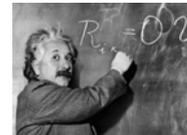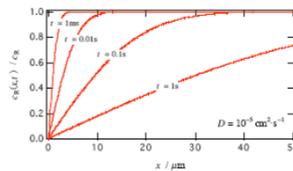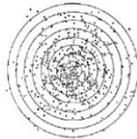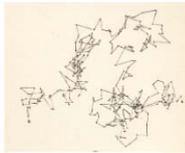Frederik Gardner Cottrell
American Chemist
1877 - 1948

Fig. 1. Adolph Fick, pioneer in the application
of physics, chemistry, and mathematics to
biological systems [Fick, 1903; frontispiece].

Physical and Interfacial Electrochemistry 2013 Lecture 7.
## Material Transport in Electrochemical Systems.

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 <u>material flux</u> 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.

$\overline{\mathbf{v}}$

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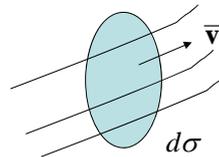
The flux of a species k through an element of area $d\sigma$ is a vector quantity given by

$$\bar{f}_k = c_k \bar{v}$$

Molar concentration (mol cm^{-3})

Fluid velocity vector cms^{-1}

Diffusive Material Transport

Diffusive material transport driven by presence of concentration gradient. Mathematically described by the <u>Fick Diffusion equations</u> (material flow expressions directly analogous to <u>Fourier heat flow</u> (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.

A.E Fick
1829-1901
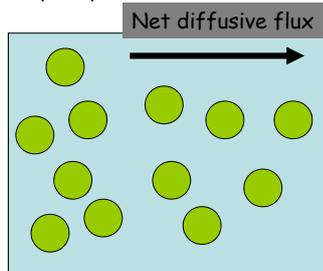
Steady State Fickian Diffusion.

We consider two cases: <u>steady state</u> (time independent) diffusion and <u>transient</u> (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 <u>chemical potential gradient</u>.

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

Net diffusive flux

High solute concentration

Low solute concentration

$$F_D = -c_k \frac{d\mu_k}{dx} \quad \boxed{\text{1-D}}$$

$$F_D = -c_k \nabla \mu_k \quad \boxed{\text{3-D}}$$

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:

$$f_k = \alpha + \beta F_D + \gamma F_D{}^2 + ...$$

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 $f_k = 0$ (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):

Introducing the definition of chemical potential:

$$f_k \cong \beta F_D = -c_k \frac{d\mu_k}{dx}$$

$$\mu_k = \mu_k^0 + RT \ln a_k$$
$$a_k = \gamma_k c_k \cong c_k$$
$$\frac{d\mu_k}{dx} = RT \frac{d \ln c_k}{dx} = \frac{RT}{c_k} \frac{dc_k}{dx}$$

<u>Ideal solution</u> approximation
Activity coefficient $\gamma = 1$.

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

$$\boxed{D \overset{.}{=} \beta RT}$$

$$f_k = \beta F_D = -\beta c_k \frac{d\mu_k}{dx}$$
$$= -\beta c_k \left\{ \frac{RT}{c_k} \frac{dc_k}{dx} \right\} = -\beta RT \frac{dc_k}{dx}$$

We arrive at the Fick equation of steady state diffusion:

$$f_k = -D_k \frac{dc_k}{dx} \quad \boxed{\text{1-D}}$$

$$f_k = -D_k \nabla c_k \quad \boxed{\text{3-D}}$$

2

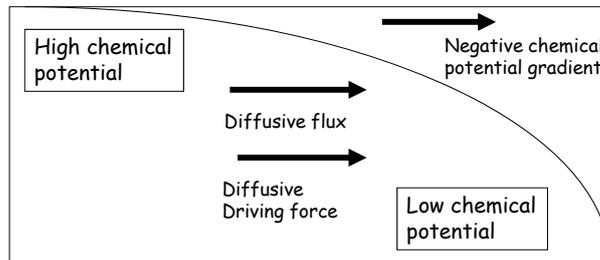More generally if the solution is not ideal the activity coefficient differs from unity.

$$f_k = -D_k \left\{ 1 + \frac{c_k}{\gamma_k} \frac{d\gamma_k}{dc_k} \right\} \frac{dc_k}{dx} = -D_k \left\{ 1 + \frac{d\ln\gamma_k}{d\ln c_k} \right\} \frac{dc_k}{dx}$$

Note that typically the diffusion coefficient is independent of concentration. Diffusion coefficients vary over many orders of magnitude. Typical values are:
<u>Ions in aqueous solution</u>: D≈ 10^{-5} – 10^{-6} cm^{2}s^{-1}.
<u>Ions in polymeric matrices</u>: D ≈ 10^{-8} – 10^{-13} cm^{2}s^{-1}.
<u>Solid state diffusion</u>: D ≈ 10^{-16}-10^{-20} cm^{2}s^{-1}.

High chemical potential

Negative chemical potential gradient

Diffusive flux

Diffusive Driving force

Low chemical potential

Time Dependent (TD) Fickian Diffusion.

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

Inward flux   Unit area

$f_k(x)$

Outward flux

$f_k(x+dx)$

x
$c_k(x)$

dx

$x+dx$
$c_k(x+dx)$
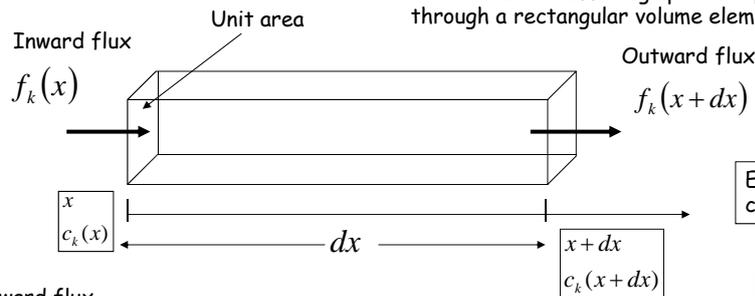
Equation of continuity

$$\frac{\partial f_k}{\partial x} = \frac{\partial c_k}{\partial t}$$

Inward flux

$$f_k(x) = -D_k \frac{\partial c_k(x)}{\partial x}$$

$$f_k(x+dx) = -D_k \frac{\partial c_k(x+dx)}{dx}$$

Outward flux

$$c_k(x+dx) \cong c_k(x) + \frac{\partial c_k(x)}{\partial x} dx$$

$$f_k \cong f_k(x) - f_k(x+dx)$$

$$= -D_k \frac{\partial c_k}{\partial x} - \left\{ -D_k \frac{\partial}{\partial x}\left(c_k + \frac{\partial c_k}{\partial x} dx\right) \right\}$$

$$f_k = D_k \frac{\partial^2 c_k}{\partial x^2} dx$$

$$\frac{\partial f_k}{\partial x} = D_k \frac{\partial^2 c_k}{\partial x^2}$$

1-D

$$\frac{\partial c_k}{\partial t} = D_k \frac{\partial^2 c_k}{\partial t^2}$$

3-D

$$\frac{\partial c_k}{\partial t} = D_k \nabla^2 c_k$$

Fick TD diffusion Equation.

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.

F_v F

$$\overline{F} = -\frac{1}{N_A}\nabla\overline{\mu}$$

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.

$$\overline{F_v} = -\zeta\,\overline{v}$$

Friction coefficient
Units: kgs^{-1}

Total force

$$\overline{F_\Sigma} = \overline{F} + \overline{F_v} = m\frac{d\overline{v}}{dt} = -\zeta\,\overline{v} - \frac{1}{N_A}\nabla\overline{\mu}$$

Material flux of ion in solution (takes Diffusion and migration into account).

$$\overline{f_k} = c_k\overline{v}_{ss} = -\frac{c_k}{N_A\zeta}\nabla\overline{\mu}_k = -c_k\overline{u}_k\nabla\overline{\mu}_k$$

Initial condition
$$t = 0 \quad v = 0$$

$$\frac{d\overline{v}}{dt} + \frac{\zeta}{m}\overline{v} + \frac{1}{N_A}\nabla\overline{\mu} = 0$$

LDE in velocity v

$$t \rightarrow \infty$$

$$\overline{v} = -\frac{1}{N_A\zeta}\nabla\overline{\mu}\left\{1 - \exp\left[-\frac{\zeta}{m}t\right]\right\} \longrightarrow \overline{v}_{ss} \cong -\frac{1}{N_A\zeta}\nabla\overline{\mu}$$

Steady state (SS) velocity

$$\overline{u}_k = \frac{1}{N_A\zeta}$$

Electrochemical mobility
Units: mol kg^{-1}s^{-1}

Steady State material flux expression for species j in fluid may be derived.

