Mass transfer by migration & diffusion (Ch. 4)

Mass transfer equation

Migration

Mixed migration & diffusion near an electrode
Mass transfer during electrolysis
Effect of excess electrolyte

Diffusion
Microscopic view
Fick's laws
Boundary conditions in electrochemical problems
Solution of diffusion equations

Mass transfer equation

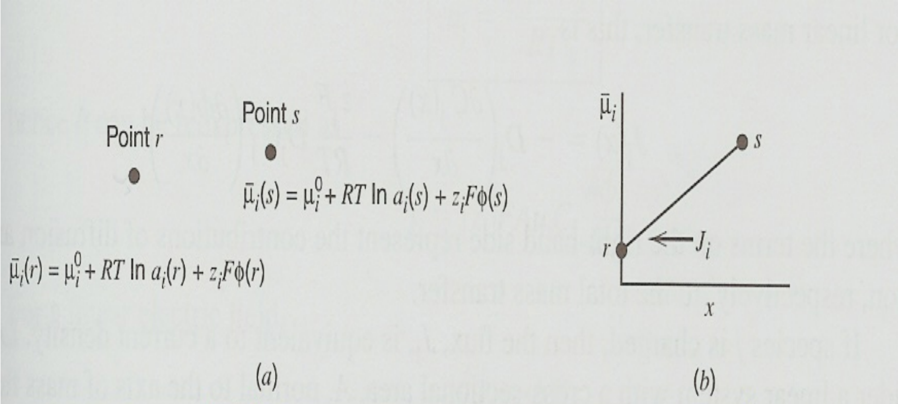
Mass transfer by diffusion, migration, convection

- Diffusion & migration result from a gradient in electrochemical potential, $\bar{\mu}$
- Convection results from an imbalance of forces on the solution

Two points in solution; r & s

→ difference of $\bar{\mu}_j$

due to conc. & electric field (ϕ) differences



Flux $\mathbf{J}_j \propto \text{grad}\bar{\mu}_j$ or $\mathbf{J}_j \propto \nabla\bar{\mu}_j$

1-D: $\nabla = \mathbf{i}(\partial/\partial x)$

3-D: $\nabla = \mathbf{i}(\partial/\partial x) + \mathbf{j}(\partial/\partial y) + \mathbf{k}(\partial/\partial z)$

$$\mathbf{J}_j = -(C_jD_j/RT)\nabla\bar{\mu}_j$$

Minus sign: flux direction opposite the direction of increasing $\bar{\mu}_j$

If solution moving with a velocity **v**

$$\mathbf{J}_j = -(C_jD_j/RT)\nabla\bar{\mu}_j + C_j\mathbf{v}$$

Nernst-Planck equations

$$J_j(x) = -D_j(\partial C_j(x)/\partial x) - (z_jF/RT)D_jC_j(\partial \phi(x)/\partial x) + C_jv(x)$$

In general

$$\underbrace{\mathbf{J}_j = -D_j \nabla C_j}_{\text{diffusion}} \underbrace{- (z_jF/RT)D_jC_j \nabla \phi}_{\text{migration}} \underbrace{+ C_j\mathbf{v}}_{\text{convection}}$$

Convection absent in this Chapter (<u>Ch.9 for convection</u>)
→ in an unstirred or stagnant solution

For linear system

$$-J_j\ (\text{mol}\,\text{s}^{-1}\text{cm}^{-2}) = i_j/z_jFA\ [\text{C/s per }(\text{C}\,\text{mol}^{-1}\text{cm}^2)] = i_{d,j}/z_jFA + i_{m,j}/z_jFA$$

With

$$i_{d,j}/z_jFA = D_j(\partial C_j/\partial x)$$

$$i_{m,j}/z_jFA = (z_jFD_j/RT)C_j(\partial \phi/\partial x)$$

$I_{d,j}$ & $i_{m,j}$: diffusion & migration currents of species j

Total current $\quad i = \sum i_j$

Migration

In the bulk soln (away from the electrode), conc gradient small: migration

$$i_j = (z_j^2 F^2 A D_j C_j/RT)(\partial\phi/\partial x)$$

Einstein-Smoluchowski equation

mobility $$u_j = |z_j|FD_j/RT$$

$$i_j = |z_j|FAu_jC_j(\partial\phi/\partial x)$$

For a linear electric field

$$\partial\phi/\partial x = \Delta E/l$$

$$i_j = |z_j|FAu_jC_j\Delta E/l$$

Total current $$i = \sum i_j = (FA\Delta E/l)\sum|z_j|u_jC_j$$

Conductance (L) $L = 1/R = i/\Delta E = (FA/l)\sum|z_j|u_jC_j = A\kappa/l$

κ: conductivity (Ω^{-1}cm^{-1})

