Material Transport Processes

- 3 main mechanisms:
  - Diffusion
    - Mass transport in concentration gradient
  - Migration (conduction)
    - Mass transport in potential gradient
  - Convection
    - Mass transport via hydrodynamic flow

- Diffusion and convection most important in electrochemistry since electromigration is usually suppressed in experiments.
- Material transport in a condensed phase may be described from either a macroscopic (in terms of partial differential equations, irreversible thermodynamics) or a microscopic (essentially statistical or stochastic) viewpoint.

Material flux.
Rate of material transport is defined in terms of a material flux $f_k$ (also denoted as $J_k$) with units mol cm$^{-2}$ s$^{-1}$. This is defined as the quantity of material flowing through a reference plane of area $A$ per unit time.

\[
\mathbf{J}_k = C_k \mathbf{v}
\]

The flux of a species $k$ through an element of area $d\sigma$ is a vector quantity given by

- Fluid velocity vector cms$^{-1}$
- Molar concentration (mol cm$^{-3}$)
Diffusive Material Transport

Diffusive material transport driven by presence of concentration gradient. Mathematically described by the Fick Diffusion equations (material flow expressions directly analogous to Fourier heat flow (energy transfer in a temperature gradient) expressions. Macroscopically, mathematical expressions previously developed for heat flow can be used with suitable modification to corresponding material transport problem.

Steady State Fickian Diffusion.

We consider two cases: steady state (time independent) diffusion and transient (time dependent) diffusion. In the first case $c = c(x)$ only whereas in the second case $c = c(x,t)$.

Assume driving force for diffusion is proportional to chemical potential gradient.

We introduce a diffusive pseudo-driving force $F_D$ which is related to the gradient in chemical potential via:

\[ F_D = -c_i \frac{d \mu_i}{dx} \quad (1-D) \]

\[ F_D = -c_i \nabla \mu_i \quad (3-D) \]

Steady State Fickian Diffusion.

A.E Fick
1829-1901

http://en.wikipedia.org/wiki/Adolf_Eugen_Fick

We now assume that diffusive pseudo force $F_D$ is associated with a diffusive Flux $f$ which serves as a measure of the diffusion rate. We use irreversible thermodynamics to relate flux and force:

\[ f_i = \alpha + \beta F_D + \gamma F_D^2 + \ldots \]

Assuming $F_D$ is small corresponding to small departure from equilibrium (linear irreversible thermodynamics) we neglect terms in $F_D^2$ and higher. Also since if $F_D = 0$ then $f_i = 0$ (no effect exists without the corresponding cause) then $\alpha = 0$. This leaves us with the assignment that we have a linear relationship between Flux (the effect) and driving force (the cause):

\[ f_i = \beta F_D = -c_i \frac{d \mu_i}{dx} \]

Introducing the definition of chemical potential:

\[ \mu_i = \mu_i^0 + RT \ln a_i \]
\[ a_i = y_i c_i \equiv c_i^* \]
\[ d \mu_i = RT \frac{d \ln c_i}{dx} = \frac{RT}{c_i} \frac{dc_i}{dx} \]

Introducing the definition of diffusive pseudo force:

\[ f_i = \beta F_D = -c_i \frac{d \mu_i}{dx} \]

\[ = -\beta c_i \left( \frac{RT}{c_i} \frac{dc_i}{dx} \right) = -\beta RT \frac{dc_i}{dx} \]

Ideal solution approximation Activity coefficient $\gamma = 1$

We introduce the phenomenological diffusion coefficient (unit: cm$^2$s$^{-1}$) $D$:

\[ D = \beta RT \]

We arrive at the Fick equation of steady state diffusion:

\[ D \frac{dc_i}{dx} \]

\[ f_i = -D_i \frac{dc_i}{dx} \]

\[ f_i = -D_i \nabla c_i \]

1-D

3-D
More generally if the solution is not ideal the activity coefficient differs from unity.

\[ f_k = -D_k \left( 1 + \frac{c_k}{\gamma_k} \frac{d\gamma_k}{dc_k} \right) \frac{dc_k}{dx} = -D_k \left( 1 + \frac{d \ln \gamma_k}{d \ln c_k} \right) \frac{dc_k}{dx} \]

Note that typically the diffusion coefficient is independent of concentration. Diffusion coefficients vary over many orders of magnitude. Typical values are:

- **Ions in aqueous solution:** \( D \approx 10^{-9} - 10^{-6} \text{ cm}^2\text{s}^{-1} \).
- **Ions in polymeric matrices:** \( D \approx 10^{-8} - 10^{-13} \text{ cm}^2\text{s}^{-1} \).
- **Solid state diffusion:** \( D \approx 10^{-16} - 10^{-20} \text{ cm}^2\text{s}^{-1} \).

---

**Time Dependent (TD) Fickian Diffusion.**

We consider a diffusing species \( k \) passing through a rectangular volume element.

**Inward flux**

\[ f_i(x) = -D_i \frac{\partial c_i}{\partial x} \]

\[ f_i(x + dx) = -D_i \frac{\partial c_i(x + dx)}{dx} \]

**Outward flux**

\[ c_i(x + dx) = c_i(x) + \frac{\partial c_i(x)}{\partial x} dx \]

\[ f_o(x) = \frac{\partial^2 c_i}{\partial x^2} dx \]

\[ f_o(x + dx) = \frac{\partial^2 c_i(x + dx)}{\partial x^2} dx \]

**Equation of continuity**

\[ \frac{\partial c_i}{\partial t} = D_i \frac{\partial^2 c_i}{\partial x^2} \]
General analysis of ion transport in electrolyte solution.

We consider the forces acting on an ion in a viscous medium such as an electrolyte solution (assumed structureless). Charged species move under the influence of a gradient in electrochemical potential with a driving force \( F \).

Movement of the ion in the viscous solvent is opposed by a viscous frictional force \( F_v \) proportional to the velocity \( v \) of the ion.

**Total force**

\[
\begin{align*}
F = \vec{F} + F_v = m \frac{dv}{dt} = -\zeta \nabla \mu - \frac{1}{N_A} \nabla \mu
\end{align*}
\]

**Initial condition**

\[
\begin{align*}
v(0,0) = 0
\end{align*}
\]

**LDE in velocity**

\[
\begin{align*}
\frac{dv}{dt} = -\frac{1}{N_A} \nabla \mu (1 - \exp \left[ -\frac{\zeta}{m} \right])
\end{align*}
\]

**Steady state (SS) velocity**

\[
\begin{align*}
v_{ss} = -\frac{1}{N_A} \nabla \mu
\end{align*}
\]

**Friction coefficient**

\[
\begin{align*}
\zeta = \frac{1}{k}\text{g.s}^{-1}
\end{align*}
\]

**Material flux of ion in solution**

\[
\begin{align*}
\nabla j_i = c_i \nabla \mu_i = -\frac{c_i}{N_A} \nabla \mu_i = -c_i \nabla \mu_i
\end{align*}
\]

