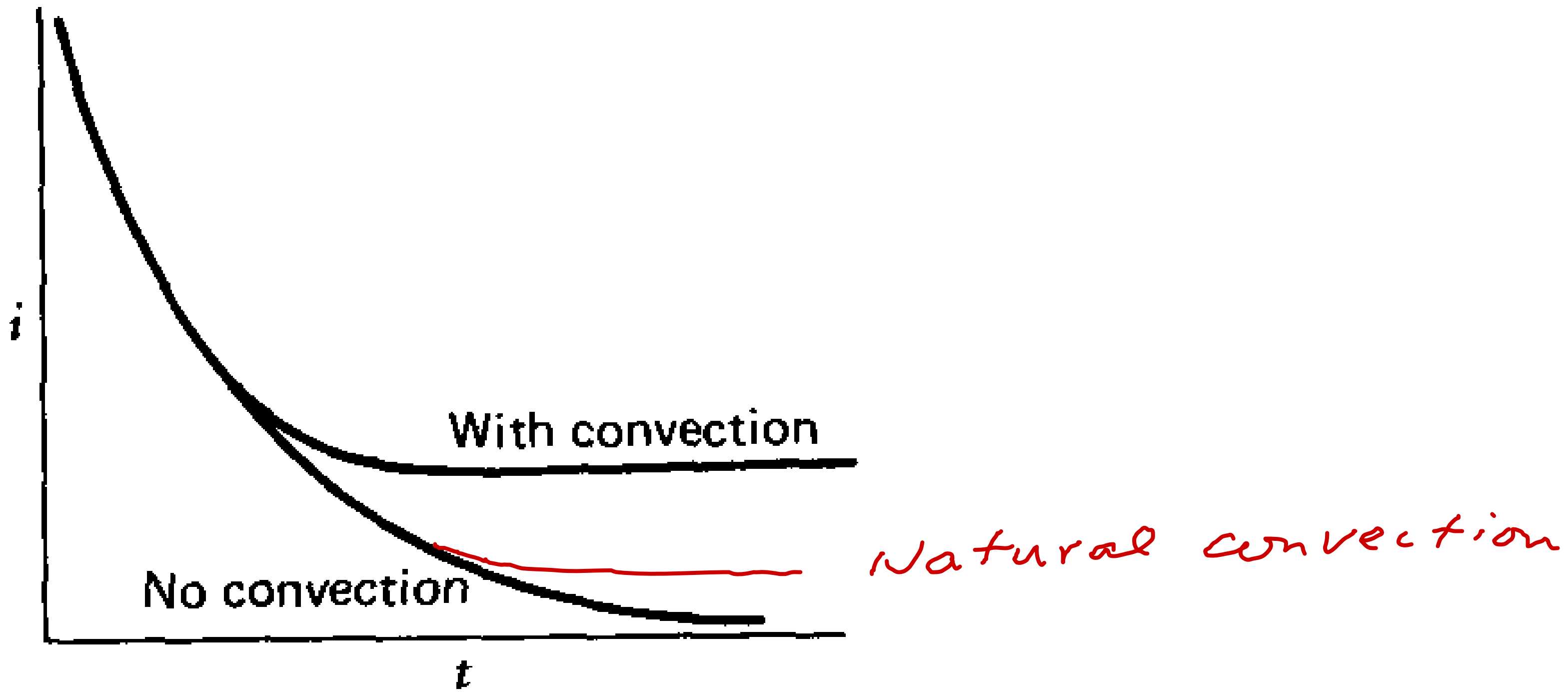
$$R_{mt} = \frac{|\eta_{conc}|}{i} = \frac{RT}{nF|i_l^c|}$$

$$\eta_{conc} = E - E_{eq}$$

(−) cathodic

(+) Anodic

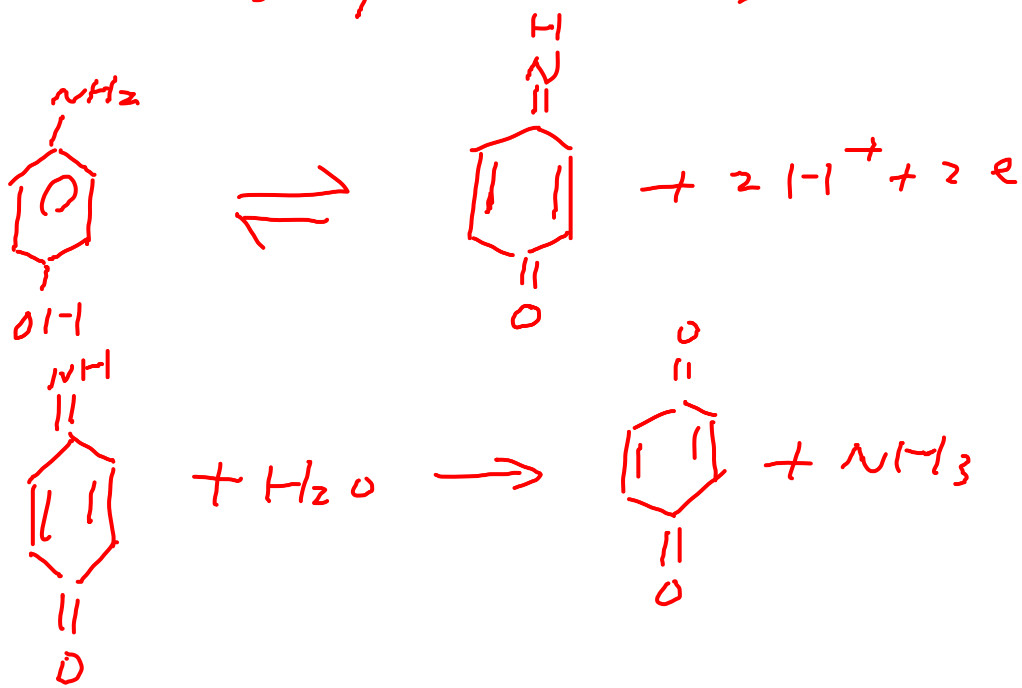
Current-time transient for a potential step