$$\kappa = F\sum|z_j|u_jC_j$$

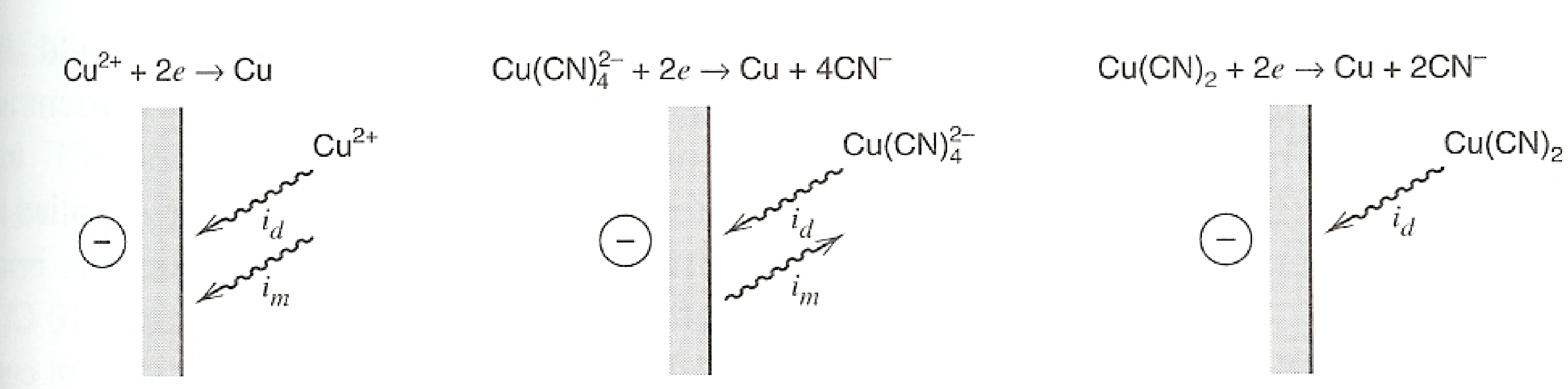
Resistivity $\rho = 1/\kappa$

Transference number

$$t_j = i_j/i = |z_j|u_jC_j/\sum|z_k|u_kC_k = |z_j|C_j\lambda_j/\sum|z_k|C_k\lambda_k$$

Mixed migration and diffusion near an active electrode

$$i = i_d + i_m$$



(a) $i = i_d + |i_m|$

(b) $i = i_d - |i_m|$

(c) $i = i_d$

Balance sheets for mass transfer during electrolysis

e.g., 4.1. Electrolysis of a solution of HCl at Pt electrode

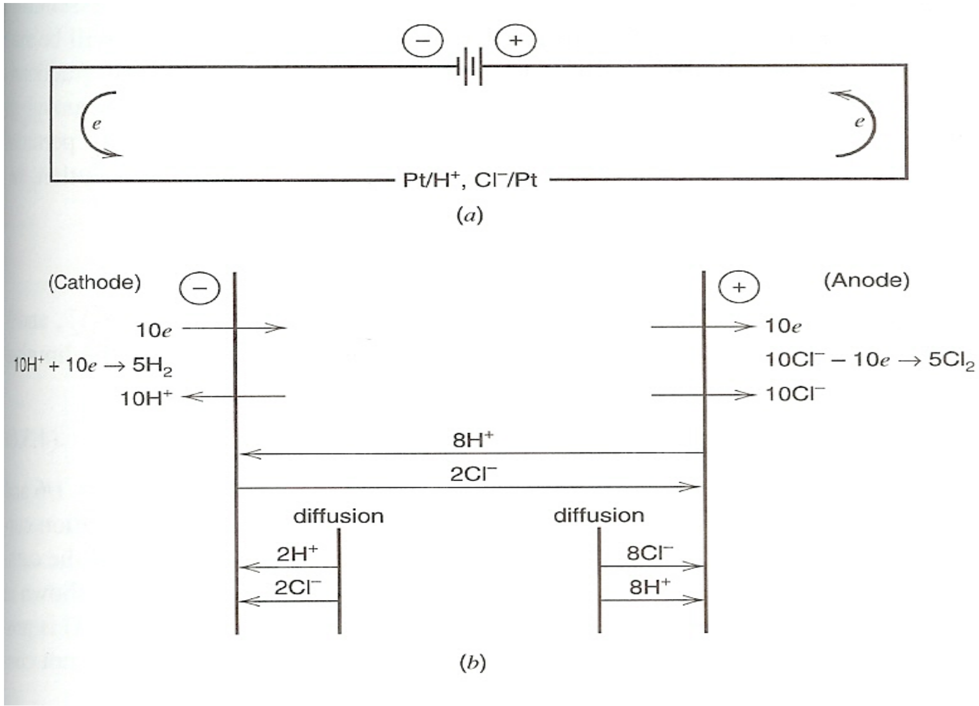
λ_+ (conductance of H^+), λ_- (conductance of Cl^-): $\lambda_+ \sim 4\lambda_- \rightarrow t_+ = 0.8$, $t_- = 0.2$