**Steady State material flux expression for species** \( j \) in fluid may be derived.

\[
\begin{align*}
j_i = -D_j \nabla c_j - \frac{z_i F}{RT} D_j c_j \nabla \phi + c_j \nabla c_i
\end{align*}
\]

**Equation of continuity (fluid mechanics)**

\[
\begin{align*}
\frac{\partial c_j}{\partial t} = D_j \nabla^2 c_j - \nabla \cdot (c_j \nabla \phi) + \nabla \cdot (\vec{f}_j)
\end{align*}
\]

**Diffusion Migration Convection**

**Time dependent material transport equation for flow of species** \( j \) in fluid medium can then be derived.

\[
\begin{align*}
\frac{\partial c_j}{\partial t} = D_j \nabla^2 c_j + \frac{z_i F}{RT} \nabla \cdot (c_j \nabla \phi) - \nabla \cdot (c_j \nabla v)
\end{align*}
\]

**Diffusion Migration Convection**

In many situations in electrochemistry we work under conditions where an excess of supporting electrolyte is used and so the migration component can be neglected. This results in the convective - diffusion equation. This expression relevant to describe transport in flowing streams or to rotating electrodes.

\[
\frac{\partial c_j}{\partial t} = D_j \nabla^2 c_j - \nabla \cdot (c_j \nabla \phi)
\]

In a stationary (unstirred) solution and if the electrodes do not rotate then we can neglect forced convection and we have the Fick time dependent diffusion equation.

\[
\frac{\partial c_j}{\partial t} = D_j \nabla^2 c_j
\]

This equation is solved subject to the stipulation of specified initial and boundary conditions via standard analytical or numerical techniques to obtain an expression for the concentration profile of reactant as a function of distance and time \( c(r,t) \). The current response may be subsequently derived via differentiation with respect to distance.
Planar Diffusion
Rectangular Cartesian Co-ordinates \((x,y,z)\):

\[ c = c(x, y, z, t) \]

Cylindrical Diffusion
Cylindrical Polar Co-ordinates \((r, \phi, z)\):

\[ c = c(r, \phi, z, t) \]

Spherical Diffusion
Spherical Polar Co-ordinates \((r, \theta, \phi)\):

\[ c = c(r, \theta, \phi, t) \]

Choice of co-ordinate system depends on type of electrode geometry.

Time dependent Fick diffusion equation (TDFDE) in various Co-ordinate systems.

<table>
<thead>
<tr>
<th>Co-ordinate System</th>
<th>Fick Diffusion Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cartesian</td>
<td>( \frac{\partial c}{\partial t} = D \nabla^2 c )</td>
</tr>
<tr>
<td>Cylindrical Polar</td>
<td>( \frac{\partial c}{\partial t} = D \left( \frac{\partial^2 c}{\partial r^2} + \frac{1}{r} \frac{\partial c}{\partial r} \right) + \frac{\partial^2 c}{\partial \phi^2} )</td>
</tr>
<tr>
<td>Spherical Polar</td>
<td>( \frac{\partial c}{\partial t} = D \left( \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial c}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial c}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 c}{\partial \phi^2} \right) )</td>
</tr>
</tbody>
</table>

Primary objective is to solve the TDFDE in a form appropriate for a particular electrode geometry, subject to various initial and boundary conditions to obtain expressions for both the concentration profile and the concentration gradient.

We consider an infinite volume of pure solvent at equilibrium. We let a sharply defined spike of solute be introduced into the central region of the solvent at time $t = 0$. This defines the origin at $x = 0$. The solute diffuses through the solvent until there is a homogeneous dispersion of solute molecules throughout the solvent. The problem is to quantify the diffusive spread of solute through the medium in either direction from the origin as a function of distance and time.

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$$

Initial condition

$$c(x,0) = c_0$$

$$c(x,t) = \frac{c_0}{\sqrt{4\pi Dt}} \exp \left[ -\frac{x^2}{4Dt} \right]$$

The solution to the initial value problem is a Gaussian function.

$$\lim_{t \to \infty} c(x,t) = 0$$

Initial injection

Solute spreads out

Short times

Long times
Passive diffusion in a finite membrane.

We examine the diffusion of a molecule through a membrane of finite thickness $L$ from a donor compartment to an acceptor compartment. This is a basic model for the transdermal delivery of drugs (nicotine patch).

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$$

where $c(x,0) = 0$ and $c(L,t) = 0$.

$k =$ partition coefficient

$c^\infty =$ concentration in membrane

We scale the boundary value problem and express in dimensionless variables.

We scale the boundary value problem and express in dimensionless variables.

Potential step chronoamperometry: reversible process.

We describe the transient electrochemical technique called Potential Step Chronoamperometry (PSCA) in which a potential step of magnitude $\Delta E$ is applied to an electrode and a Nernstian electrochemical redox transformation occurs in response to the potential step perturbation causing a current to flow.

$$\Psi(t) = \int_0^t \frac{N(t)}{N_0} \Psi(t) \, dt - \tau \cdot \frac{N(t)}{N_0}$$

where $\tau = 1/6$.

$\Psi(t) = \int_0^t \Psi(t) \, dt - \tau \cdot \frac{N(t)}{N_0} \exp\left[-\frac{nE^2}{RT}\right]$

and

$$\Delta E = 0.8 \text{ V}$$

$C_0^\infty = 1 \text{ mM}$

$D = 1.0 \times 10^{-5} \text{ cm}^2/\text{s}$

Frederick G. Cottrell
American Chemist
1877 - 1948
\[
\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}
\]

\[
c(x,0) = c^* \quad c(0,t) = 0 \quad c(x,t) = c^* 
\]

\[
\Gamma = \frac{x}{2\sqrt{Dt}}
\]

\[
\frac{d^2 c}{d\Gamma^2} + 2\Gamma \frac{dc}{d\Gamma} = 0 
\]

\[
x = 0, \quad \Gamma(0) = 0, \quad c = 0 
\]

\[
x = \infty, \quad \Gamma(\infty) = \infty, \quad c = c^* 
\]

\[
c = A\text{erfc}[\Gamma] + B\text{erfc}[-\Gamma] 
\]

\[
erfc[0] = 1 \quad \text{erfc}[x] = 0 \quad \text{erfc}[\infty] = 2 \quad \text{erfc}[-\Gamma] = 2 - \text{erfc}[\Gamma] 
\]

\[
B = -A
\]

\[
c = c^* [1 - \text{erfc}[\Gamma]] = c^* \text{erf}[\Gamma] 
\]

\[
c^*(x,t) = c^* \left[1 - \text{erf} \left( \frac{x}{2\sqrt{Dt}} \right) \right] = c^* \text{erf} \left( \frac{x}{2\sqrt{Dt}} \right)
\]

\[
c^*_t(x,t) = c^* \left[1 - \text{erf} \left( \frac{x}{2\sqrt{Dt}} \right) \right] = c^* \text{erf} \left( \frac{x}{2\sqrt{Dt}} \right)
\]

\[
\text{Red(aq)} \rightarrow \text{Ox(aq)} + n\text{e}^-
\]

\[
\text{Reactant R completely oxidized at electrode surface}
\]

\[
C^* = 1 \text{ mM} 
\]

\[
D = 1.0 \times 10^{-5} \text{ cm}^2 \text{s}^{-1}
\]

\[
\text{Diffusive depletion (diffusion layer)}
\]
Potential step chronoamperometry.