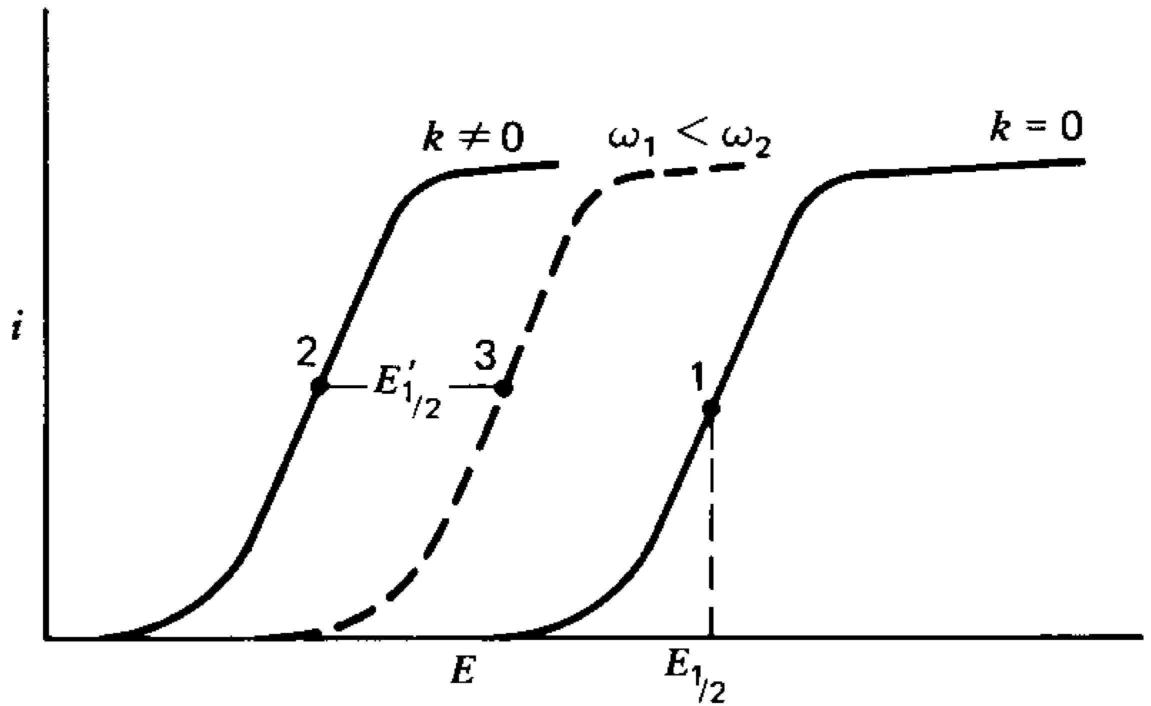
Coupled Irreversible Chemical rxns

$$O + ne = R \quad (E)$$

$$R \xrightarrow{k} T \quad (C)$$



Effect of an irreversible following homogeneous chemical reaction on nernstian i-E curves at a RDE



10.25 (四)

10.26 (五)

Assignments

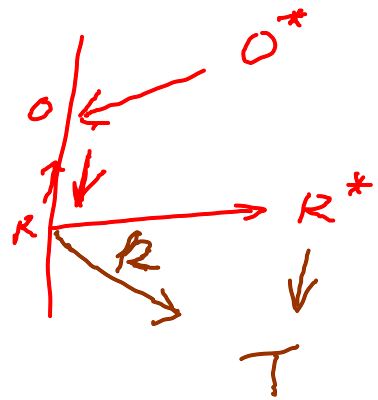
1.2

1.8

1.12

$C_R^* = 0)$

$$\frac{i}{nFA} = m_O\left[C_O^* - C_O\right] = m_R C_R + \mu k\, C_R$$



Nernstian rxn

$$E = E^{0'} + \frac{RT}{nF} \ln \frac{C_O}{C_R}$$

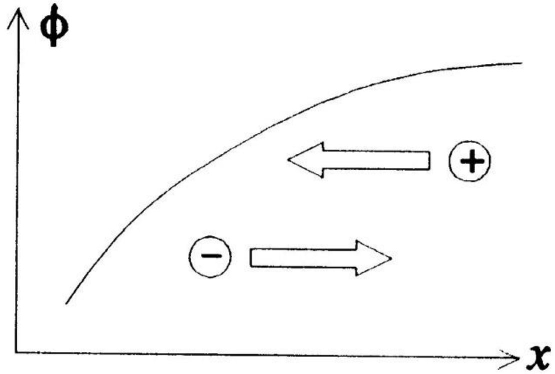
$$C_O = \frac{i_l^c - i}{nFA\, m_O}$$

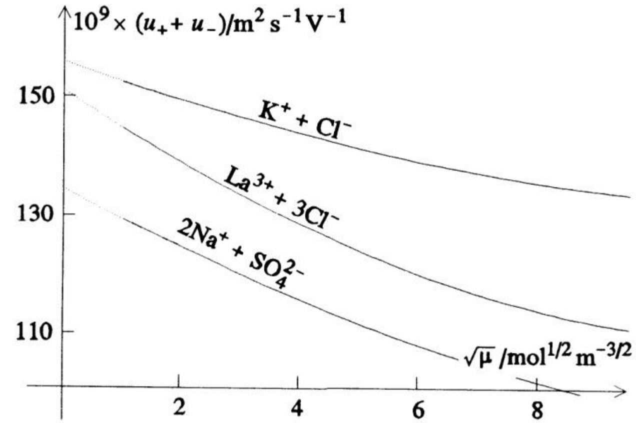
$$C_R = \frac{i}{(m_R + \mu k)\, nFA}$$

$$E = E^{0'} + \frac{RT}{nF} \ln \frac{m_R + \mu k}{m_O} + \frac{RT}{nF} \ln \frac{i_l^c - i}{i}$$