Assume total current of 10e/unit time producing $5H_2$ (cathode) & $5Cl_2$ (anode)

Total current in bulk soln: $8H^+ + 2Cl^-$

→ diffusion of 2 additional H^+ to cathode with $2Cl^-$ for electroneutrality
   diffusion of $8Cl^-$ with $8H^+$

For H^+: $i_d = 2$, $i_m = 8$, for Cl^-: $i_d = 8$, $i_m = 2 \rightarrow$ total current $i = i_d + i_m = 10$
(same direction of i_d & i_m)



For mixture of charged species, current by jth species $i_j = t_j i$

→ # of moles of jth species migrating per sec = $t_j i/z_j F$

→ # of moles arriving at the electrode per sec by migration = $\pm i_m/nF$

(positive sign for reduction of j, negative sign for oxidation)

$$\pm i_m/nF = t_j i/z_j F$$

$$i_m = \pm(n/z_j)t_j i$$

$$i_d = i - i_m = i(1 \mp nt_j/z_j)$$

Negative sign for cathodic current, positive sign for anodic current)

e.g., 4.2. Electrolysis of a solution of 10^{-3} M $Cu(NH_3)_4^{2+}$, 10^{-3} M $Cu(NH_3)_2^{+}$, 3 x 10^{-3} M Cl^- in 0.1 M NH_3 at two Hg electrodes

Assume $\lambda_{Cu(II)} = \lambda_{Cu(I)} = \lambda_{Cl-} = \lambda$

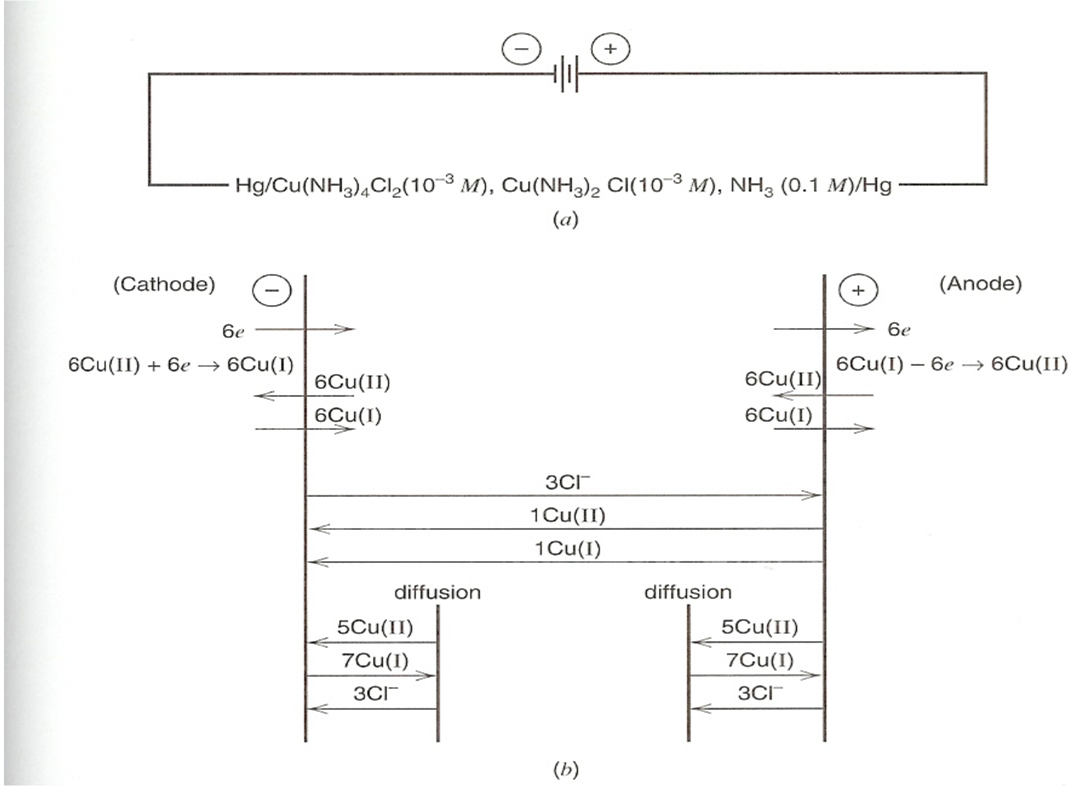
From $t_j = i_j/i = |z_j|u_jC_j/\sum|z_k|u_kC_k = |z_j|C_j\lambda_j/\sum|z_k|C_k\lambda_k$

$t_{Cu(II)} = 1/3$, $t_{Cu(I)} = 1/6$, $t_{Cl-} = 1/2$

Assume total current of 6e/unit time, $i = 6$, $n = 1$

For Cu(II) at cathode: $|i_m| = (1/2)(1/3)(6) = 1$, $i_d = 6 - 1 = 5$,

for Cu(I) at anode: $|i_m| = (1/1)(1/6)(6) = 1$, $i_d = 6 + 1 = 7$



Effect of adding excess electrolyte

e.g., 4.3. Electrolysis of a solution of 10^{-3} M $Cu(NH_3)_4^{2+}$, 10^{-3} M $Cu(NH_3)_2^{+}$, 3 x 10^{-3} M Cl^- in 0.1 M NH_3 + 0.1 M $NaClO_4$ (as excess electrolyte) at two Hg electrodes