- Apply potential step of amplitude $\Delta E$ to an electrode.
- Redox reaction occurs as a result of the potential step perturbation.
- Measure resulting current variation with time.
- Analyse $i$ vs $t$ response curve to obtain transport and kinetic information.
- If ET process is Nernstian (facile ET) then the transient current response is governed by the Cottrell equation.
- The diffusion coefficient $D$ may be obtained readily.
- If both $D$ and $c^\infty$ are both known then electrode area $A$ may be evaluated via PSCA analysis.

\[ i(t) = \frac{nFA_c}{\sqrt{\pi}} \frac{Dc^\infty}{2} \frac{t^{-1/2}}{S_C} \]


\[
f_c = \frac{D}{2\sqrt{\pi}} \left( \frac{\partial c}{\partial t} \right)_{r=a} = \frac{D}{2\sqrt{\pi}} \frac{2c^\infty}{\sqrt{\pi}} = \sqrt{\frac{Dc^\infty}{\pi}}
\]

\[
f_c = \frac{i}{nFA} = B \left( \frac{\partial c}{\partial t} \right)_{r=a} = \frac{D}{2\sqrt{\pi}} \left( \frac{\partial c}{\partial t} \right)_{r=a}
\]

\[
\frac{d}{dz} \text{erf}[z] = \frac{2}{\sqrt{\pi}} \exp[-z^2]
\]

\[
\left( \frac{\partial c}{\partial t} \right)_{r=a} = \frac{2c^\infty}{\sqrt{\pi}}
\]

Cottrell Plot

\[
\delta \quad \mu m \quad \tau / s
\]

<p>| | |</p>
<table>
<thead>
<tr>
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</tr>
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<tbody>
<tr>
<td>1</td>
<td>10^{-3}</td>
</tr>
<tr>
<td>10</td>
<td>0.1</td>
</tr>
<tr>
<td>100</td>
<td>10</td>
</tr>
</tbody>
</table>

\[
r = \frac{\delta^2}{2D}
\]

\[
D = \frac{\pi S_C^2}{n^2 F^2 A^2 c^\infty}
\]
As potential step experiment proceeds the depletion of reactant species near the electrode surface increases. This is termed the diffusion layer $\delta$ of the electrode. Electroactive material must diffuse across this zone in order to react at the electrode. Hence as time progresses the diffusion layer becomes thicker and the rate of diffusive transport falls and so does the observed diffusion limited current.

At long times however, rather than the current falling off to zero as predicted by the Cottrell equation, the experimentally measured current tends to an approximately steady value. This is consistent with a model in which the bulk solution beyond a critical distance $d$ from the electrode is well mixed due to the onset of natural convection (movement of the solution brought about by density differences), so that the concentration of the electroactive species is maintained at a constant bulk value $c^\infty$.

In the Nernst model the concentration changes linearly in the diffusion layer and the diffusive flux and diffusion limited current is readily determined from Fick’s first law.

\[
\tau = \frac{\delta^2}{2D}
\]

<table>
<thead>
<tr>
<th>$\delta$ / $\mu$m</th>
<th>$\tau$ / s</th>
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<tr>
<td>1</td>
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</table>

![Diagram of Nernst diffusion layer](image)

**Nernst diffusion layer**

**Transport and kinetics in electrochemical systems: Nernst diffusion layer approximation.**

Simple diffusion layer model neglects convection effects and also simplifies analysis of Fick diffusion equations. Important to note that NDL model is approximate. In reality the zone of mixing via natural convection and the stagnant zone of diffusion merge into one another.
Potential Step Chronocoulometry.

The charge $q(t)$ passed during the application of a potential step can be readily evaluated via integration of the Faradaic current transient response curve.

$$q(t) = \int_0^t i(t) \, dt = \frac{nF \Delta C}{\sqrt{\pi}} \int_0^{t^{1/2}} dt$$

$$= 2nFAC \frac{D}{\pi} t^{1/2}$$

Analysis indicates that the charge increases with the square root of electrolysis time.

The extent of electrolysis expressed in terms of the amount of reactant species consumed can also be readily evaluated and is shown to depend on the electrode area, the reactant concentration and on the square root of time and reactant diffusion coefficient.

$$N(t) = \frac{q(t)}{nF} = 2A \frac{D^{1/2}}{\pi} C^{1/2}$$

The total chronocoulometric response contains contributions from the Faradaic ET reaction, double layer charging and possibly, reactant adsorption. A plot of $q(t)$ versus $t^{1/2}$ is linear and is termed an Anson Plot.

$$S_q = 2nFAC \sqrt{D \pi}$$

Anson equation:

$$q(t) = q_{dc} + q_{dl} + 2nFAC \frac{D^{1/2}}{\pi} t^{1/2}$$

Anson Plot:

$$I_s = q_{dc} + nF \Delta I_G$$
Charging and Faradaic currents.

Voltammetric measurements rely on the examination of ET processes at solid/liquid interfaces. Analytical uses of voltammetry rely on measuring current flow as a function of analyte concentration. However applying a potential programme to an electrode necessitates the charging of the solid/liquid interface up to the new applied potential. This causes a current to flow which is independent of the concentration of analyte. Hence the observed current is the sum of two contributions, the charging current and the Faradaic current.

The Faradaic current $i_F$ is of primary analytical interest since this quantity is directly proportional to the bulk concentration of the analyte species of interest. The objective is to maximise $i_F$ and minimise $i_C$. Note that $i_C$ is always present and has a constant residual value. As the concentration of analyte decreases $i_F$ decreases and will approach the value of the residual value of $i_C$. This places a lower limit on analyte detection and hence on the use of voltammetry as an analytical application.

Potential Step Chronoamperometry: Double Layer Charging.

At the beginning of a potential step the current flowing is mainly attributed to double layer charging. The current flowing at short times (tens of milliseconds or less) is due to supporting electrolyte ion movement near the electrode which causes the interfacial double layer to form. We model the interface region in the absence of Faradaic activity as an equivalent circuit consisting of a resistor $R_S$ and a capacitor $C_{DL}$ in series. We calculate the charge flowing when a potential $\Delta E$ is applied across this $RS$ series assembly.