$E_{1/2}$

Law of migration





Kohlrausch limiting law (in sufficiently dilute solution)

$$u_i = u_i^o - \text{constant}\ (\mu)^{1/2}$$

where is μ the ionic strength of solution.

$$\mu = (1/2)\sum z_i^2 C_i$$

Onsager theory

Onsager theory for the constant,

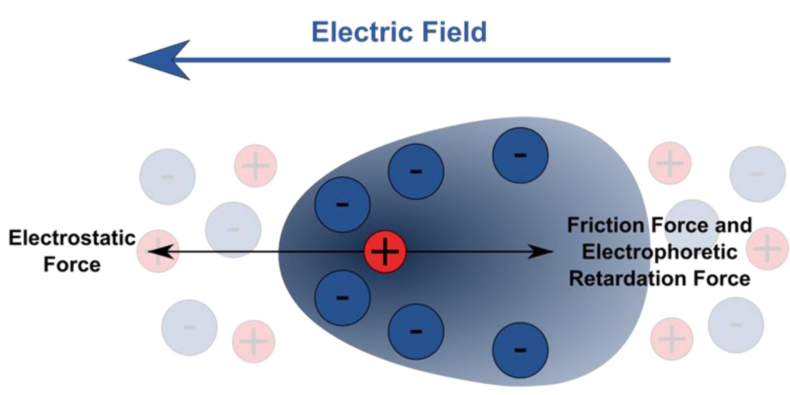
Electrophoretic effect: Electrostatic drag that an anion going in one direction has on a cation heading in the opposite direction.

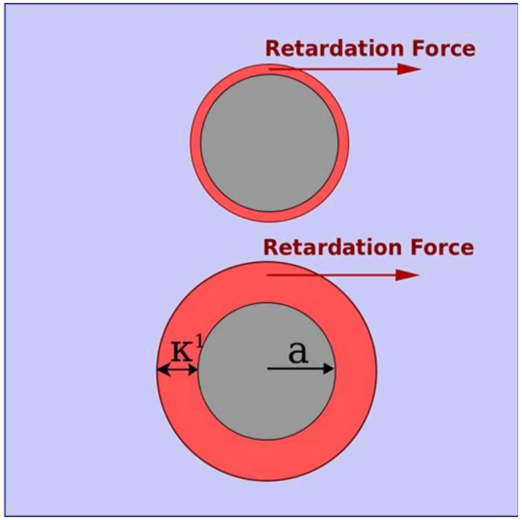
Relaxation effect: Spatial offset between a moving ion and its accompanying ionic atmosphere.

Onsager limiting law for a binary electrolyte

$$(u_i/u_i^0) \quad = 1 \quad - \quad [(39.4\text{x}10^{-9} m^2 V^{-1} s^{-1} |z_i|)/\ u_i^0 \quad - \quad (z_i z_j h/(1+h^{1/2}))(\ \mu/1567 \text{ mol } m^{-3})^{1/2}$$