Assume $\lambda_{Na+} = \lambda_{ClO4-} = \lambda$

→ $t_{Na+} = t_{ClO4-} = 0.485$, $t_{Cu(II)} = 0.0097$, $t_{Cu(I)} = 0.00485$, $t_{Cl-} = 0.0146$

*Na^+ & ClO_4^- do not participate in e-transfer rxns, but because their conc are high, they carry 97% of the current in the bulk solution

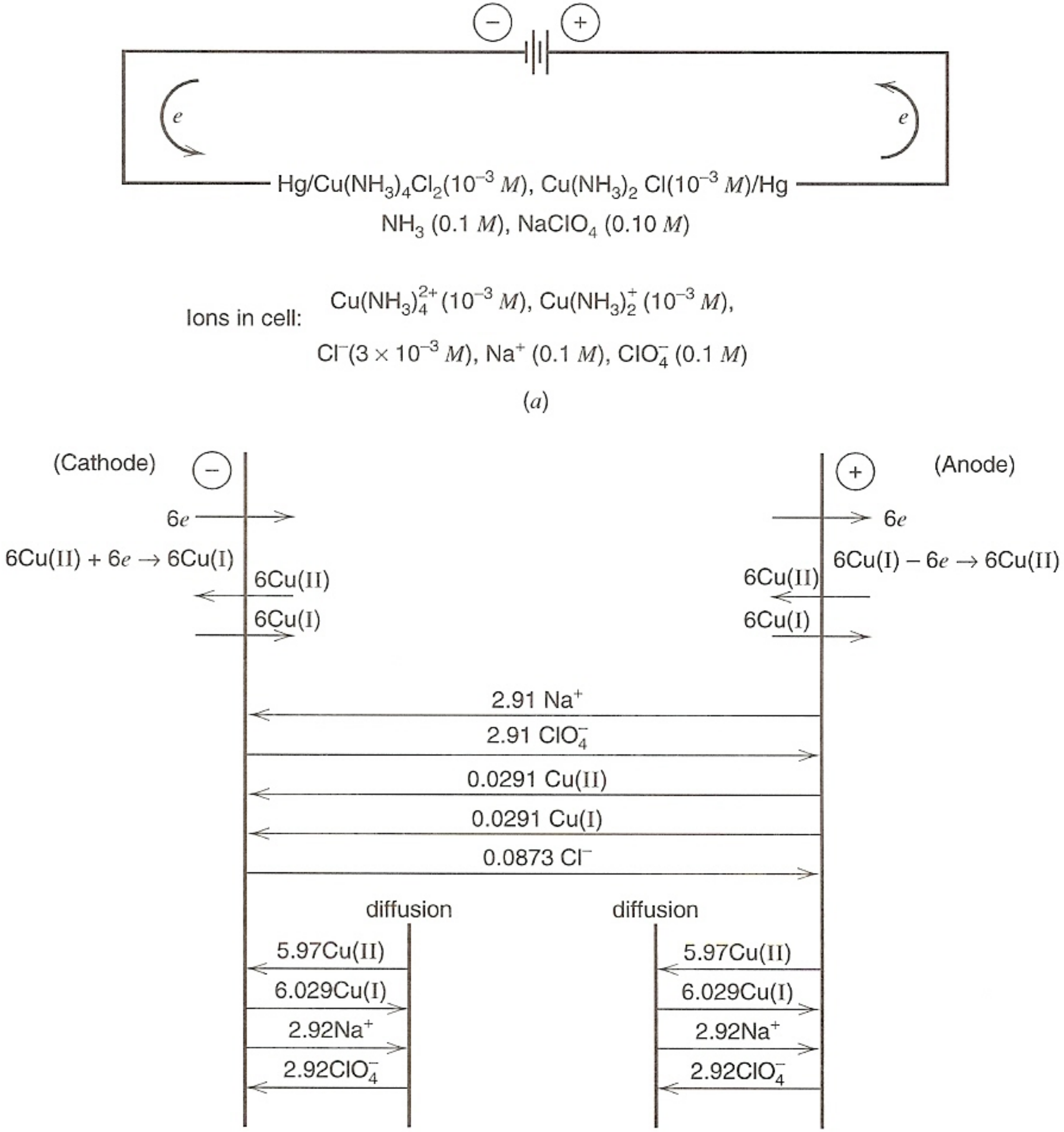
→ Most of Cu(II) reaches the cathode by diffusion & 0.5% flux by migration

Addition of an excess of nonelectroactive ions (a *supporting electrolyte*):