We introduce the relationship between current and charge to obtain a differential equation which may be readily integrated subject to a suitable initial condition using standard methods (e.g. Laplace Transforms).

$$\Delta E = i R_S + \frac{q}{C_{DL}}$$
$$\frac{dq}{dt} = -\frac{q}{R_S C_{DL}} + \frac{\Delta E}{R_S}$$
$$q(t) = \Delta E C_{DL} \left[ 1 - \exp \left( \frac{-t}{R_S C_{DL}} \right) \right] = \Delta E C_{DL} \left[ 1 - \exp \left( \frac{-\tau}{R_S C_{DL}} \right) \right]$$
$$l_i(t) = \frac{dq}{dt} = \frac{\Delta E}{R_S} \exp \left( \frac{-t}{R_S C_{DL}} \right)$$

We predict that a plot of $\ln l_i$ versus time $t$ should be linear with a slope $S = 1/R_S C_{DL}$ and intercept $I = \ln(\Delta E/R_S)$. Hence the solution resistance $R_S$ and the double layer capacitance $C_{DL}$ may be evaluated from this semi-logarithmic plot.

The current charging the double layer capacitance drops to $1/e$ or 37% of its initial value at a time $t = \tau$ and to 5% of its initial value at $t = 3\tau$. Hence if $R_S = 1\Omega$ and $C_{DL} = 20\mu F$ then $t = 20\mu s$ and DL charging is 95% complete at $t = 60\mu s$. 

$$\ln I = \ln \left( \frac{\Delta E}{R_S} \right) = \frac{1}{R_S C_{DL}} t$$
Charging current and Faradaic current contribution can be computed for various transient electrochemical techniques. Potential step technique.

\[
i_c = \frac{\Delta E}{R_s} \exp \left( -\frac{t}{R_s C_{dl}} \right)
\]

\[
i_F = nFAD^{1/2}c^\infty
\]

Charging current decays much more rapidly than Faradaic current.

\[
i_F(t) = i_F \exp \left( -\frac{D c(t)}{2uz} \right)
\]

\[
i_c(t) = i_c \left( 1 - \exp \left( -\frac{2uz}{D c(t)} \right) \right)
\]

Take reading when \( i_c \) is small.

A similar quantitative analysis can be done for other EC methods such as cyclic and linear potential sweep voltammetry.

**Reversible ET**

Electrode

Solution

- \( A_0 \)
- \( k_b \)
- \( k_0 \)
- \( B_0 \)

| \( f_b = k_b a^\infty = Da^\infty \delta \) |

Mass transport

**Heterogeneous ET**

- Normalised steady state diffusion equations
  - \( \frac{\partial^2 \chi}{\partial x^2} = 0 \)
  - \( \frac{\partial \chi}{\partial x} = 0 \)
  - \( \chi = 0 \quad u = u_0 \quad v = v_i \)
  - \( \chi = 1 \quad u = 1 \quad v = 0 \)
  - \( u = \frac{a}{a} \quad v = \frac{b}{a} \quad \chi = \frac{x}{\delta} \)

- Boundary conditions

- Normalised current
  - \( \Psi = \frac{f_i}{f_b} \)
  - \( \Psi = \frac{1}{1 + \exp \left( -\frac{\xi}{\eta_i} \right)} \)
  - \( \xi = \frac{F}{RT}(E - \chi) = \theta - \theta_i \)
  - \( \exp \left( \xi \right) = \frac{\eta_i}{\eta_i} \)
  - \( \theta = \theta_i + \ln \left( \frac{v_i}{v_o} \right) \)
  - \( a_i = \frac{a}{a} \quad v_i = \frac{b}{a} \)

**Situation pertains when ET kinetics are fast and Nernst**
Irreversible ET

Normalised Current

\[ \psi = \frac{f_z}{f_D} = \frac{1}{1 + \zeta^{-1} \exp[-\beta \xi]} \]
\[ \zeta = \frac{k^0}{k_D} \]
\[ \xi = \theta - \theta_0 = \frac{F}{RT} (E - E^0) \]
\[ \theta = \theta_{1/2} \quad \text{when} \quad \Psi = 1/2 \]
\[ \theta_{1/2} = \theta_0 + \beta^{-1} \ln \left( \frac{\xi}{\zeta} \right) \]

Situation pertains when ET kinetics are very sluggish.

Quasi reversible ET

Normalised current

\[ \Psi = \frac{f_z}{f_D} = \frac{\exp[\beta \xi]}{\zeta^{-1} + \exp[\beta \xi] \left[ 1 + \exp[-\xi] \right]} \]

Most general situation: Intermediate between reversible and irreversible limits.
General shape adopted by current/voltage curve for a simple outer sphere redox couple A/B.

Region of mixed Rate control. Both ET and MT Important.

Diffusion: material transport due to existence of a concentration gradient.

Material transport via diffusion rate limiting

Electrode

Solution

Interfacial ET Kinetics rate limiting

Normalised current

Material transport

Normalised potential


General current/potential response for outer sphere ET process, both forms of redox couple present in solution.
Random walk model of diffusion

We now examine diffusive matter transport from a microscopic point of view. The most appropriate description of molecular movement on a microscopic scale is that of a random or stochastic process. Molecular displacements are best analyzed using statistical methods and probability theory.

The trajectory or path of a diffusing molecule is described in terms of a random walk. The diffusing particles move in a series of small uncorrelated random steps and gradually move away from their original positions.

We assume that the particles can jump through a distance \( L \) and do so in a time \( \tau \). Hence the distance covered by a particle in a time \( t \) is given by \( (t/\tau)L \).

We consider the following 1D problem. The particle starts off from \( x = 0 \) and can move right or left: each choice is equally probable hence the probability = \( \frac{1}{2} \) for each case. In a random process each successive step is independent of the previous one (analogous to the meandering of a drunken undergraduate). The direction which the particle will take is not influenced by preceding steps.

The problem is to determine the probability that the particle will be found at a distance \( x \) from the origin at a time \( t \) after taking a certain number \( n \) of steps. This corresponds to a specific walk (experiment). We then repeat the process many times in order to obtain good statistical averaging (one has many walks).

During this time interval the diffusing particle will have taken \( n \) steps where the net displacement \( s = t/\tau \). The total number of steps is given by \( n = n_R + n_L \). Also the net distance travelled, \( x = n_R L - n_L L \), where \( L \) is the step length. Hence \( n_R - n_L = x/L \).

The probability of the particle being located at a distance \( x \) after \( n \) steps of length \( L \) is simply given by the probability that of the \( n \) steps, \( n_R \) occurred to the right and \( n_L \) occurred to the left.