Mobility coff. **Electrophoretic term** **Relaxation term**





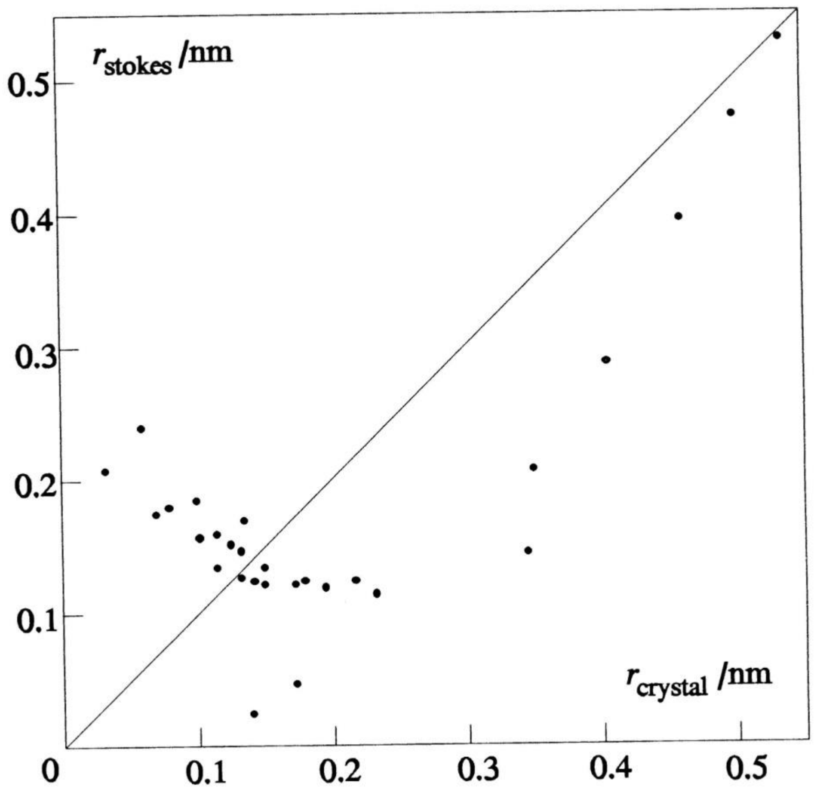
Stokes' law

Stokes' law

$$|z_i|\, e\, \Xi = 6\pi\eta r_i v_i$$

$$u_i = v_i/\Xi = |z_i|\, e/6\pi\eta r_i$$

$$r_{stokes} = |z_i|\, e/6\pi\eta\, u_i^0$$



Grothuss or Vehicle mechanism

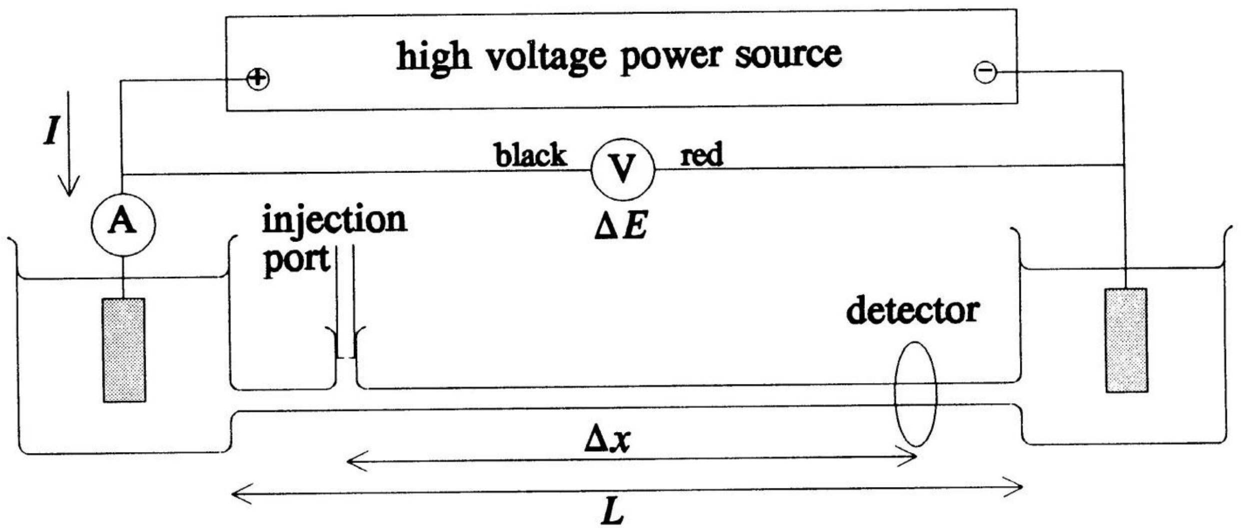
Hopping mechanism

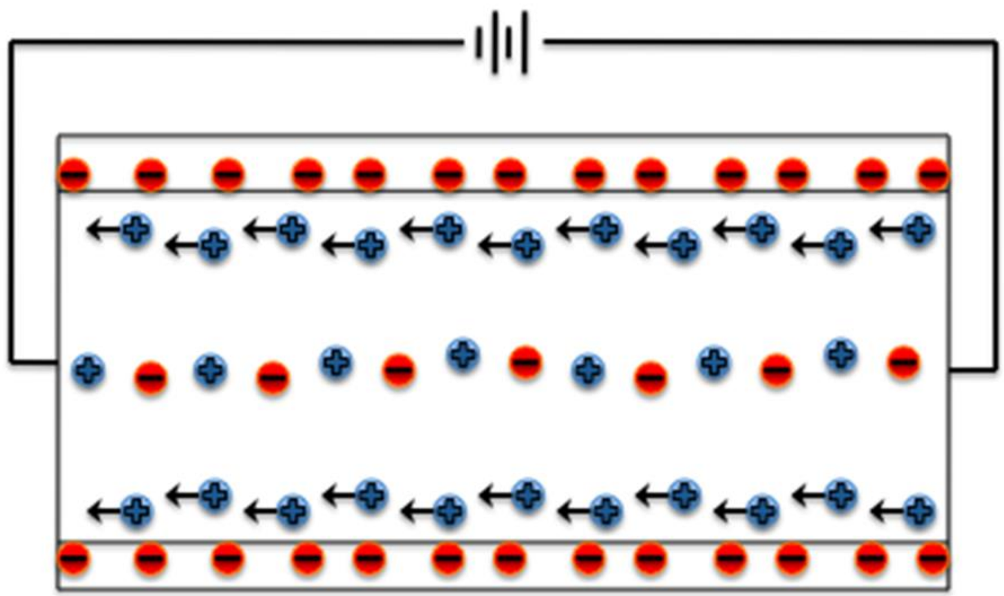
Hydrogen ions - Hydronium ion

Hydroxide ions

Electrophoresis

7 Transport



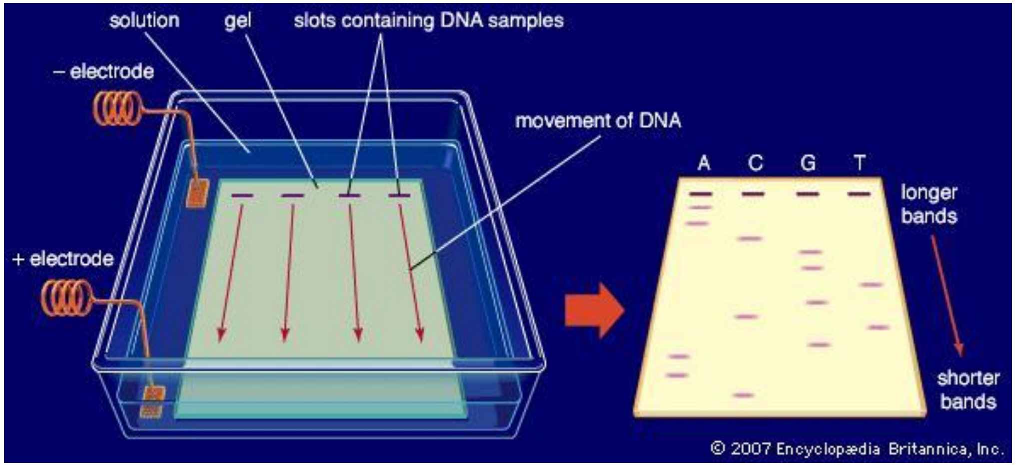


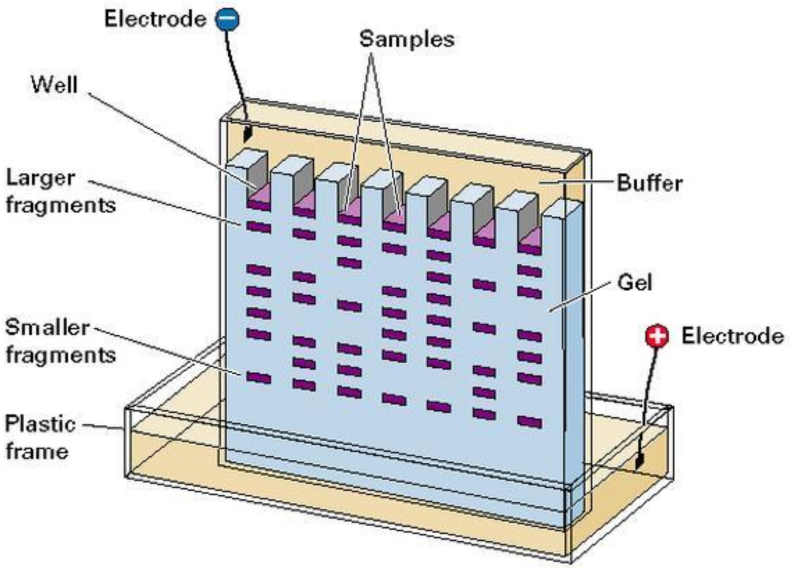
Electrophoresis

$$u_i = v_i/\Xi = \Delta x/\Xi\Delta t_i$$

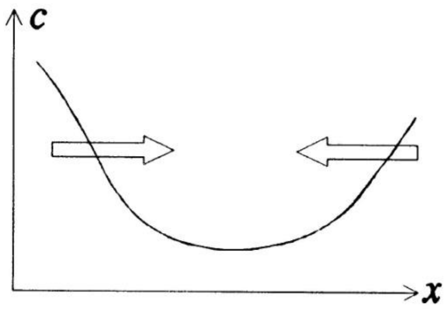
Electroosmosis ~ solution flow

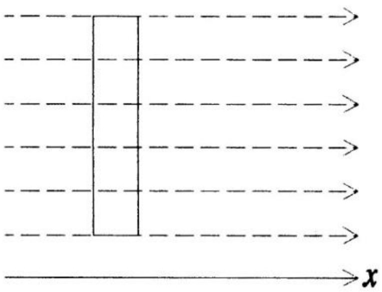
Separation of DNA samples

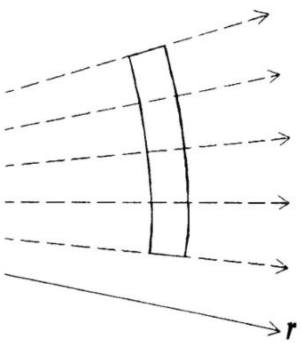




Law of diffusion







Fick's 2nd law for planar diffusion

$$\partial C/\partial t \quad = \quad D\, \partial^2 C/\partial x^2$$

