4.4 DIFFUSION

- Diffusion leads to the homogenization of a mixture

  → can be described using the model of a "random walk" process.

- Consider a one-dimensional random walk.

  → Consider a molecule constrained to a linear path

  → moving in steps of length, l, with one step being made per unit time, τ.

- In a random walk,

  → all paths that can be traversed in any elapsed period are equal

  → the probability that the molecule has arrived at any particular point

$$= \frac{\text{the number of paths leading to that point}}{\text{the total of possible paths to all accessible points}}$$

4.4 DIFFUSION

- Number of cases

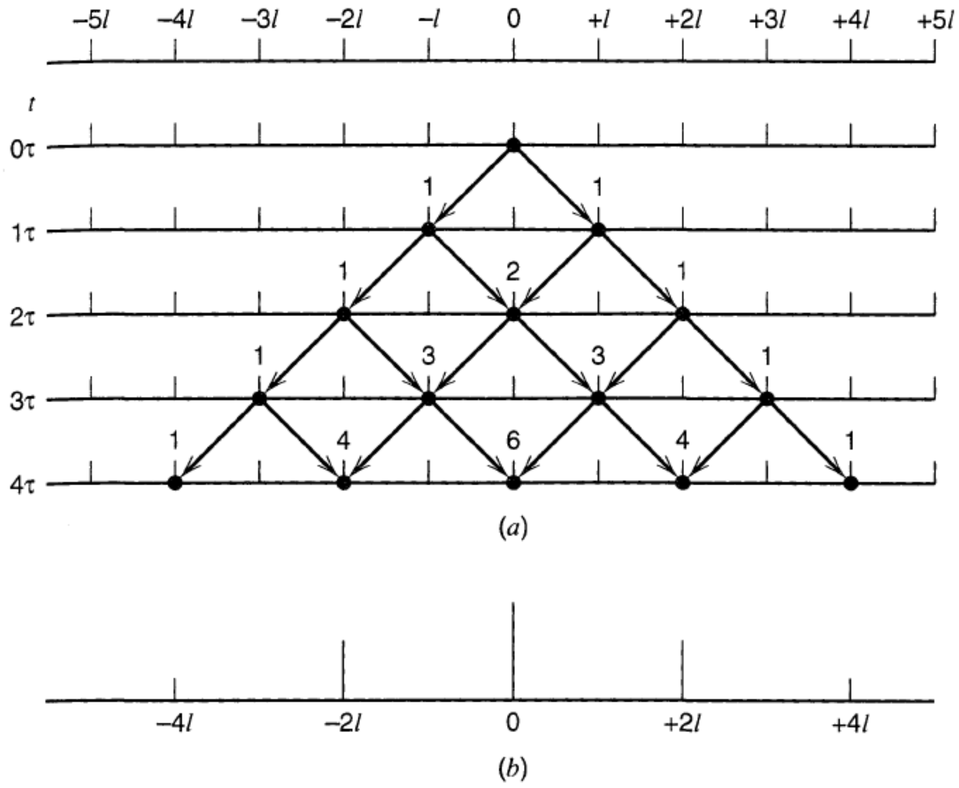


Figure 4.4.2 (*a*) Probability distribution for a one-dimensional random walk over zero to four time units. The number printed over each allowed arrival point is the number of paths to that point. (*b*) Bar graph showing distribution at $t = 4\tau$. At this time, probability of being at $x = 0$ is 6/16, at $x = \pm 2l$ is 4/16, and at $x = \pm 4l$ is 1/16.

- At time τ,

→ it is equally likely that the molecule is at +l and -l

- At time 2 τ,

→ the relative probabilities of being at +2l, 0, and -2l, are 1, 2, and 1, respectively.

4.4 DIFFUSION

- The probability, P(m, r), that the molecule is at a given location after m time units (m = t/τ) is given by

$$P(m,r) = \frac{m!}{r!(m-r)!}\left(\frac{1}{2}\right)^m$$

: where the set of locations is defined by x = (-m + 2r)l, with r = 0, 1 , . . . m.

- The mean square displacement of the molecule, $\bar{\Delta}^2$

$$= \frac{\text{Sum of the squares of the displacements}}{\text{Total number of possibilities } (2^m)}$$

→ The squares of the displacements are used, because movement is possible in both the positive and negative directions,

→ the sum of the displacements is always zero.