$$\overline{\mathbf{f}}_j = -D_j\nabla c_j - \frac{z_j F}{RT}D_j c_j\nabla\phi + c_j\overline{v}$$

$$= f_{j,D} + f_{j,M} + f_{j,C}$$

Diffusion | Migration | Convection

Equation of continuity (fluid mechanics) relates time rate of change of species concentration with the divergence of the material flux. Hence relates _steady state_ and _time varying_ material transport equations.

$$\frac{\partial c_j}{\partial t} = -\nabla\bullet\overline{\mathbf{f}}_j$$

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

$$\frac{\partial c_j}{\partial t} = D_j\nabla^2 c_j + \frac{z_j F}{RT}\nabla\bullet\left(c_j\nabla\phi\right) - \nabla\bullet\left(c_j\overline{v}\right)$$
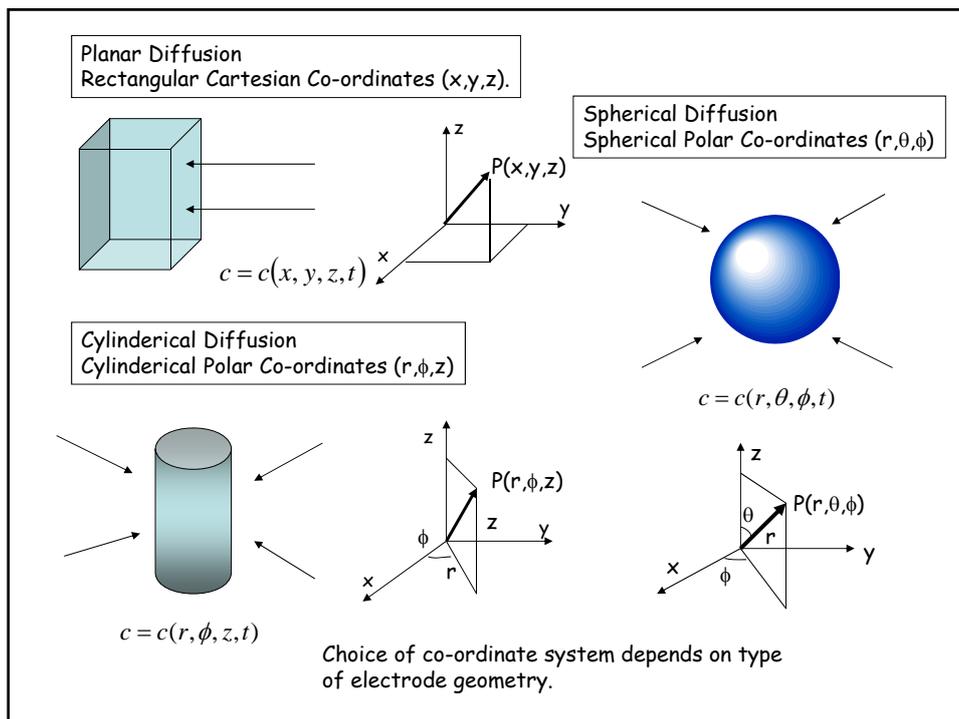
Diffusion | Migration | Convection

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.

$$\frac{\partial c_j}{\partial t} = D_j\nabla^2 c_j - \nabla\bullet\left(c_j\overline{v}\right)$$

In a stationary (unstirred) solution and if the electrode does 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 i 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).

$c = c(x, y, z, t)$

Spherical Diffusion
Spherical Polar Co-ordinates (r,θ,φ)

$c = c(r, \theta, \phi, t)$

Cylinderical Diffusion
Cylinderical Polar Co-ordinates (r,φ,z)

$c = c(r, \phi, z, t)$

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

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

Co-ordinate System	Fick Diffusion Equation $$\frac{\partial c}{\partial t} = D\nabla^2 c$$
Cartesian	$$\frac{\partial c}{\partial t} = D\left\{\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2}\right\}$$
Cylinderical Polar	$$\frac{\partial c}{\partial t} = D\left\{\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c}{\partial r}\right) + \frac{1}{r^2}\frac{\partial^2 c}{\partial \phi^2} + \frac{\partial^2 c}{\partial z^2}\right\}$$
Spherical Polar	$$\frac{\partial c}{\partial t} = D\left\{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial c}{\partial r}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial c}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2 c}{\partial\phi^2}\right\}$$

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.

Diffusion in a medium of infinite extent: a prototype diffusion problem.

t=0	t=t$_1$	t=t$_2$	t → ∞

x=0   x=0   x=0   x=0
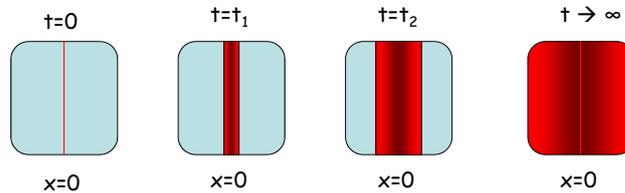
We consider an infinite volume of pure solvent at equilibrium. We let a sharply defined spike of solute be introduced into the central region of the solvent at time t = 0. This defines the origin at x = 0. The solute diffuses through the solvent until there is a homogeneous dispersion of solute molecules throughout the solvent. The problem is to quantify the <u>diffusive spread</u> 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

$$c(x,0) = c_0$$
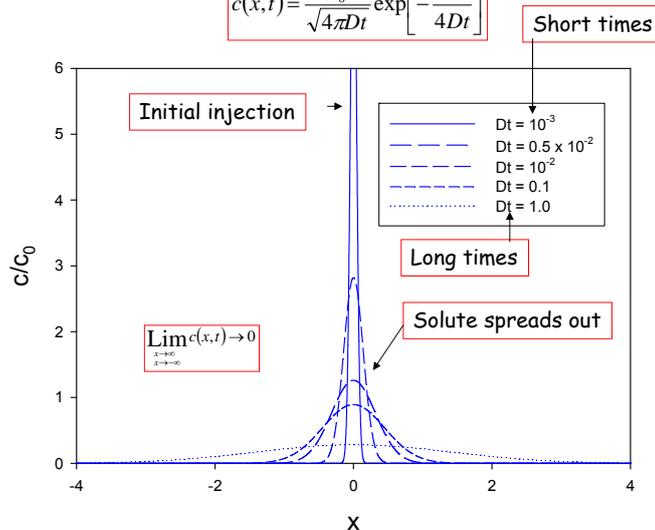
$$c(x,t) = \frac{c_0}{\sqrt{4\pi Dt}}\exp\left[-\frac{x^2}{4Dt}\right]$$

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

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

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

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

Short times

Initial injection →

	Dt = 10^{-3}
	Dt = 0.5 x 10^{-2}
	Dt = 10^{-2}
	Dt = 0.1
	Dt = 1.0

Long times

Solute spreads out

$$\underset{\substack{x\to\infty\\x\to-\infty}}{\text{Lim}}c(x,t)\to 0$$

c/c$_0$

x

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).
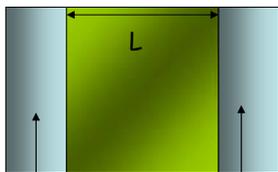
$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$$
$$c(x,0) = 0$$
$$c(0,t) = \kappa c^\infty \quad c(L,t) = 0$$

κ = partition coefficient
κc^∞ = concentration in membrane

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

L

Donor compartment | membrane | Acceptor compartment

Membrane concentration profile

$$u(\chi,\tau) = 1 - \chi + 2\sum_{n=1}^{\infty}\frac{\sin[n\pi(1-\chi)]}{n\pi}\exp[-n^2\pi^2\tau]$$

Normalised variables
$$u = \frac{c}{\kappa c^\infty} \quad \chi = \frac{x}{L} \quad \tau = \frac{Dt}{L^2}$$

$$\frac{\partial u}{\partial \tau} = \frac{\partial^2 u}{\partial \chi^2}$$

Normalised Initial & boundary conditions
$$u(\chi,0) = 0 \quad u(0,\tau) = 1 \quad u(1,\tau) = 0$$

$$\Psi_\Sigma = \frac{f_\Sigma L}{Dc^\infty} = -\left(\frac{\partial u}{\partial \chi}\right)_{\chi=1}$$

Diffusion Flux (rate)

Diffusive flux
$$\Psi = -\left(\frac{\partial u}{\partial \chi}\right)_{\chi=1} = 1 + 2\sum_{n=1}^{\infty}(-1)^n\exp[-n^2\pi^2\tau]$$