Fick's 2nd law for sperical diffusion

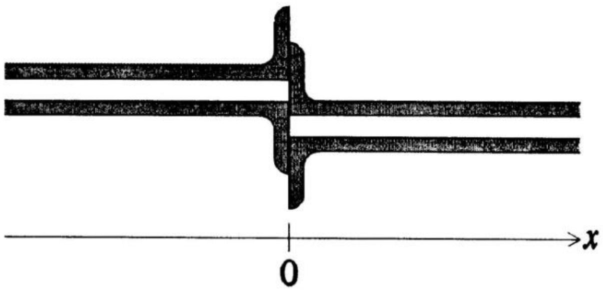
$$\partial C/\partial t \quad = \quad D\, \partial^2 C/\partial r^2 \quad + \quad (2D/r)\, \partial C/\partial r$$

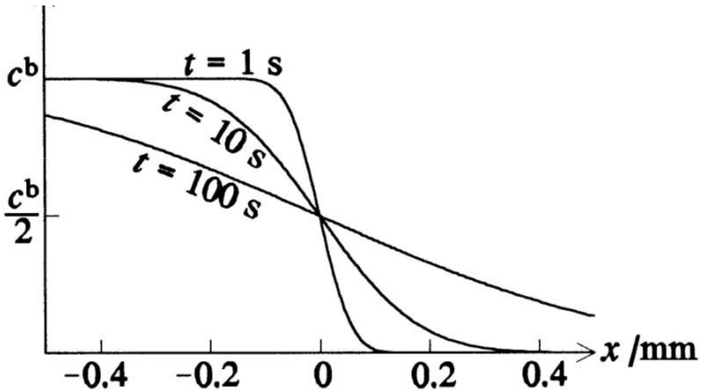
Diffusivity of species

Values of the diffusivity of species in various media at 25°C

Diffusant	$D/m^2\ s^{-1}$	Medium
H_2O	2.44×10^{-9}	H_2O
$O_2(aq)$	2.26×10^{-9}	H_2O
$Cd^{2+}(aq)$	0.690×10^{-9}	0.1 M KNO_3
	0.715×10^{-9}	0.1 M KCl
	0.681×10^{-9}	1.0 M KCl
$Zn^{2+}(aq)$	0.638×10^{-9}	0.1 M KNO_3
	0.620×10^{-9}	1.0 M KNO_3
	0.654×10^{-9}	0.1 M NaOH
$Pb^{2+}(aq)$	0.828×10^{-9}	0.1 M KNO_3
	0.867×10^{-9}	0.1 M KCl
$IO_3^-(aq)$	1.015×10^{-9}	0.1 M KCl
	0.989×10^{-9}	1.0 M KCl
$Fe(CN)_6^{4-}(aq)$	0.650×10^{-9}	0.1 M KCl
ascorbic acid(aq)	1.027×10^{-9}	0.1 M NaCl
Cd(amal)	1.66×10^{-9}	Hg
Zn(amal)	1.89×10^{-9}	Hg
Pb(amal)	1.41×10^{-9}	Hg