4.4 DIFFUSION

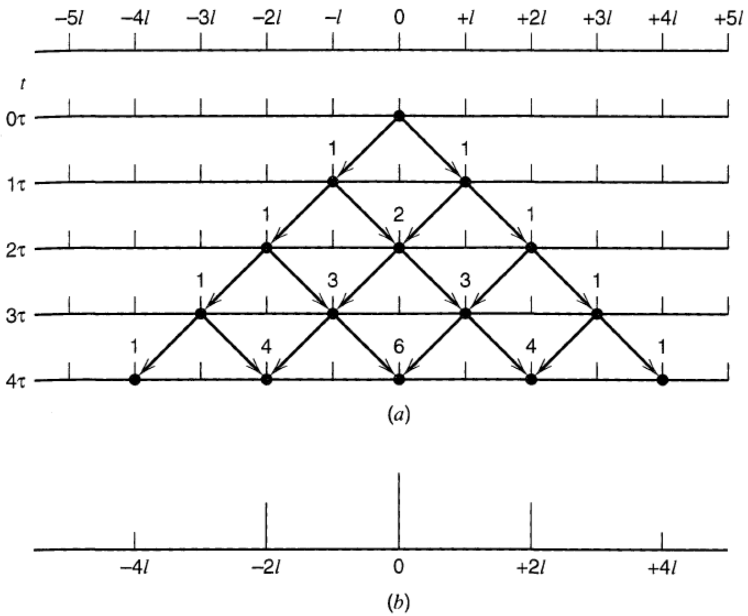
TABLE 4.4.1 Distributions for a Random Walk Process[a]

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	$4(=2^2)$	$0(2),\ \pm 2\,l(1)$	$8l^2$	$2\,l^2$
3τ	$8(=2^3)$	$\pm l(3),\ \pm 3l(1)$	$24l^2$	$3l^2$
4τ	$16(=2^4)$	$0(6),\ \pm 2\,l(4),$ $\pm 4l(1)$	$64l^2$	$4l^2$
$m\tau$	2^m		$mnl^2(=m2^ml^2)$	$m\,l^2$

[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.



(a)

(b)

4.4 DIFFUSION

- In general, $\bar{\Delta}^2$ is given by

$$\overline{\Delta^2} = ml^2 = \frac{t}{\tau}l^2 = 2Dt$$

→ where the diffusion coefficient, D, identified as $l^2/2\tau$, is a constant related to the step size and step frequency. (derived by Einstein)

→ It has units of length^2/time, usually cm^2/s.

- The root-mean-square displacement at time t is thus

$$\boxed{\bar{\Delta} = \sqrt{2Dt}}$$

- This equation provides a handy rule of thumb for estimating the thickness of a diffusion layer (e.g., how far product molecules have moved, on the average, from an electrode in a certain time).

→ A typical value of D for aqueous solutions is 5 X 10^{-6} cm^2/s, so that a diffusion layer thickness of 10^{-4} cm is built up in 1 ms, 10^{-3} cm in 0.1 s, and 10^{-2} cm in 10 s.

4.4 DIFFUSION

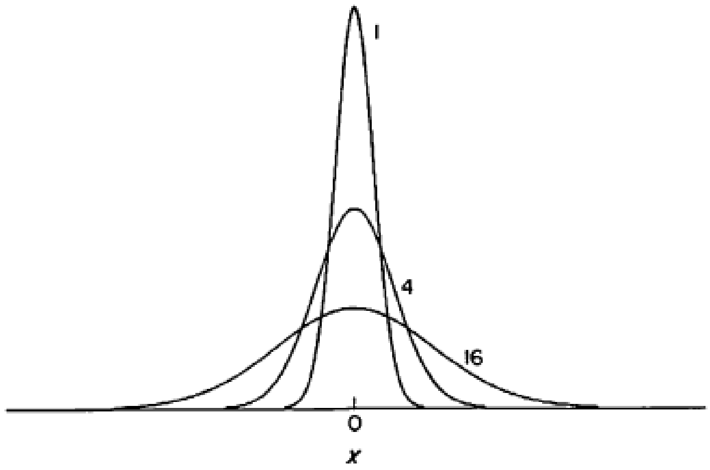
- As m becomes large, a continuous form can be obtained.

- For N_0 molecules located at the origin at t = 0,

  → a Gaussian curve will describe the distribution at some later time, t.