Since each step can occur in one of two directions (left or right) each with a probability of \( \frac{1}{2} \), then after \( n \) steps, the probability of a right step or a left step is \( \left(\frac{1}{2}\right)^n \). We now must determine the number of ways of taking \( n_R \) steps in a total of \( n \) steps. This problem is the same as determining the number of ways of choosing \( n_R \) objects from a box containing \( n \) objects irrespective of the order. This can be readily calculated from simple probability theory as the binomial coefficient:

\[
\binom{n}{n_R} = \frac{n!}{n_R!(n-n_R)!}.
\]

Hence the probability \( P_n(x) \) of being at position \( x \) after taking (in a total of \( n \) steps) \( n_R \) steps to the right and \( n_L = n-n_R \) steps to the left in any order is simply obtained by multiplying the probability of this sequence, \( \left(\frac{1}{2}\right)^n \), by the number of possible sequences of such steps (the Binomial coefficient). This yields the Binomial Distribution Function:

\[
P_n(x) = \binom{n}{n_R} \left(\frac{1}{2}\right)^{n} = \frac{n!}{n_R!(n-n_R)!} \left(\frac{1}{2}\right)^{n}
\]

Binomial Distribution Function

\[
P_n(x) = \frac{n!}{\left(\begin{array}{c} n+1 \choose 2 \end{array}\right)} \times \frac{1}{2^n} \left(\frac{n+x}{2}\right) \left(\frac{n-x}{2}\right).
\]
Random Walk Binomial Distribution Function.

The Binomial distribution function has been calculated for \( n = 10, 20, 100 \) and 500 and presented in histogram form.

We note that as the number of steps \( n \) increases, then the distribution function \( P_n(s) \) becomes more defined and approaches the symmetric ‘bell shape’ characteristic of the Gaussian distribution.

We can calculate the average and root mean square displacement using standard methods.

\[
\langle s \rangle = \sum_{s=0}^{n} s P_n(s) = 0
\]
\[
\langle s^2 \rangle = \sum_{s=0}^{n} s^2 P_n(s) = n
\]
\[s_{rms} = \sqrt{\langle s^2 \rangle} = \sqrt{n}
\]

Hence the width of the probability distribution varies as \( n^{1/2} \).

The mean square distance travelled by a diffusion particle after \( n \) steps, each step being of length \( L \) can also be readily evaluated. This is called the mean free path.

\[
\langle s^2 \rangle = \frac{s_{rms}^2}{L} = \sqrt{nL}
\]
\[
\langle x^2 \rangle = nL^2
\]

When \( n \) is very large one can show (the maths are tedious) that the Binomial distribution function changes to a Gaussian function.

\[
P_n(s) \approx \frac{2}{\sqrt{2\pi n}} \exp \left[ -\frac{s^2}{2n} \right]
\]

Now only even values of \( s \) are allowed if \( n \) is even.
And only odd values are allowed if \( n \) is odd.
Hence this expression is valid for \( n \) and \( s \) values of similar parity (even/odd characteristic).

\( P_n(s) \) will be zero if there is a difference in parity between \( n \) and \( s \).
Hence we must develop an expression for the probability as a function of the distance parameter \( x \).
We therefore calculate the probability that a particle is located in an interval between \( x \) and \( x + dx \) at some time \( t \):

\[
P(x)dx = P(x)dx = \frac{2}{\sqrt{2\pi m}} \exp \left( -\frac{x^2}{2m} \right) dx = \frac{1}{\sqrt{2\pi mL^2}} \exp \left( -\frac{x^2}{2L^2} \right) dx
\]

We now assume that the diffusing molecule takes \( z \) steps per unit time and we note that \( n = zt = t/\tau \). Hence the probability expression reduces to the following form.

\[
P(x,t)dx = \frac{1}{\sqrt{2\pi zL^2}} \exp \left( -\frac{x^2}{2zL^2} \right) dx
\]

Hence the probability that a particle which was initially located at \( x = 0 \) at \( t = 0 \) will be found at a position \( x \) at a subsequent time \( t \) can be readily defined. The expression provides an expression for the diffusive spread as a function of time.

\[
P(x,t) = \frac{1}{\sqrt{4\pi dL^2 t}} \exp \left( -\frac{x^2}{4dLt} \right)
\]

The fundamental step frequency \( z = 1/\tau \) (where \( \tau \) denotes the fundamental jump time) and the mean free path \( L \) are now combined together in a new constant factor called the diffusion coefficient \( D \). This results in a modified form of the probability for diffusive spread.

\[
D = \frac{L^2}{2} \quad \frac{D}{t} = \frac{L^2}{6t}
\]

We recall the solution to the Fick diffusion equation for infinite diffusion from a point source.

\[
x(x,t) = \frac{c_0}{\sqrt{4\pi dL t}} \exp \left( -\frac{x^2}{4dLt} \right)
\]

Hence both the macroscopic solution to the diffusion equation and the microscopic solution derived via application of probability theory to many small steps of a randomly diffusing molecule, yield the same result.

Hence both the macroscopic solution to the diffusion equation and the microscopic solution derived via application of probability theory to many small steps of a randomly diffusing molecule, yield the same result.

\[
x_{rms} = \sqrt{\langle x^2 \rangle} = \sqrt{4\pi dL t} = \sqrt{2dLt}
\]

We recall that \( \langle x^2 \rangle = nL^2 \) and also \( n = zt \). Hence the mean square distance travelled in a time \( t \) is \( \langle x^2 \rangle = 2L^2t \). Hence the mean distance travelled is related to the diffusion coefficient as follows.

\[
x_{rms} = \sqrt{\langle x^2 \rangle} = \sqrt{2L^2 t} = \sqrt{2Lt}
\]

**Einstein-Smoluchowski Equation**

**Diffusion regarded as an activated rate process (Eyring).**

We can adopt a more detailed view of the fundamental random hopping event. We have introduced two fundamental parameters, the mean jump distance \( L \) and the jump frequency \( z = 1/\tau \). The diffusion coefficient is related to these two quantities via well defined expressions which depend on whether the diffusive process is 1D or 3D.

We now examine the structure of a liquid medium in which diffusion is taking place. The structure of a liquid is local in extent and transitory in time and mobile in space.

During a random walk the diffusing species jumps out of one site in the liquid structure and enters into another adjacent site. The mean jump distance \( L \) represents the average distance between sites and will therefore depend on the detail of the liquid structure.

There is a formal analogy here between ion jumping and chemical reaction \( AB + C \rightarrow A + BC \), since formally we have a jump of an atom \( B \) from a site in \( A \) to a site in \( C \). Both are activated rate processes. We discuss the approach adopted by Eyring to diffusion when it is viewed as an activated rate process.

The fundamental idea behind the Eyring approach is that the potential energy (or the Gibbs energy) of a system of particles involved in a rate process varies as the particles move to accomplish the process. If the Gibbs energy of the system is plotted versus the position of the moving particle then the energy of the system has to attain a critical value termed the activation free energy \( \Delta G^* \) for the process to be accomplished.
The number of times per second, $z$, that the rate process occurs (the jump frequency) for diffusive hopping from site to site can be evaluated via the Eyring equation:

$$
z = \frac{1}{\tau} = \frac{k_0}{h} \exp\left(\frac{-\Delta G^*}{RT}\right) = \frac{k_0}{h} \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(\frac{\Delta H^*}{RT}\right)
$$

We develop the Eyring expression for the diffusion coefficient $D$ as follows.

$$
D = \rho \frac{L^2}{\tau} = \rho \frac{L^2}{h} \exp\left(\frac{-\Delta G^*}{RT}\right) = \rho \frac{L^2}{h} \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(\frac{-\Delta H^*}{RT}\right)
$$

Numerical factor defining Dimension of diffusion process.