Diffusion experiments

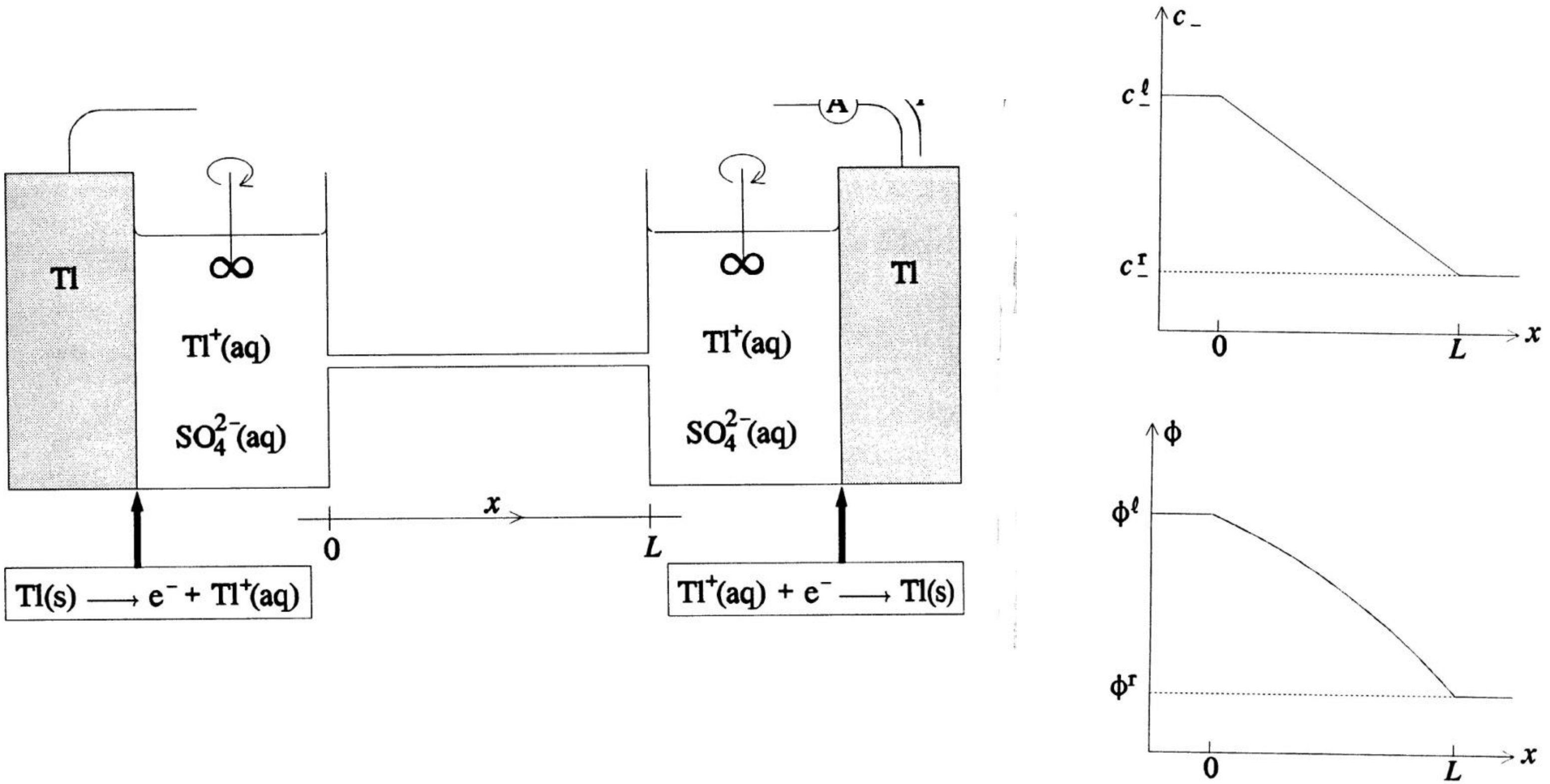




Diffusion experiments

$$C = (C^b/2)\text{erfc}\{x/(2(Dt)^{1/2})\}$$

Nernst-Einstein law



Nernst-Einstein law

Electroneutrality

$z_+C_+ = z_-C_-$

Nernst-Einstein law

$0 = j_-^{diff} + j_-^{mig} = -D_-dC_-/dx - z_-/|z_i|u_-C_-d\Phi/dx$

$|z_i|D_-\ln(C_-^r/C_-^l) = -z_-u_-(\Phi^r - \Phi^l)$

$a_-^r/a_-^l = \exp\{(-z_-u_-/|z_i|D_-)(\Phi^r - \Phi^l)\}$

Anion must be unifrom throughout the cell,

$a_-^r/a_-^l = \exp\{(-z_-F/RT)(\Phi^r - \Phi^l)\}$

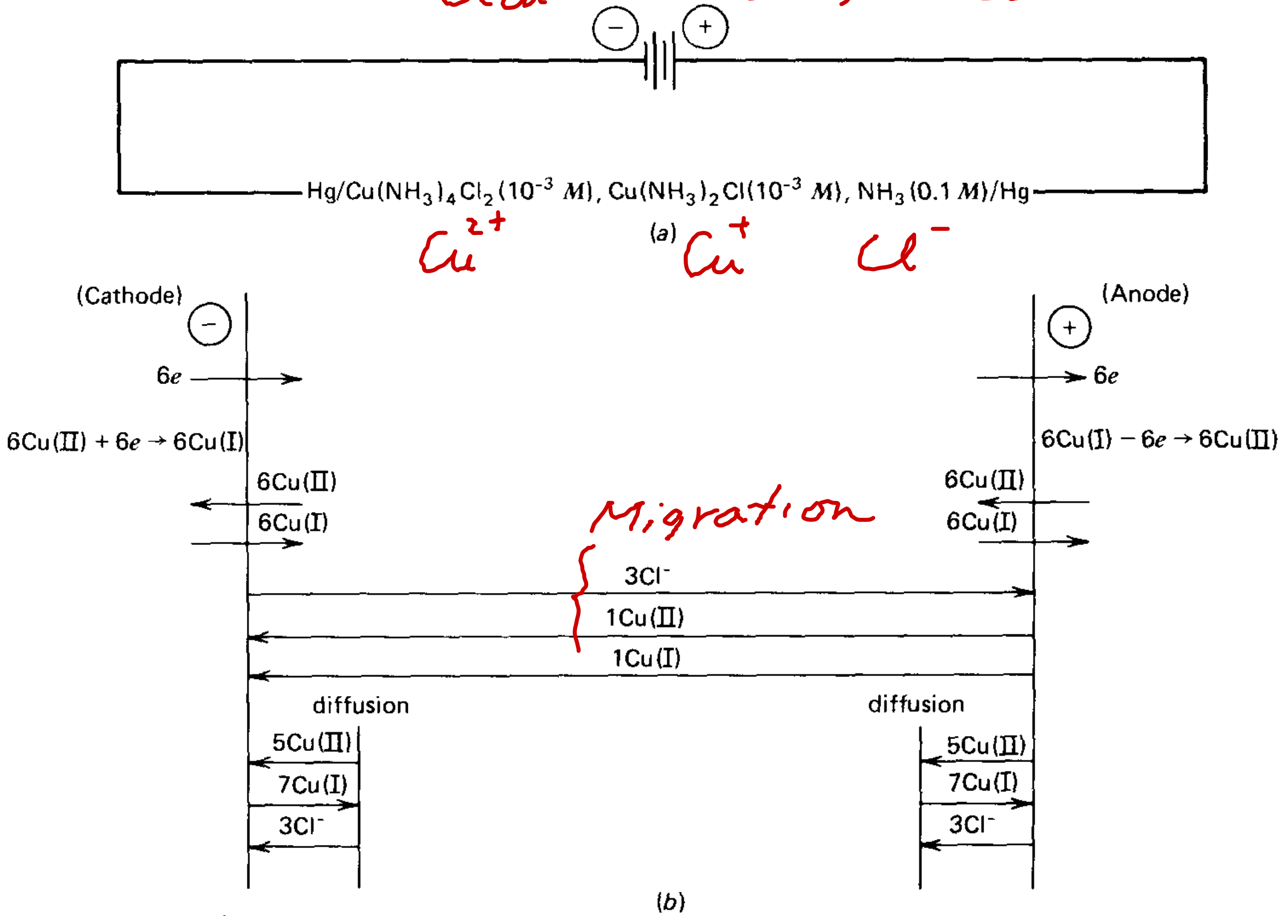
Nernst-Einstein equation,

$u_-/D_- = |z_i|F/RT$

Balance sheet

$C_{Cu^{2+}} = C_{Cu^{+}}$ $C_{Cl^-} = 3\, C_{Cu^{2+}}$

$u_{Cu^{2+}}$, $u_{Cu^{+}}$, u_{Cl^-}

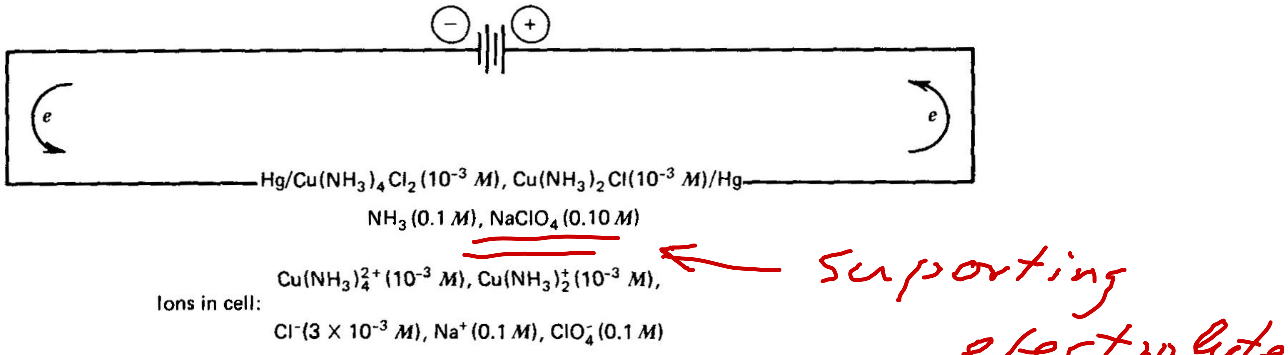


$t_{Cl^-} = 0.5$

$t_{Cu^{2+}}$

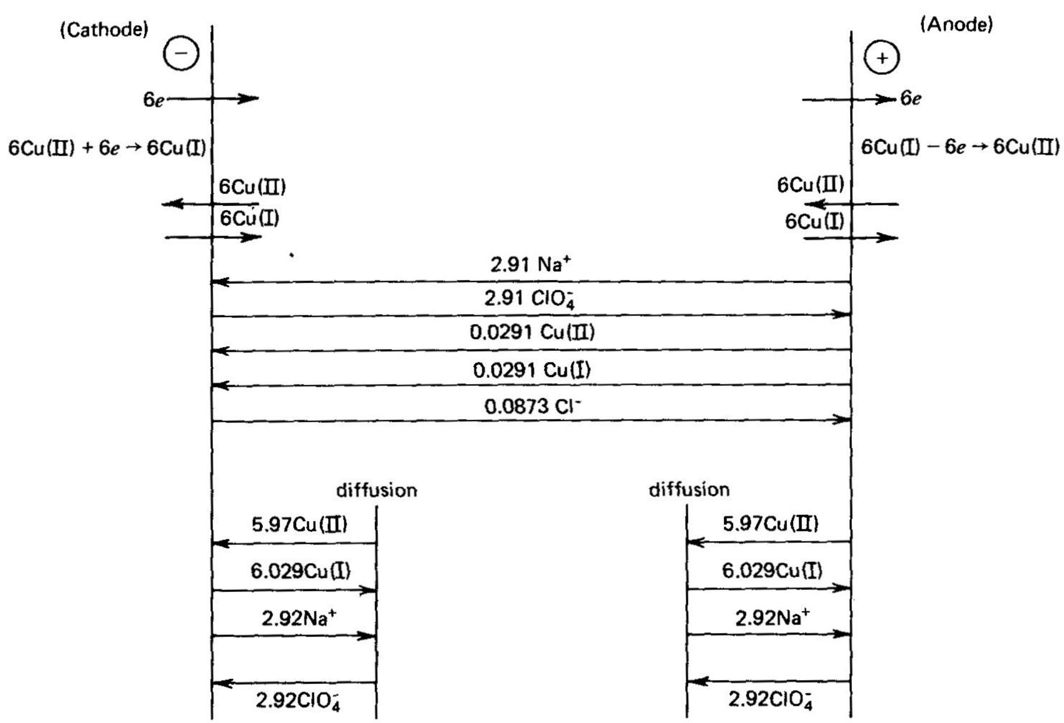
$t_{Cu^{+}}$

$6\, Cu^{2+} + 6e^- = 6 Cu^{+}$ $6\, Cu^{+} = 6\, Cu^{2+} + 6e^-$