Total amount transferred through Membrane.
$$\theta(\tau) = \frac{N(\tau)}{N_\infty} = \int_0^\tau \Psi(\tau)d\tau \quad \boxed{\tau_L = 1/6}$$
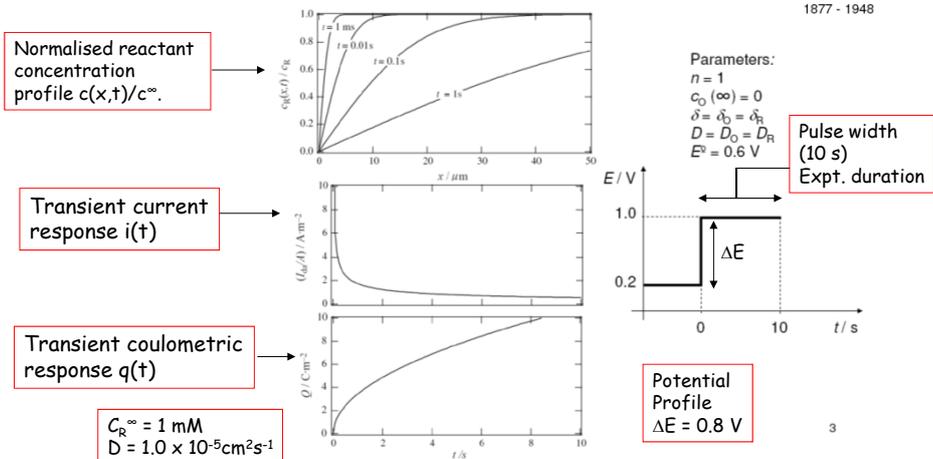
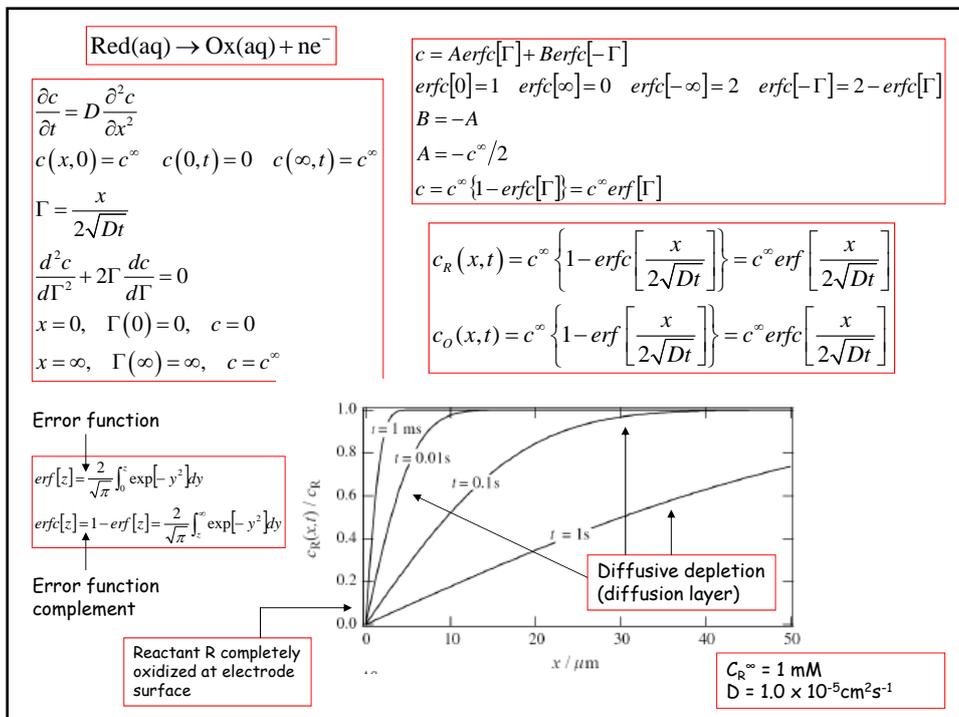$$\theta(\tau) = \tau - \tau_L - 2\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2\pi^2}\exp[-n^2\pi^2\tau]$$
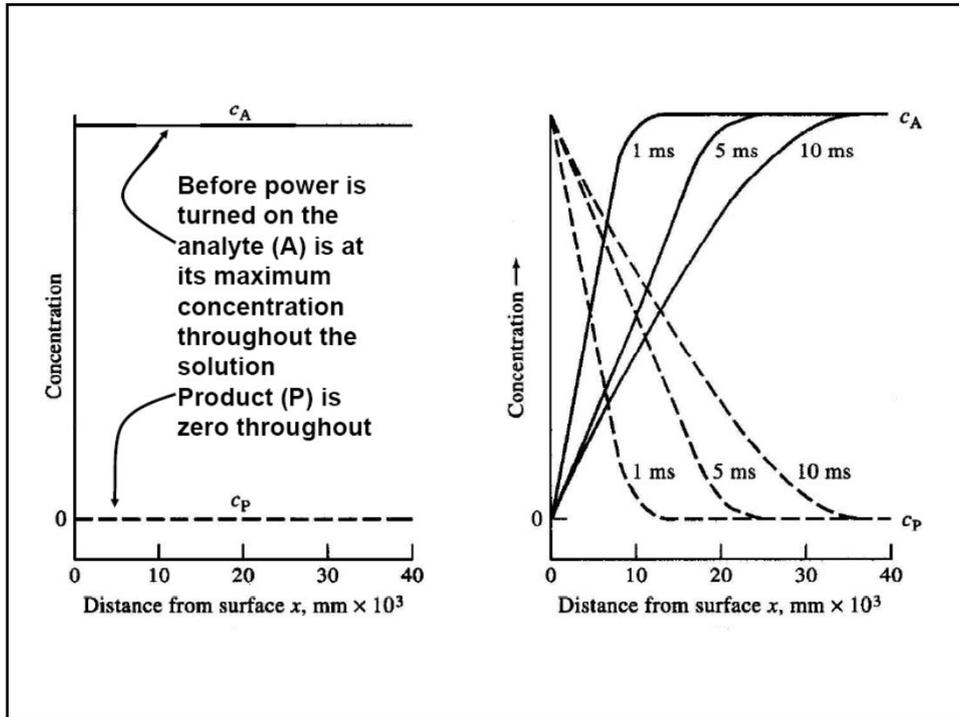

Potential step chronoamperometry : reversible process.

We describe the transient electrochemical technique called <u>Potential Step Chronoamperometry</u> (PSCA) in which a potential step of magnitude ΔE is applied to an electrode and a Nernstian electrochemical redox transformation occurs in response to the potential step perturbation causing a current to flow. We solve the Fick diffusion equation for the problem to derive an expression for the transient <u>Faradaic</u> current response as a function of time.

Frederik Gardner Cottrell
American Chemist
1877 - 1948

Normalised reactant concentration profile c(x,t)/c∞.

Transient current response i(t)

Transient coulometric response q(t)

C_R^∞ = 1 mM
D = 1.0 × 10⁻⁵cm²s⁻¹

Parameters:
$n = 1$
$c_O(\infty) = 0$
$\delta = \delta_O = \delta_R$
$D = D_O = D_R$
$E^9 = 0.6$ V

Pulse width (10 s)
Expt. duration

ΔE

Potential Profile
ΔE = 0.8 V

3

Before power is turned on the analyte (A) is at its maximum concentration throughout the solution

Product (P) is zero throughout

c_A

c_P

1 ms   5 ms   10 ms

$$\text{Red(aq)} \rightarrow \text{Ox(aq)} + ne^-$$

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

$$c(x,0) = c^\infty \quad c(0,t) = 0 \quad c(\infty,t) = c^\infty$$

$$\Gamma = \frac{x}{2\sqrt{Dt}}$$

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

$$x = 0, \quad \Gamma(0) = 0, \quad c = 0$$

$$x = \infty, \quad \Gamma(\infty) = \infty, \quad c = c^\infty$$

$$c = Aerfc[\Gamma] + Berfc[-\Gamma]$$

$$erfc[0] = 1 \quad erfc[\infty] = 0 \quad erfc[-\infty] = 2 \quad erfc[-\Gamma] = 2 - erfc[\Gamma]$$

$$B = -A$$

$$A = -c^\infty/2$$

$$c = c^\infty\{1 - erfc[\Gamma]\} = c^\infty erf[\Gamma]$$

$$c_R(x,t) = c^\infty\left\{1 - erfc\left[\frac{x}{2\sqrt{Dt}}\right]\right\} = c^\infty erf\left[\frac{x}{2\sqrt{Dt}}\right]$$

$$c_O(x,t) = c^\infty\left\{1 - erf\left[\frac{x}{2\sqrt{Dt}}\right]\right\} = c^\infty erfc\left[\frac{x}{2\sqrt{Dt}}\right]$$