- The number of molecules, N(x, t), in a segment Δx wide centered on position x is

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



4.4.2 Fick's Laws of Diffusion

- **Fick's laws**

→ differential equations describing the flux of a substance and its concentration as functions of time and position.

- Consider the case of linear (one-dimensional) diffusion.
- The flux of a substance O at a given location x at a time t, written as $J_O(x, t)$
  - → the net mass-transfer rate of O
  - → expressed as amount per unit time per unit area (e.g., mol s^{-1} cm^{-2}).

- Thus $J_O(x, t)$ represents the number of moles of O that pass a given location per second per cm^2 of area normal to the axis of diffusion.

4.4.2 Fick's Laws of Diffusion

- Fick's first law

→ states that the flux is proportional to the concentration gradient, $\partial C_O/\partial x$:

$$\boxed{-J_O(x,t) = D_O \frac{\partial C_O(x,t)}{\partial x}}$$

- This equation can be derived from the microscopic model
- Consider location x, and assume $N_O(x)$ molecules are immediately to left of x, and $N_O(x+\Delta x)$ molecules are immediately to the right, at time t

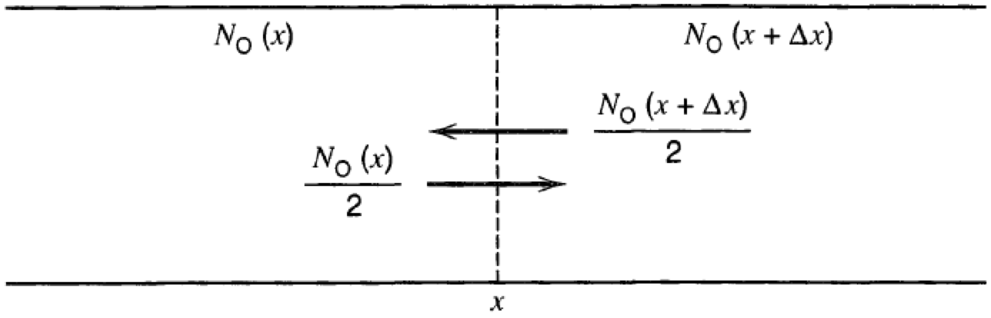


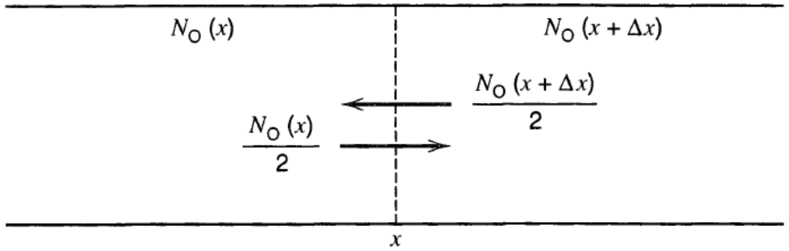
Figure 4.4.3 Fluxes at plane x in solution.

4.4.2 Fick's Laws of Diffusion

- All of the molecules are understood to be within one step-length, Δx, of location x.

- During the time increment, Δt, half of them move Δx in either direction by the random walk process, so that the net flux through an area A at x is given by the difference between the number of molecules moving from left to right and the number moving from right to left:

$$J_O(x,t) = \frac{1}{A}\,\frac{\dfrac{N_O(x)}{2} - \dfrac{N_O(x+\Delta x)}{2}}{\Delta t}$$



- Multiplying by $\Delta x^2/\Delta x^2$ and noting that the concentration of O is $C_O = N_O/A\Delta x$, we derive

$$-J_O(x,t) = \frac{\Delta x^2}{2\Delta t}\,\frac{C_O(x+\Delta x) - C_O(x)}{\Delta x}$$

4.4.2 Fick's Laws of Diffusion

- From the definition of the diffusion coefficient, $D_O = \Delta x^2/2\Delta t$, and allowing Δx and Δt approach zero, we obtain the Fick's first law

$$-J_O(x,t) = \frac{\Delta x^2}{2\Delta t}\,\frac{C_O(x+\Delta x) - C_O(x)}{\Delta x} \quad \Rightarrow \quad \boxed{-J_O(x,t) = D_O\,\frac{\partial C_O(x,t)}{\partial x}}$$

4.4.2 Fick's Laws of Diffusion

- **Fick's second law** → the change in concentration of O with time:

$$\boxed{\frac{\partial C_O(x, t)}{\partial t} = D_O \left(\frac{\partial^2 C_O(x, t)}{\partial x^2} \right)}$$

- This equation is derived from the first law
- The change in concentration at a location x is given by the difference in flux into and flux out of an element of width dx

$$\frac{\partial C_O(x, t)}{\partial t} = \frac{J(x, t) - J(x + dx, t)}{dx}$$

- Note that J/dx has units of (mol s^{-1} cm^{-2})/cm or change in concentration per unit time.