$\rho = \frac{1}{2} (1-D), \rho = \frac{1}{6} (3-D)$

We can define an Arrhenius equation for diffusion. The diffusion coefficient exhibits an Arrhenius type behaviour with changes in temperature $T$. Typically the activation energy for diffusion is ca. 15 kJ/mol.

$$
D = A_0 \exp\left[\frac{E_{A,D}}{RT}\right]
$$

$$
A_0 = \rho \frac{L^2}{h} \exp\left[\frac{\Delta S^*}{R}\right]
$$

$E_{A,D} = -R \left(\frac{d \ln D}{d(1/T)}\right)$
Linear sweep and cyclic voltammetry.

- Linear sweep voltammetry (LPSV) and cyclic voltammetry (CV) are the most well known and popular electrochemical technique in use today.
- In both techniques a defined time varying potential ramp is applied to a working electrode causing an interfacial ET reaction to occur. The current flowing from this process is monitored and the resulting plot of current versus applied potential (the voltammogram) is recorded.
- Again the quantitative basis of the method is the solution of the time dependent Fick diffusion equation.
- This initial and boundary value problem cannot be solved totally analytically but the integral equation obtained which describes the voltammetric current response has to be solved numerically.

### Linear Potential Sweep Voltammetry.

**Reversible ET**

**Normalised Current**

\[ i = \frac{nFA \sqrt{nFDu/RT}}{a} \phi \]

**Normlised variables**

\[ u = \frac{a}{a^2} \quad v = \frac{b}{a} \]

\[ \tau = \frac{nFA}{RT} \]

\[ \xi = \frac{nE}{RT} (E(t) - E^*) \]

\[ E(t) = E_0 \pm \xi \]

\[ \xi(t) = \xi \pm \tau \]

**Integral equation for normalised current**

\[ \int_1^{\xi+\xi} \frac{1}{\sqrt{\pi}} \frac{1}{\sqrt{\tau - \lambda}} d\lambda = \int_1^{\xi+\xi} \frac{1}{1 + \exp[-\xi(t)]]} \]

\[ \Psi(\xi) = \int_1^{\xi+\xi} \frac{1}{1 + \exp[-\xi(t)]]} \]

\[ \Psi(\xi) = \frac{1}{\sqrt{\pi}} \sech \frac{\xi}{2} \]

**Randles Sevcik equation for peak current**

\[ I_p = nFA\sqrt{nFDu/RT} a^* \Psi_p \]

\[ I_p = 0.446 \]

**Integral defining normalised current**

\[ E_p = E^* \]

\[ \Psi_p = 0.446 \]
Analytical Approximation to LPS Voltammogram for reversible ET

\[ \Psi_{NS} = \frac{nF(A\sqrt{nFD\nu})}{RT \alpha^2} = \sqrt{\pi X_{NS}} \]

\[ \frac{1}{\sqrt{\pi}} \int_{0}^{\xi} \frac{\Psi(\lambda)}{\sqrt{\tau - \lambda}} d\lambda = \frac{1}{1 + \exp[-\xi(\tau)]} \]

\[ \Psi_{NS}(\xi) \approx \frac{a_1 \theta + a_2 \theta^2}{b_1 + b_2 \theta + b_3 \theta^2} \]

\[ a_1 = 0.9933 \]
\[ a_2 = 0.0944 \]
\[ b_1 = 1.0000 \]
\[ b_2 = 1.5221 \]
\[ b_3 = 0.3349 \]

Prasad & Sangaranarayanan
JEC, 2003

LPS Voltammetry. Reversible ET

D = 10^{-5} \text{ cm}^2\text{s}^{-1}; T = 298K; n = 1; c = 0.001 M
Sweep rate = 0.1 V s^{-1}

DigiSim Programme
Cyclic Voltammetry (CV) is a form of electrochemical spectroscopy. In CV the potential applied to the electrode is swept in a linear manner from an initial value \( E_i \) to a given intermediate value \( E_l \) and then the direction of the potential scan is reversed to a final value \( E_f \). Usually the initial and final potentials are the same.

The output obtained is called a voltammogram and is a plot of current versus applied potential. A series of peaks appears at definite potentials corresponding to the occurrence of oxidation and reduction reactions at the electrode surface. A major experimental variable is the sweep rate \( \frac{dE}{dt} = v \). This defines the experimental time scale.

Typically the shape of the voltammogram as a function of sweep rate is examined. Peak potentials \( E_p \), peak currents \( i_p \), peak separations \( \Delta E \) and peak widths at half peak heights \( d \) are measured as a function of sweep rate.

Cyclic Voltammetry. Reversible ET.

- CV profile obtained via Digital Simulation (using commercial software, CH Instruments) of Time Dependent Fick Diffusion equations for A and B.
- Implicit Finite Difference Method Used.
- Analytical solution of diffusion equations even for the simple case of reversible ET, results in the generation of an integral equation which can only be solved numerically.
- Hence digital simulation is a powerful technique when more complicated situations (irreversible ET, coupled ET and homogeneous chemical reactions) are considered.

CV profile for a reversible ET process will exhibit sharp and well defined peaks with a defined peak separation.
CV : Diagnostic Features

- If ET process is rapid (Nernstian $E_{\text{rev}}$ process) then we expect that:
  - Peak current varies linearly with both the bulk concentration of the reactant and the square root of the sweep rate according to the Randles-Sevcik equation.
  - The voltammetric peak potentials are invariant with respect to changing sweep rate.
  - The oxidation/reduction peak current ratio is approximately unity at all sweep rates.
  - The standard redox potential is the average of the anodic and cathodic peak potentials.

$$i_p = 0.446nFAC^c\sqrt{\frac{nFE}{RT}} \left(\frac{0.446nFAC^c}{nF/RT}\right)^{1/2}$$

$$\Delta E_p = E_{\text{red}} - E_{\text{ox}} = \frac{0.058}{n} V \quad (T = 298K)$$

Cyclic Voltammetry. Reversible ET

D = $10^{-5}$ cm$^2$s$^{-1}$; T = 298K; n = 1; c = 0.001 M
Sweep rate = 0.1 Vs$^{-1}$
LPS Voltammetry: Irreversible ET.

- $k_0 = 10^{-4}$ cm/s
- $D = 10^{-5}$ cm$^2$/s
- $b = 0.5$
- $E^0 = 0.3$ V

$E_{1/2} \neq E^0$

Electrode kinetics are finite: cause distortion of voltammogram.