Error function

$$erf[z] = \frac{2}{\sqrt{\pi}}\int_0^z \exp[-y^2]dy$$

$$erfc[z] = 1 - erf[z] = \frac{2}{\sqrt{\pi}}\int_z^\infty \exp[-y^2]dy$$

Error function complement

Reactant R completely oxidized at electrode surface

Diffusive depletion (diffusion layer)

C_R^∞ = 1 mM
D = 1.0 × 10^{-5}cm^{2}s^{-1}

t = 1 ms t = 0.01s t = 0.1s t = 1s

8

Slide 1

$$f_\Sigma = \frac{i}{nFA} = D\left(\frac{\partial c}{\partial x}\right)_{x=0} = \frac{D}{2\sqrt{Dt}}\left(\frac{\partial c}{\partial \Gamma}\right)_{\Gamma=0}$$

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

$$\left(\frac{\partial c}{\partial \Gamma}\right) = \frac{\partial}{\partial \Gamma}\left\{c^\infty erf[\Gamma]\right\} = c^\infty \frac{2}{\sqrt{\pi}}\exp\left[-\Gamma^2\right]$$

$$\left(\frac{\partial c}{\partial \Gamma}\right)_{\Gamma=0} = \frac{2c^\infty}{\sqrt{\pi}}$$

Typical chronoamperometric current
Transient response profile to applied
Potential step.

$$f_\Sigma = \frac{D}{2\sqrt{Dt}}\left(\frac{\partial c}{\partial \Gamma}\right)_{\Gamma=0} = \frac{D}{2\sqrt{Dt}}\cdot\frac{2c^\infty}{\sqrt{\pi}} = \sqrt{\frac{D}{\pi}}\frac{c^\infty}{\sqrt{t}}$$

$$i(t) = nFAf_\Sigma = \frac{nFA\sqrt{D}c^\infty}{\sqrt{\pi t}}$$

$$S_C = \frac{di}{d(1/\sqrt{t})} = \frac{nFA\sqrt{D}c^\infty}{\sqrt{\pi}}$$

Cottrell Equation

Diffusion controlled conditions.

i

$1/\sqrt{t}$

Cottrell Plot

Diffusion layer thickness	Characteristic diffusion time
δ / μm	τ / s
1	10^{-3}
10	0.1
100	10

$$\tau = \frac{\delta^2}{2D}$$

Slide 2

Potential step chronoamperometry.

• Apply potential step of amplitude ΔE 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^∞ are both known then electrode area A may be evaluated via PSCA analysis.

E_2

E_1 ΔE

Potential E

Time t

Current i

Time t

Diffusion coefficient

$$D = \frac{\pi S_C^2}{n^2 F^2 A^2 c^{\infty 2}}$$

S_C

i

Cottrell Plot

$t^{-1/2}$

$$i(t) = \frac{nFA\sqrt{D}c^\infty}{\sqrt{\pi}}t^{-1/2}$$
$$= S_C\, t^{-1/2}$$

Nernst diffusion layer

As potential step experiment proceeds the depletion of reactant species near the electrode surface increases. This is termed the <u>diffusion layer</u> δ 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.

$$\tau = \frac{\delta^2}{2D}$$

Diffusion layer thickness   Characteristic diffusion time

δ / μm	τ / s
1	10^{-3}
10	0.1
100	10

Diffusion limited flux

Diffusive mass Transport coefficient

$$f_D = D\frac{\partial c}{\partial x} = \frac{Dc^{\infty}}{\delta} = k_D c^{\infty}$$

$$i_D = nFAf_D = \frac{nFADc^{\infty}}{\delta}$$

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^{∞}. In the Nernst model the concentration changes linearly in the diffusion layer and the diffusive flux and diffusion limited current is readily determined from Ficks 1st law.

Transport via Molecular diffusion only

Diffusion layer (stagnant)

Double layer region

Interfacial ET

Electrode

δ

c^{∞}

A ⟵ **A**

k_{ET} k_D

B

c_0

Material flux ⟶

$$f_{\Sigma} \cong \frac{D(c^{\infty} - c_0)}{\delta}$$

Bulk solution (well stirred)

Hydrodynamic 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.

Slide 1

Distance scales in electrochemistry

Electrode

Distance	Label
0.1 nm	Inner Helmholtz Plane
1 nm	Outer Helmholtz Plane
10 nm	Diffuse Double Layer
0.1 μm	
1 μm	**Aqueous solution**
10 μm	Diffusion Layer δ
0.1 mm	
1 mm	Hydrodynamic Boundary Layer δ_0

distance

Slide 2

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.

$$q(t) = \int_0^t i(t)dt = \frac{nFA\sqrt{D}c^\infty}{\sqrt{\pi}}\int_0^t t^{-1/2}dt$$

$$= 2nFAc^\infty\sqrt{\frac{D}{\pi}}t^{1/2}$$

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.

$$N(t) = \frac{q(t)}{nF} = 2A\sqrt{\frac{Dt}{\pi}}c^\infty$$

Anson equation $\quad q(t) = q_{DL} + q_{ads} + 2nFAc^\infty\sqrt{\frac{D}{\pi}}t^{1/2}$
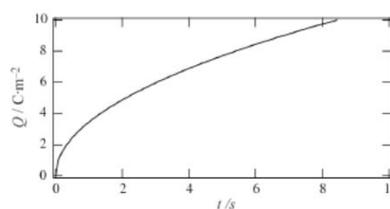
The total chronocoulometric response contains contributions from the Faradaic ET reaction, double layer charging and possibly, reactant adsorption.
A plot of q(t) versus $t^{1/2}$ is linear and is termed an <u>Anson Plot</u>.

$q(t)$

$S_A = 2nFAc^\infty\sqrt{D/\pi}$

Anson Plot

$I_A = q_{DL} + nFA\Gamma_\Sigma$

$\sqrt{t}$
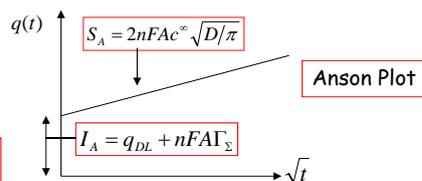
Charging and Faradaic currents.

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.

$$i = i_F + i_C$$
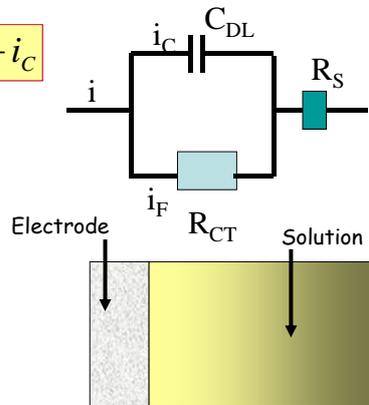
The objective is to **maximise i_F** and **minimise i_C** . Note that i_C is always present and has a constant residual value. As the concentration of analyte decreases i_F decreases and will approach the value of the residual value of i_C. This places a lower limit on analyte detection and hence on the use of voltammetry as an analytical application.

Potential Step Chronoamperometry: Double Layer Charging.

At the beginning of a potential step experiment the current flowing is mainly attributed to underlined 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 ΔE 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).

$$\Delta E = iR_S + \frac{q}{C_{DL}}$$

$$i = \frac{dq}{dt}$$
$$\frac{dq}{dt} = -\frac{q}{R_S C_{DL}} + \frac{\Delta E}{R_S}$$
$$t = 0 \quad q = 0$$

$$q_c(t) = \Delta E C_{DL}\left\{1 - \exp\left[-\frac{t}{R_S C_{DL}}\right]\right\} = \Delta E C_{DL}\left\{1 - \exp\left[-\frac{t}{\tau}\right]\right\}$$

$$i_c(t) = \frac{dq_c}{dt} = \frac{\Delta E}{R_S}\exp\left[-\frac{t}{R_S C_{DL}}\right]$$

RC time constant

$$\tau = R_S C_{DL}$$

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

$$\ln i_c = \ln\left\{\frac{\Delta E}{R_S}\right\} - \frac{1}{R_S C_{DL}}t$$

The current charging the double layer capacitance drops to 1/e or 37% of its initial value at a time t = τ and to 5% of its initial value at t = 3τ. Hence if R_S = 1Ω and C_{DL} = 20 μF then t = 20μs and DL charging is 95 % complete at t = 60 μs.