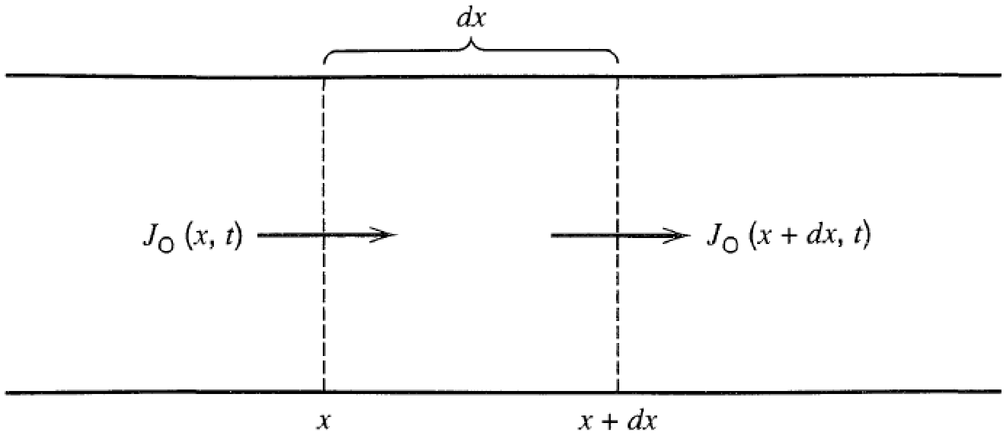
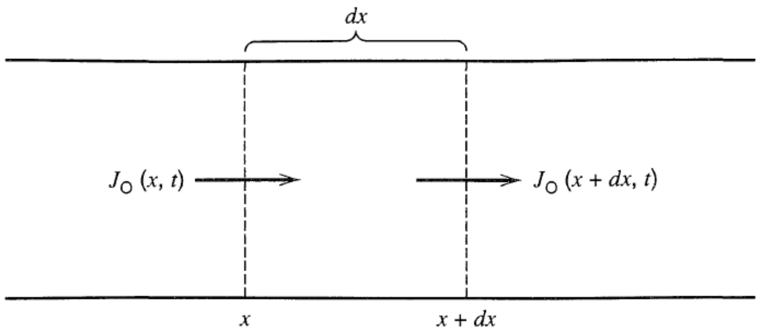


Figure 4.4.4 Fluxes into and out of an element at *x*.

4.4.2 Fick's Laws of Diffusion

- From the Fick's first law, we obtain

$$-\frac{\partial J(x,t)}{\partial x} = \frac{\partial}{\partial x} D_{\mathrm{O}} \frac{\partial C_{\mathrm{O}}(x,t)}{\partial x}$$



- Combination of the equations yields

$$\left.\begin{aligned}
&\frac{\partial C_{\mathrm{O}}(x,t)}{\partial t} = \frac{J(x,t) - J(x+dx,t)}{dx} \\
&J(x+dx,t) = J(x,t) + \frac{\partial J(x,t)}{\partial x}\,dx \\
&-\frac{\partial J(x,t)}{\partial x} = \frac{\partial}{\partial x} D_{\mathrm{O}} \frac{\partial C_{\mathrm{O}}(x,t)}{\partial x}
\end{aligned}\right\} \quad \frac{\partial C_{\mathrm{O}}(x,t)}{\partial t} = \left(\frac{\partial}{\partial x}\right)\left[D_{\mathrm{O}}\left(\frac{\partial C_{\mathrm{O}}(x,t)}{\partial x}\right)\right]$$

4.4.2 Fick's Laws of Diffusion

- When D_O is not a function of x,

$$\frac{\partial C_O(x,t)}{\partial t} = \left(\frac{\partial}{\partial x}\right)\left[D_O\left(\frac{\partial C_O(x,t)}{\partial x}\right)\right] \quad \Rightarrow \quad \boxed{\frac{\partial C_O(x,t)}{\partial t} = D_O\left(\frac{\partial^2 C_O(x,t)}{\partial x^2}\right)}$$

➔ In most electrochemical systems, the changes in solution composition caused by electrolysis are sufficiently small that variations in the diffusion coefficient with x can be neglected.