Cyclic Voltammetry: Effect of slow ET kinetics

- $k_0 = 10^{-7}$ cm s$^{-1}$
- $k_0 = 1$ cm s$^{-1}$
- $k_0 = 10^{-3}$ cm s$^{-1}$
- $k_0 = 10^{-6}$ cm s$^{-1}$

Sweep rate = 0.1 V/s
- $D = 10^{-5}$ cm$^2$/s
- $C = 1$ mM

Peak shapes become less sharp as ET kinetics become more sluggish.
**Determination of kinetic parameters using CV.**

- Shape of CV response depends on kinetic facility of interfacial ET.
- As electrochemical rate constant $k_0$ decreases, the anodic/cathodic peak separation $\Delta E_p$ increases and the peak current decreases.
- ET processes are termed
  - Reversible ($E_{rev}$) if $k_0 > 0.1$ cm/s
  - Quasi-reversible ($E_{qr}$) if $(10^{-5} < k_0 < 0.1)$ cm/s
  - Irreversible ($E_{irrev}$) if $k_0 < 10^{-5}$ cm/s.
- CV profiles become more drawn out if interfacial ET kinetics are sluggish.
- It can sometimes be difficult to distinguish between the effects of slow ET kinetics and finite solution resistance effects when analysing the shape of the CV profile since both effects can result in CV profile distortion.
- We can evaluate $k_0$ by noting $DEP$ at some given scan rate $n$. Using the theoretical working curve shown across we can then calculate the corresponding value of $Y_N$ and hence evaluate $k_0$.

$$\Psi_N = \left( \frac{D_{OX}}{D_{RED}} \right)^{\beta/2} k_0^\gamma$$


---

**Cyclic Voltammetry**

**Quasi Reversible ET Kinetics**
Effect of capacitative current flow.

- Net current consists of both Faradaic ($i_F$) and Charging ($i_C$) components. These vary with sweep rate in different ways.
- The charging current component becomes important when the concentration of redox species is low or the scan rate is large.
- This is a major limitation of CV as a technique.
- This can be addressed using ultramicroelectrodes.

\[
i_F = 0.446nFAdc \left( \frac{\nu F D}{RT} \right)^{1/2}
\]

\[
i_C = C_{dl} \left( \frac{E}{R_t} \right) + C_{dc} \exp \left( \frac{t}{\tau} \right)
\]

\[
\tau = \text{time constant} = R_t C_{dc}
\]

Limitations of cyclic voltammetry

- **Charging current contribution**
  - Important when sweep rate is large and when concentration of electroactive species is low.
- **Uncompensated solution resistance**
  - Important especially in non-aqueous solutions and at fast sweep rates.
- Both effects can be minimized if the size of the working electrode is made very small.
- Hence electrochemical studies using ultramicroelectrodes (UME) are now very common.
  - UME systems minimize both charging current and uncompensated solution resistance effects in CV studies and also result in greatly enhanced rates of material transport to the electrode surface. This facilitates measurement of fast ET processes.
Ultramicroelectrodes

- Ultramicroelectrodes (UME's) are of small size, typically between 0.6 – 100 mm radius.
- Most common construction involves sealing a wire into soft glass and exposing the end to form an inlaid disc electrode.
- Have a wide range of microelectrode geometries including disc, disc array, microring, interdigitated array, hemisphere, etc.
- Diffusion to a microelectrode is not planar but is convergent and can be approximated as spherical.
- UME systems minimize both charging current and uncompensated solution resistance effects in CV studies.
- In CV the charging current has a limiting value given by the product n CDL. Since the double layer capacitance is proportional to the electrode area then it will vary as the square of the electrode radius. The Faradaic current under steady state conditions varies as the electrode radius. Hence the ratio of the Faradaic to the charging current is improved as the electrode radius decreases. This advantage more than offsets any disadvantage derived from the small current flow that must be measured at microelectrodes.
- Diffusion to a microelectrode is very efficient and results in greatly enhanced rates of material transport to the electrode surface. This facilitates measurement of fast ET processes.

Typical range of electrode size.

Small size = new chemistry and physics!
Better space, time and energy resolution.
Literature references


*Figure 1* Illustrations of the most common microelectrode geometries, and their diffusion fields.
Microelectrode Gallery

Sigmoidal shape: characteristic of radial diffusion.

Peak Shape: characteristic of Planar diffusion.

Figure 3 Cyclic voltammetric response at slow scan rates for the oxidation of 10 mM ferrocene at a gold disk microelectrode ($r = 65 \mu m$). Supporting electrolyte is 0.1 M tetrabutyl ammonium perchlorate in acetonitrile. (a) Scan rate is 0.1 V s$^{-1}$, (b) scan rate is 10 V s$^{-1}$.
UME's Radial vs. Planar Diffusion

Radial Diffusion

- Redox wave:
  - sigmoidal shape
- \( I_{ss} = 4nF \nu D_o C^* \)
  - \( I_{ss} \) scan rate independent \( \propto D_o C^* \)

Planar Diffusion

- Redox wave:
  - normal shape
- \( I_p \propto \nu^{1/2} \propto D_o^{1/2} C \)

Planar and non planar diffusion.

- Potential sweep voltammetry performed on macroelectrodes results in characteristic peak shaped current / voltage curves whereas sigmoidal shaped responses are obtained for microelectrodes.
- The rms distance travelled by a diffusion species \( d = (2Dt)^{1/2} \). When \( d \geq a \), the electrode radius non planar convergent diffusion will predominate, and the voltammetric response will be sigmoidal rather than peak shaped.
**Microelectrode geometries:** Some quantitative results.

**Spherical/Hemispherical electrode**

\[
\frac{\partial c}{\partial t} = D \left( \frac{\partial^2 c}{\partial r^2} + \frac{2 \partial c}{r \partial r} \right)
\]

- \(i_D = 4\pi nFDc^e a\) Sphere
- \(i_D = 2\pi nFDc^e a\) Hemisphere

**Inlaid Disc electrode**

\[
\frac{\partial c}{\partial t} = D \left( \frac{\partial^2 c}{\partial r^2} + \frac{1 \partial c}{r \partial r} + \frac{\partial^2 c}{\partial z^2} \right)
\]

- \(i_D = 2nFDc^e d_s\) Sphere
- \(i_D = \pi a\) Hemisphere
- \(i_D = 2a\) Inlaid Disc

**Microelectrode experiments produce sigmoidal voltammograms characteristic of steady state conditions**

Diffusion layer thickness: \(\delta = r_0\)

Diffusion limited current: \(i_d = 2\pi nFD c r_0\)

Microdisc & Microhemisphere Electrodes

Diffusion layer thickness: \(\delta = \frac{r_0}{4}\)

Diffusion limited current: \(i_d = 4nFD c r_d\)

Experiments using ultramicroelectrodes very good for performing accurate kinetic measurements. Disadvantages include low currents and difficult theory!
We make an approximate calculation of the $i_F/i_C$ ratio for an inlaid microdisc electrode of radius $a$ under steady state conditions.

$$i_F = 4nFDc^\infty a$$

$$\frac{i_F}{i_C} \approx \frac{4nFDc^\infty a}{u(\varepsilon \pi / X_H)a^2} = K \left(\frac{c^\infty}{u a}\right)$$

$$K = \frac{4nFDX_H}{\varepsilon \pi}$$

- The ratio of Faradaic current to charging or capacitive current increases with:
  - Smaller electrode radii
  - Slower sweep rates
  - Larger redox species concentrations.
Nano-sized carbon fibre electrodes.