1. nearly eliminates the contribution of migration to the mass transfer of the electroactive species → eliminate $\nabla\phi$ or $\partial\phi/\partial x$ in mass transfer equations

2. Decreases the solution resistance, improve the accuracy of WE potential

Disadvantage: impurities, altered medium


−
+
e
e
Hg/Cu(NH$_3$)$_4$Cl$_2$(10^{-3} M), Cu(NH$_3$)$_2$ Cl(10^{-3} M)/Hg
NH$_3$ (0.1 M), NaClO$_4$ (0.10 M)
Ions in cell: Cu(NH$_3$)$_4^{2+}$ (10^{-3} M), Cu(NH$_3$)$_2^+$ (10^{-3} M),
Cl$^-$(3 × 10^{-3} M), Na$^+$ (0.1 M), ClO$_4^-$ (0.1 M)
(Cathode)
−
6e
6Cu(II) + 6e → 6Cu(I)
6Cu(II)
6Cu(I)
+
(Anode)
6e
6Cu(I) − 6e → 6Cu(II)
6Cu(II)
6Cu(I)
2.91 Na$^+$
2.91 ClO$_4^-$
0.0291 Cu(II)
0.0291 Cu(I)
0.0873 Cl$^-$
diffusion
diffusion
5.97Cu(II)
6.029Cu(I)
2.92Na$^+$
2.92ClO$_4^-$
5.97Cu(II)
6.029Cu(I)
2.92Na$^+$
2.92ClO$_4^-$

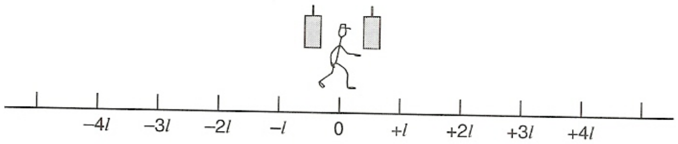
(a)

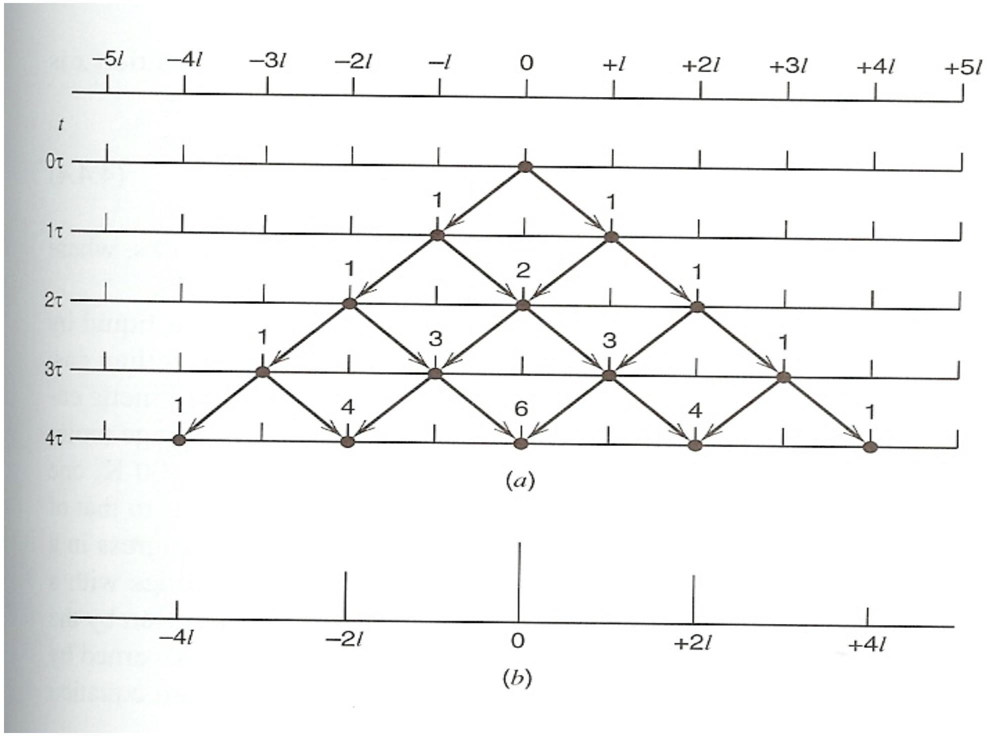
(b)

Diffusion

A microscopic view-discontinuous source model

Diffusion occurs by a “random walk” process





Probability, $P(m, r)$ after m time units ($m = t/\tau$)

$$P(m, r) = (m!/r!(m - r)!)(1/2)^m$$

where $x = (-m + 2r)l$ with $r = 0, 1, \ldots m$

Mean square displacement of the molecule

$$\overline{\Delta^2} = ml^2 = (t/\tau)l^2 = 2Dt$$

D: diffusion coefficient (= $l^2/2\tau$), cm^2/s (Einstein in 1905)