- Solutions of this equation yield concentration profiles, $C_O(x, t)$.

4.4.2 Fick's Laws of Diffusion

- The general formulation of Fick's second law for any geometry is

$$\boxed{\frac{\partial C_O}{\partial t} = D_O \nabla^2 C_O}$$

: where ∇^2 is the Laplacian operator.

- Forms of ∇^2 for different geometries are given in Table 4.4.2.

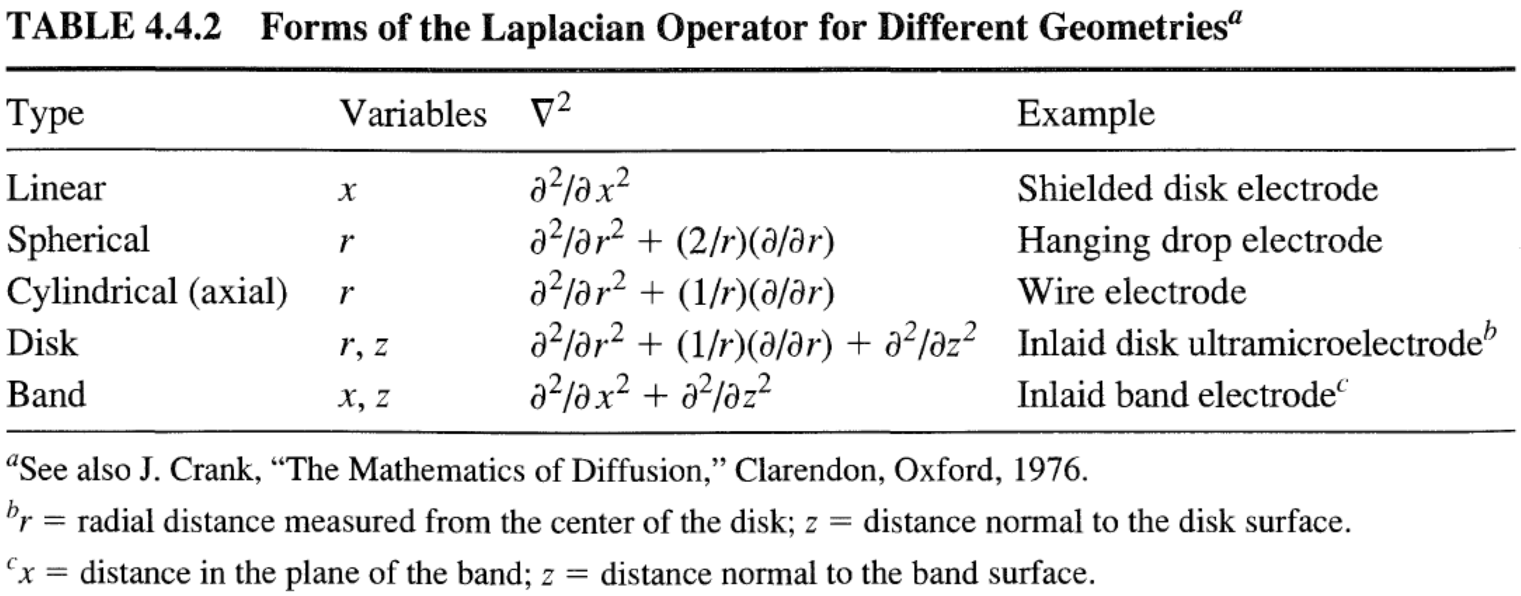


TABLE 4.4.2 Forms of the Laplacian Operator for Different Geometries[a]

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.

4.4.2 Fick's Laws of Diffusion

- Thus, for problems involving a planar electrode,

→ the linear diffusion equation is appropriate.