e
e
Hg/Cu(NH3)4Cl2 (10^-3 M), Cu(NH3)2Cl(10^-3 M)/Hg
NH3 (0.1 M), NaClO4 (0.10 M)
Ions in cell:
Cu(NH3)4^2+ (10^-3 M), Cu(NH3)2^+ (10^-3 M),
Cl^- (3 X 10^-3 M), Na^+ (0.1 M), ClO4^- (0.1 M)
suporting electrolyte

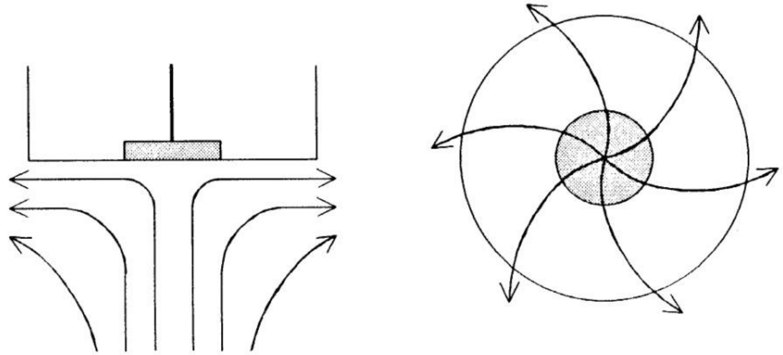
(a)



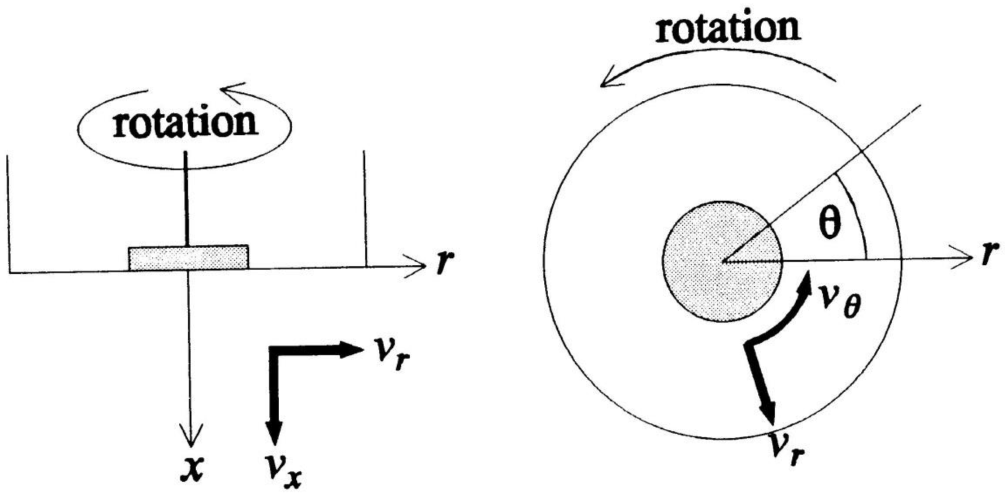
(Cathode)
(Anode)
6e
6e
6Cu(II) + 6e → 6Cu(I)
6Cu(I) − 6e → 6Cu(II)
6Cu(II)
6Cu(I)
6Cu(II)
6Cu(I)
2.91 Na+
2.91 ClO4-
0.0291 Cu(II)
0.0291 Cu(I)
0.0873 Cl-
diffusion
diffusion
5.97Cu(II)
6.029Cu(I)
2.92Na+
2.92ClO4-
5.97Cu(II)
6.029Cu(I)
2.92Na+
2.92ClO4-

(b)

Transport to a rotating disk



Rotating disk



Consevation law

$$\partial C/\partial t = D\, \partial^2 C/\partial x^2 - v_x \partial C/\partial x$$

Continuity condition

$$(1/r)\, \partial (r v_r)/\partial r + \partial v/\partial x = 0$$

Navier-Stokes equations for x-direction