Root-mean square displacement

$$\overline{\Delta} = \sqrt{2Dt}$$

→ estimating the thickness of diffusion layer

e.g., D = 5 x 10^{-5} cm^2/s: diffusion layer thickness 10^{-4} cm in 1 ms, 10^{-3} cm in 0.1 s, 10^{-2} cm in 10 s

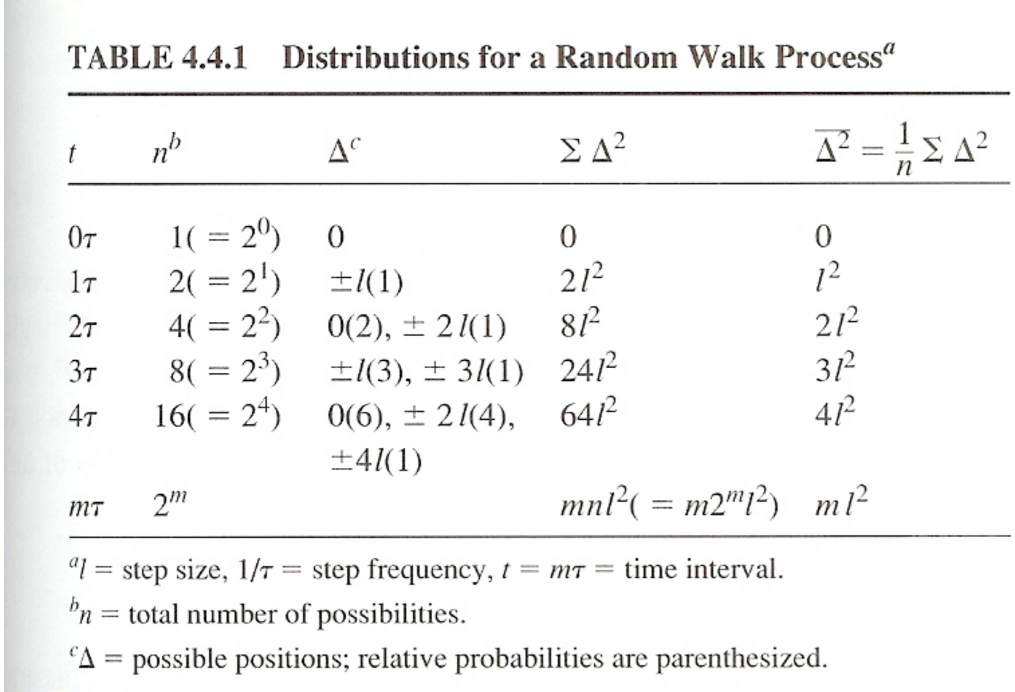


TABLE 4.4.1 **Distributions for a Random Walk Process**[a]

t	n[b]	Δ[c]	$\Sigma\,\Delta^2$	$\overline{\Delta^2} = \frac{1}{n}\Sigma\,\Delta^2$
0τ	$1(=2^0)$	0	0	0
1τ	$2(=2^1)$	$\pm l(1)$	$2l^2$	l^2
2τ	$4(=2^2)$	$0(2), \pm 2l(1)$	$8l^2$	$2l^2$
3τ	$8(=2^3)$	$\pm l(3), \pm 3l(1)$	$24l^2$	$3l^2$
4τ	$16(=2^4)$	$0(6), \pm 2l(4),$ $\pm 4l(1)$	$64l^2$	$4l^2$
$m\tau$	2^m		$mnl^2(=m2^ml^2)$	ml^2

[a] l = step size, $1/\tau$ = step frequency, $t = m\tau$ = time interval.

[b] n = total number of possibilities.

[c] Δ = possible positions; relative probabilities are parenthesized.

For N_0 molecules at the original position at $t = 0$ → Gaussian distribution later
$N(x, t)$ in a segment Δx wide on x

$$N(x, t)/N_0 = (\Delta x/2\sqrt{\pi D t})\exp(-x^2/4Dt)$$

2-D: $\overline{\Delta} = \sqrt{4Dt}$, 3-D: $\overline{\Delta} = \sqrt{6Dt}$

Diffusional velocity (v_d)

$$v_d = \overline{\Delta}/t = (2D/t)^{1/2}$$

Migration ($v = u_i E$) vs. diffusion (v_d)

Einstein-Smoluchowski equation

mobility $u_j = |z_j| F D_j/RT$

$$v = |z_j| F D_j E/RT$$ (E: electric field strength)