Slide 1
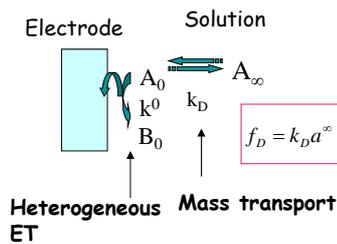
Charging current and Faradaic current contribution can be computed for various transient electrochemical techniques

Charging current decays much more rapidly than Faradaic current.

i

E_F

E_i

$\Delta E = E_f - E_i$

$i_F(t)$

$i_F \gg i_C$
$i \cong i_F$

$i_C(t)$

t

$i_C = \dfrac{\Delta E}{R_S} \exp\left[-\dfrac{t}{R_S C_{DL}} \right]$

$i_F = \dfrac{nFAD^{1/2}c^\infty}{\pi^{1/2}t^{1/2}}$

Take reading when i_C is small.
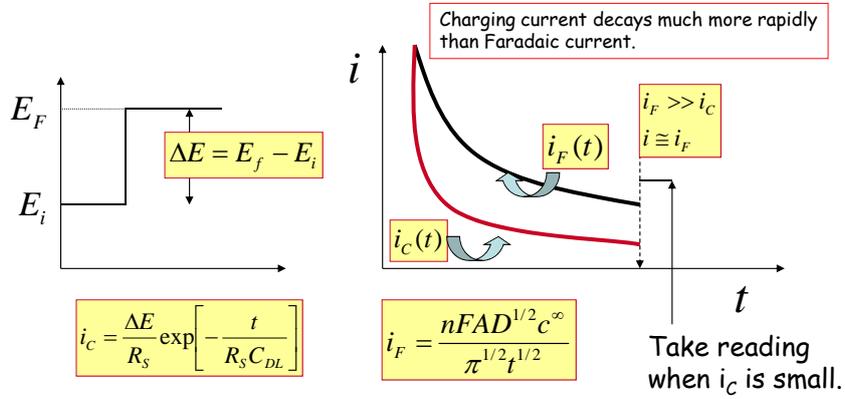
Potential step technique.

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

Slide 2

Reversible ET

Normalised steady State diffusion equations

Electrode   Solution

A_0 A_∞
k^0 k_D
B_0

$f_D = k_D a^\infty = \dfrac{Da^\infty}{\delta}$

Heterogeneous ET   **Mass transport**

Boundary conditions

$\dfrac{\partial^2 u}{\partial \chi^2} = 0 \quad \dfrac{\partial^2 v}{\partial \chi^2} = 0$

$\chi = 0 \quad u = u_0 \quad v = v_0$

$\chi = 1 \quad u = 1 \quad v = 0$

$u = \dfrac{a}{a^\infty} \quad v = \dfrac{b}{a^\infty} \quad \chi = \dfrac{x}{\delta}$

Situation pertains when ET kinetics are fast and Nernstian.
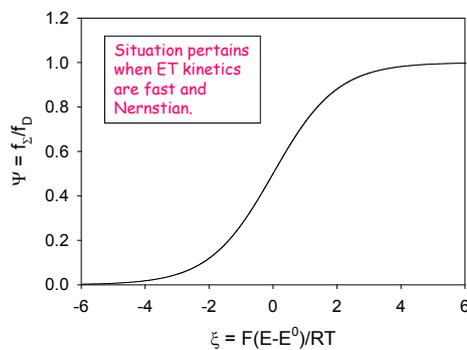
$\Psi = \dfrac{f_\Sigma}{f_D}$ Normalised current

$\Psi = \dfrac{1}{1+\exp[-\xi]} = \dfrac{1}{1+\exp[-(\theta - \theta_0)]}$

$\xi = \dfrac{F}{RT}(E - E^0) = \theta - \theta_0$

$\exp[\xi] = \dfrac{v_0}{u_0}$ Nernst equation

$\theta = \theta_0 + \ln\left\{ \dfrac{v_0}{u_0} \right\}$

$u_0 = \dfrac{a_0}{a^\infty} \quad v_0 = \dfrac{b_0}{a^\infty}$

Y-axis: $\Psi = f_\Sigma/f_D$ (values 0.0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2)

X-axis: $\xi = F(E-E^0)/RT$ (values -6, -4, -2, 0, 2, 4, 6)

Irreversible ET

Electrode   Solution

Heterogeneous ET

Mass transport

Normalised Current

$$\Psi = \frac{f_\Sigma}{f_D} = \frac{1}{1+\zeta^{-1}\exp[-\beta\xi]}$$

$$\zeta = \frac{k^0}{k_D}$$

$$\xi = \theta - \theta_0 = \frac{F}{RT}(E - E^0)$$

$$\theta = \theta_{1/2} \quad \text{when} \quad \Psi = 1/2$$

$$\theta_{1/2} = \theta_0 + \beta^{-1}\ln\{\zeta^{-1}\}$$

Situation pertains when ET kinetics are very sluggish

$$\zeta = \frac{k^0}{k_D}\downarrow$$

$\zeta = 0.1$
$\zeta = 10^{-2}$
$\zeta = 10^{-3}$
$\zeta = 10^{-4}$

$\xi = \theta - \theta_0 = F(E-E^0)/RT$

Quasi reversible ET

$$\beta = 0.5$$

$\zeta = 10$
$\zeta = 1$
$\zeta = 0.1$
$\zeta = 10^{-2}$
$\zeta = 10^{-3}$
$\zeta = 10^{-4}$

$$\zeta = \frac{k^0}{k_D}\downarrow$$

Rapid ET

Slow ET

Most general situation: Intermediate between reversible and irreversible limits.

$\xi = F(E-E^0)/RT$

Normalised current

$$\Psi = \frac{f_\Sigma}{f_D} = \frac{\exp[\beta\xi]}{\zeta^{-1} + \exp[\beta\xi]\{1 + \exp[-\xi]\}}$$

Top slide

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

Interfacial ET Kinetics rate limiting

Normalised current

Ψ

$A \xrightarrow{k_{ox}} B + e^-$

$B + e^- \xrightarrow{k_{red}} A$

1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5

-10   -5   0   5   10

$\xi = F(E-E^0)/RT$

Normalised potential

Net current zero. Interfacial ET balanced. Nernst eqn. pertains.

Electrode   Solution

A_0 A_∞
k^0
B_0 B_∞
k_D

Heterogeneous ET

Mass transport

Bottom slide

Normalised flux

$$\Psi = \frac{f_\Sigma \delta}{D a^\infty}$$

$$\Psi = \frac{\exp[\beta\xi]\{1 - \kappa \exp[-\xi]\}}{\zeta^{-1} + \exp[\beta\xi]\{1 + \exp[-\xi]\}}$$

$$\kappa = \frac{b^\infty}{a^\infty}$$

$$\zeta = \frac{k^0}{k_D} = \frac{k^0 \delta}{D}$$

$$\xi = \frac{F}{RT}(E - E^0)$$

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

large ζ limit MT control

Oxidation

$\kappa = 1, \beta = 0.5$

small ζ limit ET control

1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5

Ψ

-15   -10   -5   0   5   10   15

$\xi = F(E-E^0)/RT$

Reduction

$\kappa = 1, \zeta = 0.01$
$\kappa = 1, \zeta = 0.1$
$\kappa = 1, \zeta = 1$
$\kappa = 1, \zeta = 10$
$\kappa = 1, \zeta = 100$

A_0 A_∞
k_D
k^0
B_0 B_∞
k_D

Heterogeneous ET

Mass transport

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 τ. 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).

origin   Step length L

-4 -3 -2 -1 0 1 2 3 4
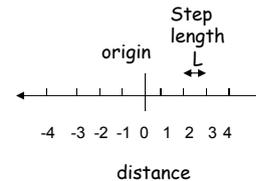
distance

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 $(\frac{1}{2})^n$. 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: $n! / n_R! . n_L! = n! / n_R!(n-n_R)!$.