Nanoelectrode

Electrophoretic paint

Fig. 3. The steady-state voltammograms (both forward and reverse scans) of reduction of 0.10 mol dm⁻³ K₂Fe(CN)₆ in 0.5 mol dm⁻³ KCl. Both electrodes were fabricated using three repeated EDP coating/rinsing cycles. The effective radii are calculated from the diffusion-limited currents at 0.9 nm, (a) and 38 nm, (b). Scan rate of 10 mV s⁻¹.

Towards Single Molecule Studies:
- Nanoelectrodes with precisely known radii may be constructed
- Zeptomoles may be measured precisely

(Fe-CH₂-N(CH₃)₂⁺PF₆⁻, 2 mM in 0.2 KCl)
UME's: advantages, disadvantages and applications.

- Advantages
  - Reduced capacitance.
  - Low IR drop.

- Disadvantages
  - Noise.
  - Electrochemical fouling
    - Analyte
    - Method of electrode preparation.
  - Stray capacitance.
  - Maintenance.
    - Cost
    - Fragile construction.

- UME applications
  - Fast electrode kinetics (high sweep rate CV).
  - Biological systems.
  - Study reactions
    - at low temperatures (frozen glasses)
    - in solvents of low to moderate permittivity
      without electrolyte
    - in solvents of high resistance
    - in solid state
    - in gas phase.
  - Development of analytical tools to probe electrode/solution interface (SECM, Bard et al.).

Scanning electrochemical microscopy (SECM)

Diameter (typically 100 nm) of UME tip determines lateral resolution, hence tip geometry important.

Hemispherical diffusion to tip.
Acquire current vs tip position (x,y).
Analyze variation of current vs normalised tip/substrate distance L.

Modes of operation:
- Feedback (positive or negative)
- Collection/Generation.
SECM Operation

- Tip mounted on a three axis positioning stage driven by piezoelectric actuators under software control.
- As tip is scanned in raster pattern across sample surface (substrate) the software produces a map of the electrochemical response of the tip.
- Generally tip current is displayed although tip voltage can also be acquired.
- If substrate is conductive then substrate potential and current can be displayed.
- Any conventional EC measurement (CV, PSCA etc) can be carried out with SECM.
- Great flexibility in operational mode employed:
  - Feedback Mode
  - Generation/Collection Mode, Potentiometric SECM
  - Penetration Experiments
  - Equilibrium Perturbation Mode
  - SECM Imaging
- Micrometer size metal tips used in form of inlaid discs.
- Nanometer scale tips fabricated via EC etching methods.
- Theory well developed using approximate analytical methods especially Finite Difference and Finite Element numerical methods.

SECM set-up for imaging
Imaging Applications

Principles

Tip positioned far from the substrate

\[ i(\infty) = 4 \text{naFDc}^* \]

Negative Feedback

\[ i < i(\infty) = i_{\text{hin}} \]

Positive Feedback

\[ i > i(\infty) = i_{\text{con}} \]
Feedback Modes

- In the feedback mode the tip potential is set to a value at which a particular species in the solution such as a redox mediator is consumed.
- Feedback is the term used to indicate that the measured tip current is influenced by the rate at which the mediator is regenerated at the substrate.
- The substrate may also be subjected to an independent bias and serve as a second working electrode, although it is not necessary that the substrate be another electrode or even be conductive.
- The feedback effect is sensitive to the tip-substrate separation and this distance can be expressed in units of tip radius as $L = d/a$.
- At large values of normalised distance $L$, the tip diffusion layer is not affected by the substrate and is independent of $L$.
- An inlaid microdisc is often used since this tip surface is parallel to the substrate surface and maximizes the feedback effect. Conical electrodes of the type used in STM produce smaller feedback effects than the disc.

- For an oxidizable redox mediator $A$ the process occurring at the tip during a feedback experiment is $A - ne^{-} \rightarrow B$. Now if $E_T$ is poised sufficiently positive then the rate of reaction is diffusion controlled. For large $L$ and if an inlaid disc is used then $i_T = 4nFDc$.
- When $L$ is smaller the product species $B$ can diffuse to the substrate where it can be reduced back to $A$ via $B + ne^{-} \rightarrow A$.
- This reaction produces an additional flux of $A$ to the tip and hence an increase in tip current and so $i_T > i_{\infty}$.
- This phenomenon is termed **positive feedback**.
- As tip-substrate distance $d$ decreases, $i_T$ increases without limit.
- Negative feedback is the terminology used for situations where the product $B$ does not react at the substrate surface since it may be insulating or the $A/B$ reaction may be kinetically irreversible.
• For negative feedback at small $L$ values $i_T < i_{T\infty}$ because the substrate now hinders diffusion of species $A$ from the bulk to the tip surface.
• The smaller $L$ gets the smaller will be the ratio $i_T/i_{T\infty}$.
• For both positive and negative feedback, variations of $i_T$ can be related to changes in $L$, and used to image the substrate topography by scanning the tip over the substrate surface.
• Since the mass transport rate in positive feedback experiments at small $L$ is typically $D/d \sim 0.1 \text{ cm/s}$, convective effects arising from tip motion (typically $10 \mu \text{m/s}$) during imaging can be neglected.
• Since the magnitude of the feedback is sensitive to the rate of mediator regeneration at the substrate surface, the measured feedback/distance behaviour (the approach curve) provides information on the kinetics of the process at the substrate.
• During imaging the $z$ position of the tip is usually fixed and therefore an independent measurement of the tip-substrate distance is useful to de-convolute substrate kinetics from the effects of topography.
• Hence feedback mode kinetic studies are often made at fixed x-y lateral positions but with the tip scanning over a range of $z$ values to generate an approach curve.

Scanning electrochemical Microscopy (SECM): Positive and negative feedback.
Generation/Collection Mode

- Generation/collection (G/C) mode refers to experiments in which species are generated at the substrate independent of the tip reaction and are subsequently detected at the tip, or vice versa.
- These two different G/C modes are referred to as substrate generation/tip collection SG/TC and tip generation/substrate collection TG/SC.
- The ratio of fluxes at the tip and the substrate defines the collection efficiency.
- Owing to the relative sizes of tip and substrate the collection efficiency approaches 100% in the TG/SC mode. Deviations of the collection from 100% can be used to investigate homogeneous chemical kinetics of unstable species in the tip/substrate gap.
- The rates of chemical reactions following an initial electron transfer may be determined by measuring the distance dependence of the collection efficiency. At small L the reverse reaction at the substrate competes with the homogeneous chemical reaction.

Dual electrode generator/collector experiments.

First attempt at ring/disc Generator collector device.

Fig. 5. A photograph of an RD electrode assembly. The diameter of the disc is 3.5 pm.

Behaviour of reaction intermediates probed.