$\mathbf{v \ll v_d}$ $D_i E/(RT/|z_i|F) \ll (2D_i/t)^{1/2}$

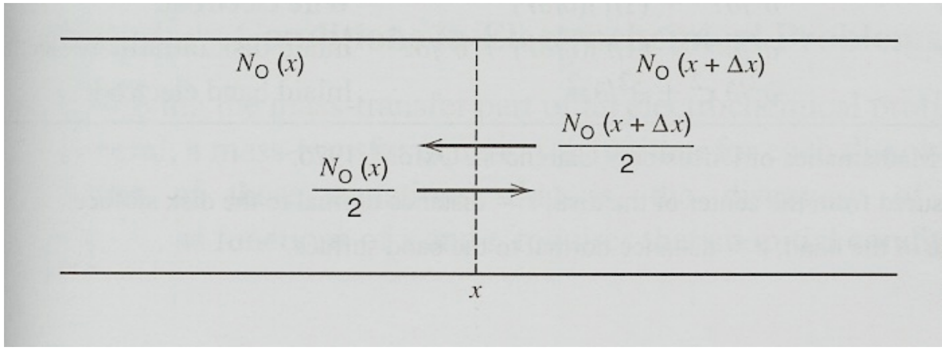
rearrange $(2D_i t)^{1/2} E \ll 2RT/|z_i|F$

→ voltage drop over length scale of diffusion $\ll 2RT/|z_i|F$: migration negligible

Fick's laws of diffusion

Fick's 1^{st} law: flux ∝ conc gradient

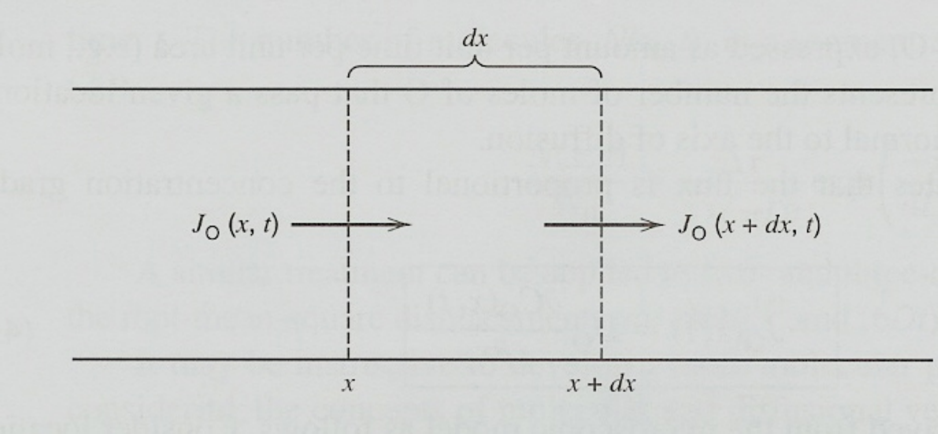
$$-J_O(x, t) = D_O(\partial C_O(x, t)/\partial x)$$



Fick's 2^{nd} law: change in concentration of O with time

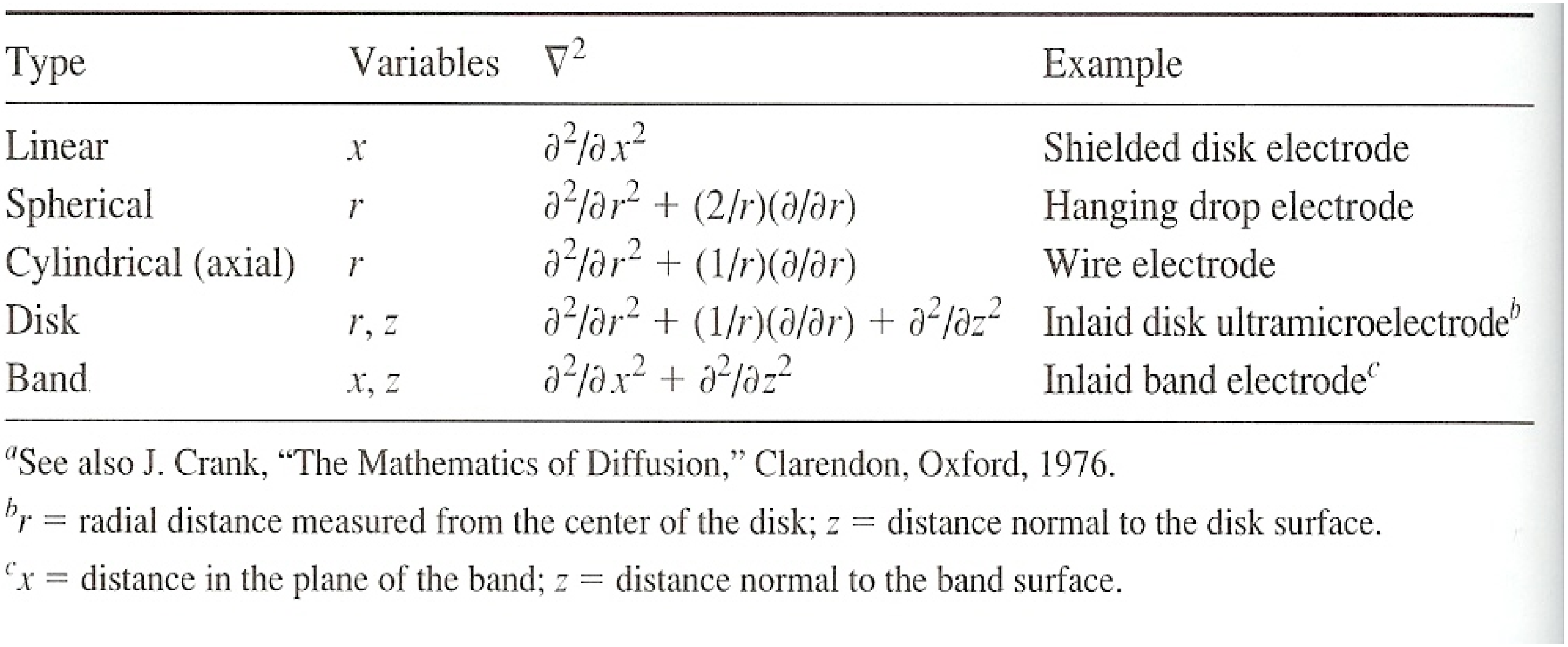
$$\partial C_O(x, t)/\partial t = D_O(\partial^2 C_O(x, t)/\partial x^2)$$