- For problems involving a spherical electrode, such as the hanging mercury drop electrode (HMDE),

→ the spherical form of the diffusion equation must be employed:

$$\boxed{\frac{\partial C_O(r,t)}{\partial t} = D_O\left(\frac{\partial^2 C_O(r,t)}{\partial r^2} + \frac{2}{r}\frac{\partial C_O(r,t)}{\partial r}\right)}$$

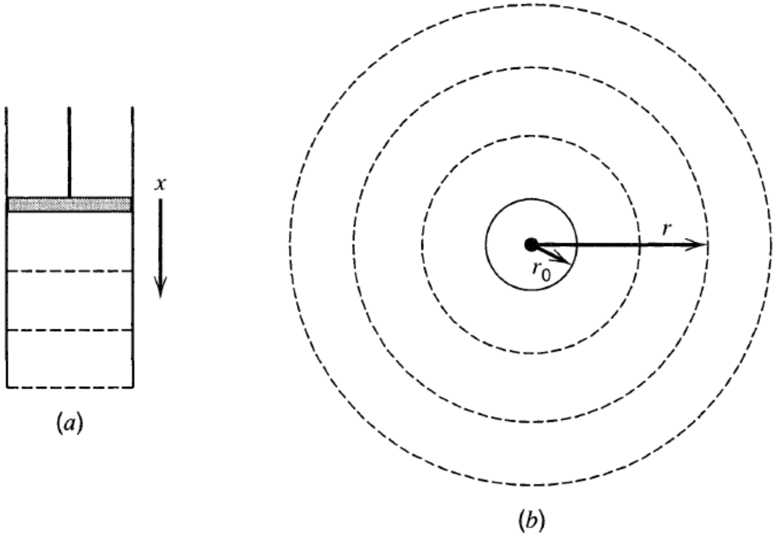


Figure 4.4.5 Types of diffusion occurring at different electrodes. (*a*) Linear diffusion to a planar electrode. (*b*) Spherical diffusion to a hanging drop electrode.

4.4.3 Boundary Conditions in Electrochemical Problems

- The solution of these equations, that is, the discovery of an equation expressing C_O, C_R, . . . as functions of x and t, requires that

→ i) an initial condition (the concentration profile at t = 0)

→ ii) two boundary conditions (functions applicable at certain values of x) be given for each diffusing species.

4.4.3 Boundary Conditions in Electrochemical Problems

- Typical initial and boundary conditions include the following.

(a) Initial Conditions

- These are usually of the form

$$C_O(x, 0) = f(x)$$

- For example, if O is uniformly distributed throughout the solution at a bulk concentration C_O* at the start of the experiment, the initial condition is

$$C_O(x, 0) = C_O^* \qquad \text{(for all } x\text{)}$$

- If R is initially absent from the solution, then

$$C_R(x, 0) = 0 \qquad \text{(for all } x\text{)}$$

4.4.3 Boundary Conditions in Electrochemical Problems

(b) Semi-infinite Boundary Conditions

- The electrolysis cell is usually large compared to the length of diffusion

→ hence the solution at the walls of the cell is not altered by the process at the electrode

- One can normally assume that at large distances from the electrode (x → ∞) the concentration reaches a constant value, typically the initial concentration, so that, for example,

$$\lim_{x\to\infty} C_O(x,t) = C_O^* \qquad \text{(at all } t\text{)}$$

$$\lim_{x\to\infty} C_R(x,t) = 0 \qquad \text{(at all } t\text{)}$$

- However, for thin-layer electrochemical cells, where the cell wall is at a distance, l, of the order of the diffusion length, one must use boundary conditions at x = l instead of those for x → ∞ (Finite boundary condition)

4.4.3 Boundary Conditions in Electrochemical Problems

(c) Electrode Surface Boundary Conditions

- Additional boundary conditions usually relate to concentrations or concentration gradients at the electrode surface. For example, if the potential is controlled in an experiment, one might have

$$C_O(0,t) = f(E)$$

$$\frac{C_O(0,t)}{C_R(0,t)} = f(E)$$

→ where f(E) is some function of the electrode potential derived from the general current-potential characteristic or one of its special cases (e.g., the Nernst equation).

- If the current is the controlled quantity, the boundary condition is expressed in terms of the flux at x = 0; for example,

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

4.4.4 Solution of Diffusion Equations

- Sometimes one is interested only in the steady-state solution (e.g., with rotating disk electrodes or ultramicroelectrodes). Since $dC_O/dt = 0$ in such a situation, the diffusion equation simply becomes

$$\boxed{\frac{\partial C_O}{\partial t} = D_O \nabla^2 C_O} \quad \Rightarrow \quad \nabla^2 C_O = 0$$

- For most cases, the electrochemical system is not a steady state
  → solve the PDEs using the Laplace transformation

$$\boxed{\frac{\partial C_O}{\partial t} = D_O \nabla^2 C_O}$$