$$\rho[v_r \partial v/\partial r + v_x \partial v/\partial x] = \eta[1/r\, \partial/\partial r(r\, \partial v/\partial r) + \partial^2 v/\partial x^2] - \partial p/\partial x$$

Karman equations

Von Kármán results; $\zeta = 2.11\exp\left\{-0.884x\sqrt{\omega d/\eta}\right\}$

$x\sqrt{\omega d/\eta}$ = dimensionless axial coordinate	$-v_x$ = upward velocity toward the disk	v_r = radial velocity away from axis	v_θ = angular velocity around the axis
0	0	0	ωr
small	$0.510x^2\sqrt{\omega^3 d/\eta}$	$0.510rx\sqrt{\omega^3 d/\eta}$	$\omega(r - 0.616x)$
1	$0.268\sqrt{\eta\omega/d}$	$0.182\omega r$	$0.477\sqrt{\eta\omega/d}$
large	$\sqrt{\eta\omega/d}[0.884-\zeta]$	$0.443\omega r\zeta$	$0.443\omega r\zeta$
∞	$0.884\sqrt{\eta\omega/d}$	0	0

Dimensionless varible

$x(\omega\rho/\eta)^{0.5}$

Hydrodynamic layer

$x = (\eta/\omega\rho)^{0.5}$ (` ~100 μm)

Flux ~ Current density

Flux density at the electrode surface

$$j_i^s = 0.62(\rho/\eta)D_i^{2/3}(C_i^s - C_i^b)(\omega)^{1/2}$$