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, $(\frac{1}{2})^n$, by the number of possible sequences of such steps (the Binomial coefficient). This yields the Binomial Distribution Function.

$$s = x/L$$

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

$$n = n_R + n_L, \quad \frac{x}{L} = n_R - n_L$$

$$n_R = \left(\frac{1}{2}\right)\left(n + \frac{x}{L}\right) = \left(\frac{1}{2}\right)(n + s)$$

$$n - n_R = \left(\frac{1}{2}\right)\left(n - \frac{x}{L}\right) = \left(\frac{1}{2}\right)(n - s)$$

Binomial Distribution Function

$$P_n(s) = \frac{n!}{2^n \left\{ \left(\frac{n+s}{2}\right)! \left(\frac{n-s}{2}\right)! \right\}}$$

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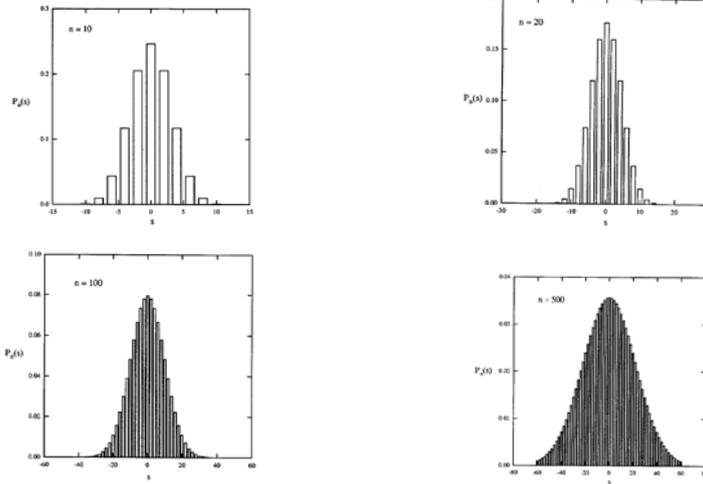
We can calculate the average and root mean square displacement using standard methods.

$$\langle s \rangle = \sum_{s=0}^{n} sP_n(s) = 0$$

$$\langle s^2 \rangle = \sum_{s=0}^{n} s^2 P_n(s) = n$$

$$s_{rms} = \sqrt{\langle s^2 \rangle} = \sqrt{n}$$

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 <u>mean free path</u>.

$$s_{rms} = \frac{x_{rms}}{L}$$

$$x_{rms} = s_{rms}L = \sqrt{n}L$$

$$\langle x^2 \rangle = nL^2$$

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

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

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).
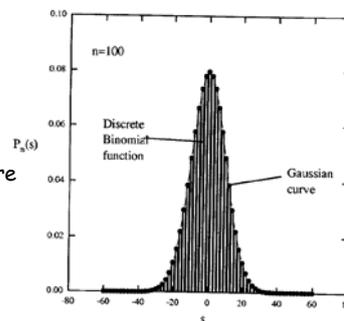
$P_n(s)$ will be zero if there is a difference in parity between n and s. Hence we must develop an expression for the probability as a function of the distance parameter x.

We therefore calculate the probability that a particle is located in an interval between x and $x + dx$ at some time t.

$$P_n(x)dx = P_n(s)ds = \frac{2}{\sqrt{2\pi n}}\exp\left[-\frac{s^2}{2n}\right]ds = \frac{2}{\sqrt{2\pi n}}\exp\left[-\frac{x^2}{2nL^2}\right]\frac{dx}{2L} = \frac{1}{\sqrt{2\pi n}L}\exp\left[-\frac{x^2}{2nL^2}\right]dx$$

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.

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

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.

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

The fundamental step frequency $z = 1/\tau$ (where τ 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.

$$D = \frac{1}{2}zL^2 = \frac{L^2}{2\tau}$$

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

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

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

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

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

$$x_{rms} = \sqrt{\langle x^2 \rangle} = \sqrt{zt}L = \sqrt{zL^2 t} = \sqrt{2Dt}$$

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.

$$D = \frac{L^2}{2\tau} \quad \text{1-D}$$

$$D = \frac{L^2}{6\tau} \quad \text{3-D}$$

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.

Occupied site   Vacant site   Vacant site   Occupied site

ion

Before ion jump

After ion jump
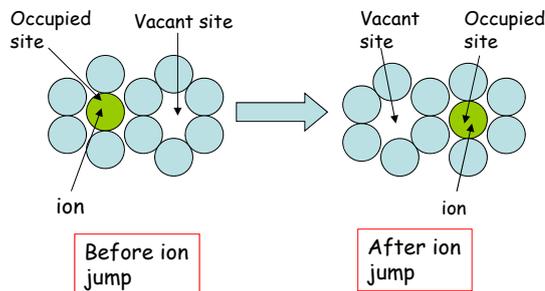
The fundamental idea behind the Eyring approach is that the potential energy (or the Gibbs energy) of a system of particles involved in a rate process varies as the particles moves to accomplish the process. If the Gibbs energy of the system is plotted versus the position of the moving particle then the energy of the system has to attain a critical value termed the activation free energy ΔG^{0*} for the process to be accomplished.

Slide 1

Jump distance L

Pre-jump site | Jumping species | Post-jump site

Activated state

Gibbs energy

ΔG^{0*}

System has to cross an activation energy barrier for rate process to occur.

Pre-jump site | Post-jump site

Position

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.

$$z = \frac{1}{\tau} = \frac{k_B T}{h} \exp\left[-\frac{\Delta G^{0*}}{RT}\right] = \frac{k_B T}{h} \exp\left[\frac{\Delta S^{0*}}{R}\right] \exp\left[-\frac{\Delta H^{0*}}{RT}\right]$$

Slide 2

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

$$D = \rho \frac{L^2}{\tau} = \rho L^2 \frac{k_B T}{h} \exp\left[-\frac{\Delta G^{0*}}{RT}\right] = \rho L^2 \frac{k_B T}{h} \exp\left[\frac{\Delta S^{0*}}{R}\right] \exp\left[-\frac{\Delta H^{0*}}{RT}\right]$$

Numerical factor defining
Dimension of diffusion process.
$\rho = \frac{1}{2}$ (1-D), $\rho = 1/6$ (3-D)

Activation energy for diffusion

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.

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

$$A_D = \rho L^2 e\left(\frac{k_B T}{h}\right) \exp\left[\frac{\Delta S^{0*}}{R}\right]$$

Pre-exponential factor

Base of natural logarithm

$\ln D$

$$E_{A,D} = -R\left(\frac{d \ln D}{d(1/T)}\right)$$

$1/T$

19

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 / Nicholson-Shain Current function

$$\Psi = \frac{i}{nFA\sqrt{nFD\upsilon/RT}\,a^{\infty}} = \sqrt{\pi}\,\mathrm{X}_{NS}$$

Integral equation for normalised current

$$\frac{1}{\sqrt{\pi}} \int_0^{\tau} \frac{\Psi(\lambda)}{\sqrt{\tau-\lambda}}\,d\lambda = \frac{1}{1+\exp[-\xi(\tau)]}$$

Normalised variables

$$u = \frac{a}{a^{\infty}} \quad v = \frac{b}{a^{\infty}} \quad \chi = \sqrt{\frac{nF\upsilon}{DRT}}\,x$$

$$\tau = \frac{nF\upsilon}{RT}t$$

$$\xi = \frac{nF}{RT}\left(E(t)-E^0\right)$$

$$E(t) = E_i \pm \upsilon t$$

$$\xi(\tau) = \xi_i \pm \tau$$

Integral defining normalised current

$$\Psi(\xi) \cong \int_0^{\infty} \frac{1}{4\sqrt{\pi\,\lambda}}\,\mathrm{sech}^2\left[\frac{\xi-\lambda}{2}\right]d\lambda$$

$$\Psi_P = 0.446$$

$$E_P \cong E^0 = 0.3\,V$$

Diffusive boundary value problem

$$\frac{\partial u}{\partial \tau} = \frac{\partial^2 u}{\partial \chi^2} \quad \frac{\partial v}{\partial \tau} = \frac{\partial^2 v}{\partial \chi^2}$$

$$\tau = 0 \quad \chi \geq 0 \quad u = 1 \quad v = 0$$

$$\tau \geq 0 \quad \chi \to \infty \quad u \to 1 \quad v \to 0$$

$$\tau \geq 0 \quad \chi = 0 \quad \frac{\partial u}{\partial \chi} = -\frac{\partial v}{\partial \chi} = \Psi$$

$$\tau \geq 0 \quad \chi = 0 \quad u_0 = v_0 \exp[-\xi(\tau)]$$
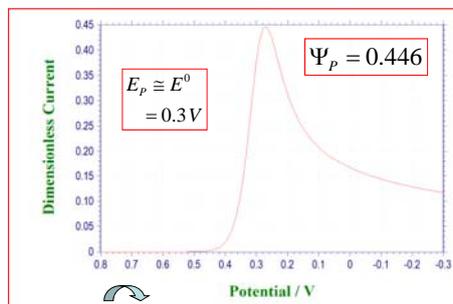
Randles Sevcik equation for peak current

$$i_P = nFA\sqrt{nFD\upsilon/RT}\;a^{\infty}\Psi_P$$

$$= 0.446\,nFA\sqrt{nFD\upsilon/RT}\;a^{\infty}$$

Analytical Approximation to LPS Voltammogram for reversible ET

Numerical Solution.