→ solution gives concentration profiles, $C_O(x, t)$



General formulation of Fick’s 2nd law

$$\partial C_O/\partial t = D_O \nabla^2 C_O$$



Type	Variables	∇^2	Example
Linear	x	$\partial^2/\partial x^2$	Shielded disk electrode
Spherical	r	$\partial^2/\partial r^2 + (2/r)(\partial/\partial r)$	Hanging drop electrode
Cylindrical (axial)	r	$\partial^2/\partial r^2 + (1/r)(\partial/\partial r)$	Wire electrode
Disk	r, z	$\partial^2/\partial r^2 + (1/r)(\partial/\partial r) + \partial^2/\partial z^2$	Inlaid disk ultramicroelectrode[b]
Band	x, z	$\partial^2/\partial x^2 + \partial^2/\partial z^2$	Inlaid band electrode[c]

[a] See also J. Crank, “The Mathematics of Diffusion,” Clarendon, Oxford, 1976.

[b] r = radial distance measured from the center of the disk; z = distance normal to the disk surface.

[c] x = distance in the plane of the band; z = distance normal to the band surface.

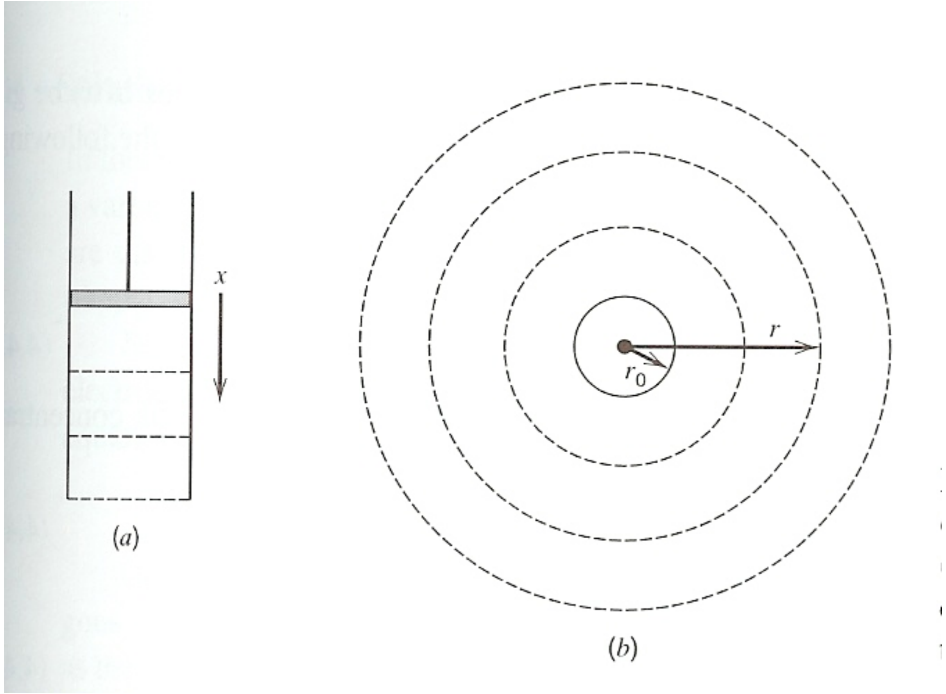


Fig. (a): Planar electrode (linear diffusion equation)

$$\partial C_O(x, t)/\partial t = D_O(\partial^2 C_O(x, t)/\partial x^2)$$

Fig. (b): spherical electrode (hanging Hg drop)

$$\partial C_O(r, t)/\partial t = D_O[(\partial^2 C_O(r, t)/\partial x^2) + (2/r)(\partial C_O(r, t)/\partial r)]$$

Consider O transported purely by diffusion to an electrode

$$O + ne = R$$

$$-J_O(0, t) = i/nFA = D_O[\partial C_O(x, t)/\partial x]_{x = 0}$$