$\xi = nF(E-E^0)/RT$

Not good for large ξ

Analytical Approximation.

$\xi = nF(E-E^0)/RT$
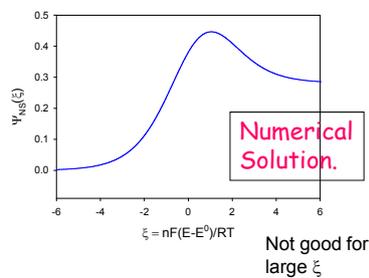
$$\Psi_{NS} = \frac{i}{nFA\sqrt{nFD\upsilon/RT}\,a^\infty} = \sqrt{\pi}\,X_{NS}$$

$$\frac{1}{\sqrt{\pi}}\int_0^\tau \frac{\Psi(\lambda)}{\sqrt{\tau-\lambda}}\,d\lambda = \frac{1}{1+\exp[-\xi(\tau)]}$$
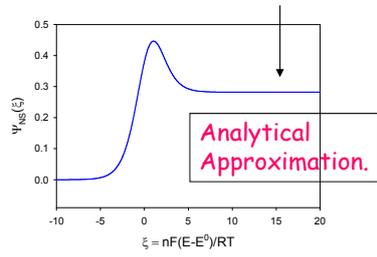
$$\Psi_{NS}(\xi) \cong \frac{a_1\vartheta + a_2\vartheta^2}{b_1 + b_2\vartheta + b_3\vartheta^2}$$

$a_1 = 0.9933$
$a_2 = 0.0944$
$b_1 = 1.0000$
$b_2 = 1.5221$
$b_3 = 0.3349$

$$\vartheta = \exp[\xi]$$

Prasad & Sangaranarayanan JEC, 2003

LPS Voltammetry. Reversible ET

D = 10^{-5} cm^{2}s^{-1}; T = 298K ; n = 1; c = 0.001 M Sweep rate = 0.1 Vs^{-1}
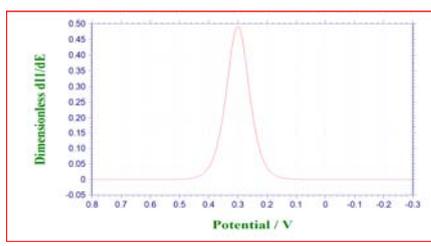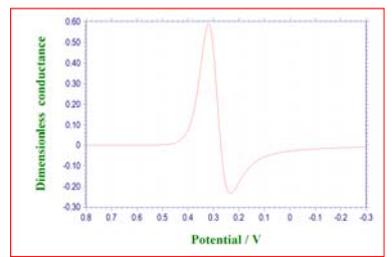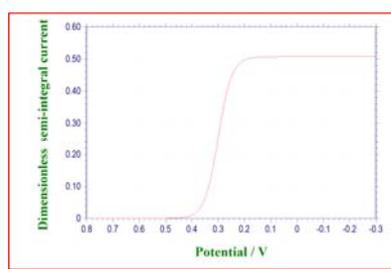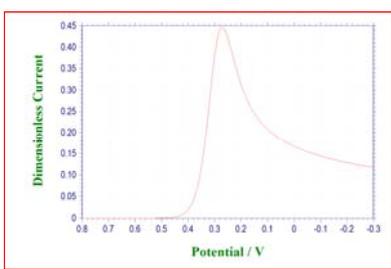
DigiSim Programme

Cyclic Voltammetry (CV)

- 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_λ 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 $dE/dt = \nu$. 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 ΔE_P and peak widths at half peak heights d are measured as a function of sweep rate.
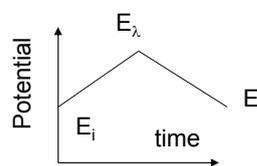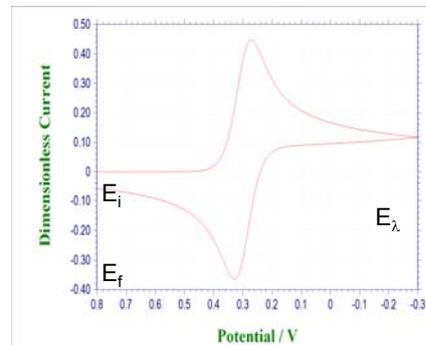
Cyclic Voltammetry. Reversible ET.

- 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.

Reduction

$E^0 = 0.3$ V

Oxidation

$$A \xrightarrow{\;+e^-\;} B$$
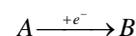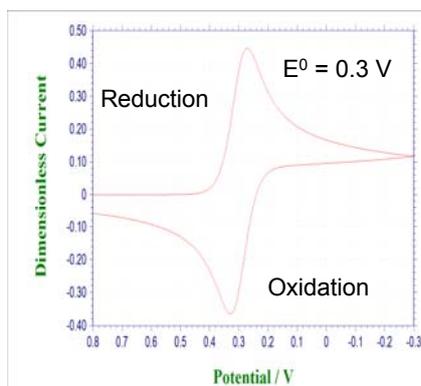
CV : Diagnostic Features

- If ET process is rapid (Nernstian E_{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.

$$E^0 \cong \frac{E_{P,ox} + E_{P,red}}{2}$$

$$i_P = 0.446 nFAc^\infty \sqrt{\frac{nF}{RT}} D^{1/2} \upsilon^{1/2} = S_{RS} \upsilon^{1/2}$$

$$\frac{i_{P,ox}}{i_{P,red}} \cong 1 \qquad D = \frac{S_{RS}^2}{\left(0.446 nFAc^\infty\right)^2 \left(nF/RT\right)}$$

$$\Delta E_P = E_{P,ox} - E_{P,red} \cong \frac{0.058}{n} \, V \qquad (T = 298K)$$

Randles-Sevcik Plot
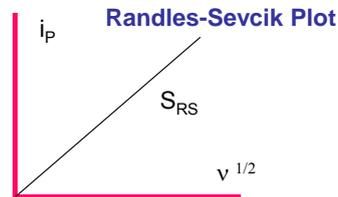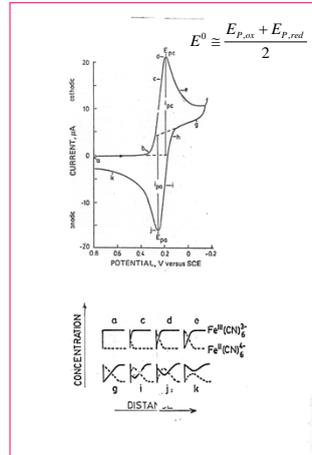
Cyclic Voltammetry. Reversible ET

$D = 10^{-5} \ cm^2 s^{-1}$; $T = 298K$;
$n = 1$; $c = 0.001$ M
Sweep rate = $0.1 \ Vs^{-1}$
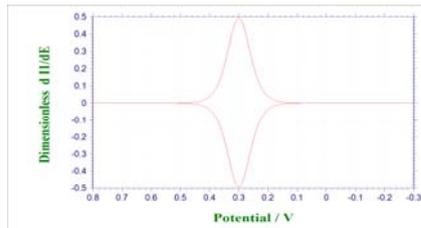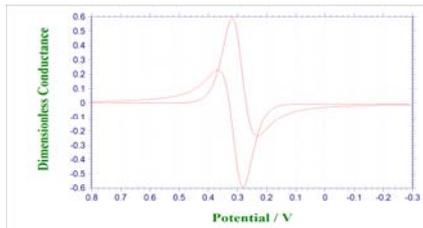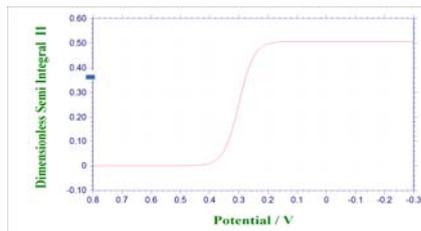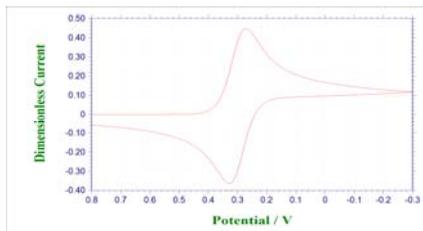
LPS Voltammetry: Irreversible ET.
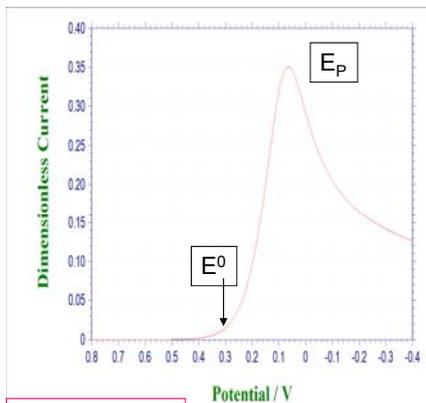
$k^0 = 10^{-4}$ cm/s
$D = 10^{-5}$ cm^2/s
$b = 0.5$
$E^0 = 0.3$ V

$E_{1/2} \neq E^0$
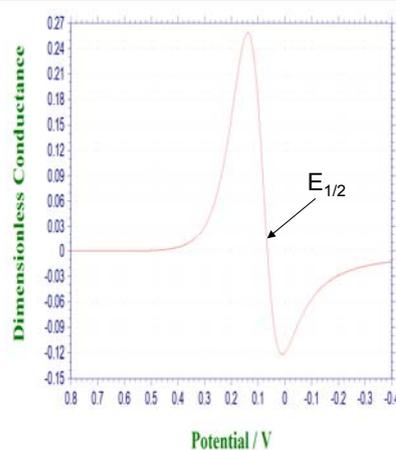
Electrode kinetics are finite: cause distortion of voltammogram.

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}
$k^0 = 10^{-5}$ cm s^{-1}
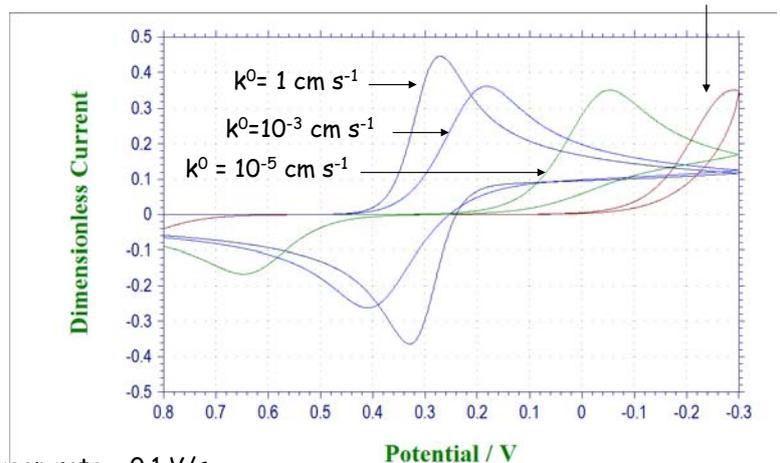
Sweep rate = 0.1 V/s
$D = 10^{-5}$ cm^2/s
$C = 1$ mM

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 ΔE_p increases and the peak current decreases.
- ET processes are termed
  - Reversible (E_{rev}) if $k^0 > 0.1$ cm/s
  - Quasireversible (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 DE_p 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.
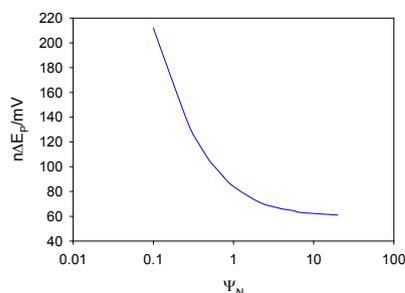
$$\Psi_N = \frac{\left(\dfrac{D_{OX}}{D_{RED}}\right)^{\beta/2}}{\sqrt{D_{OX}\,\pi\,\upsilon\left(\dfrac{nF}{RT}\right)}}\ k^0$$

R.S. Nicholson, Anal. Chem. 1965, 37, 1351-1355.

Cyclic Voltammetry
Quasi Reversible ET Kinetics
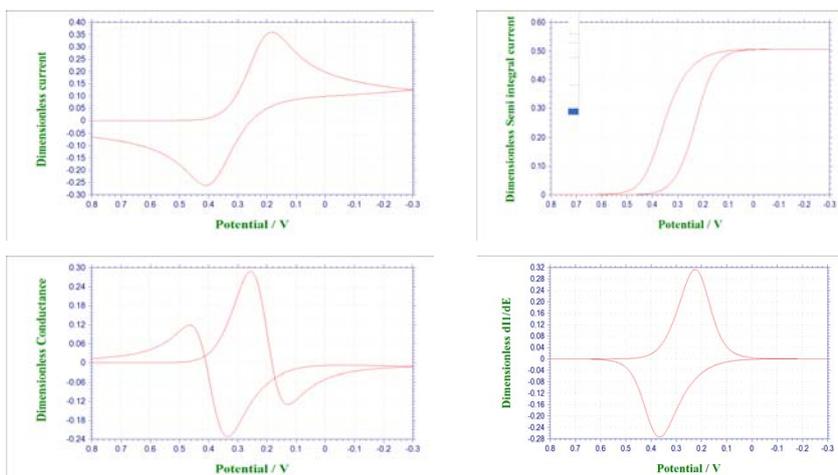
Effect of capacitative current flow.

- 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.
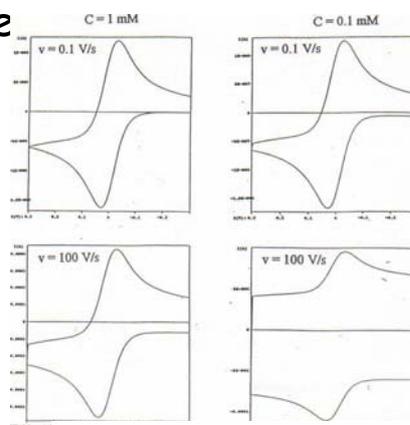
$$i_F = 0.446 nFAc^\infty \sqrt{\frac{nFD}{RT}}\, \upsilon^{1/2}$$

$$i_C = \upsilon C_{DL} + \left\{ \left(\frac{E_i}{R_S} - \upsilon C_{DL} \right) \exp\left[-\frac{t}{\tau} \right] \right\}$$

$$\tau = \text{time constant} = R_S C_{DL}$$
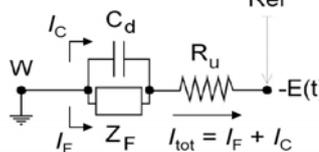
Limitations of cyclic voltammetry

- **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 C_{DL}. 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.

Planar Diffusion

Spherical Diffusion

Diffusive rate constant

$$k_D \cong \frac{D}{a}$$

electrode radius
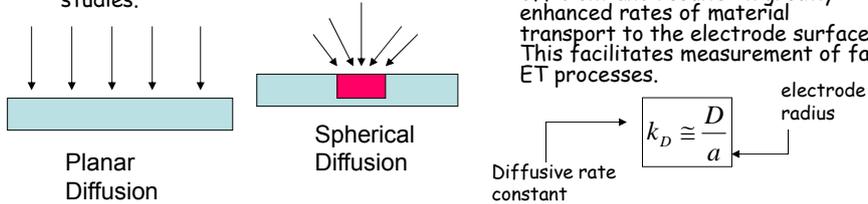
Typical range of electrode size.

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

- 1 mm — Standard electrode size
- 100 µm — **Microelectrodes**
- 10 µm — Much current research
- 1 µm — **Ultramicroelectrodes**
- 100 nm — **Nanodes** — Lots of new Chemistry here!

Carbon fiber

Epoxy

Glass micropipette

10 µm
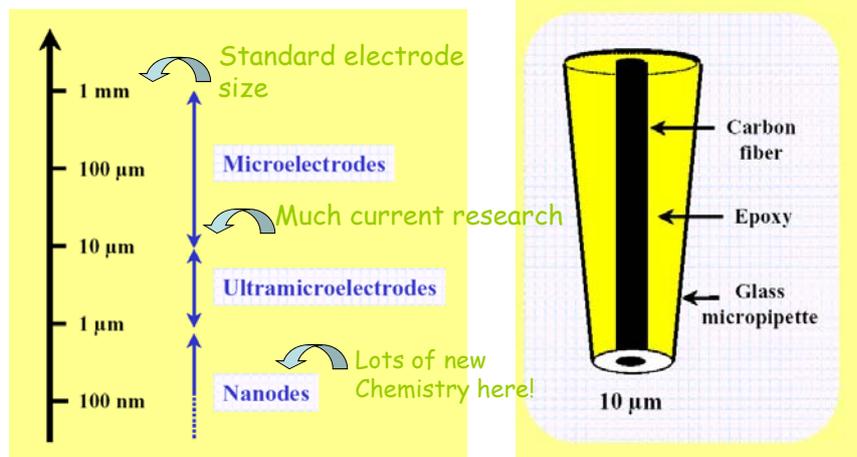
Literature references

- K. Stulik et al. Microelectrodes :definitions, characterization and applications. *Pure Appl. Chem.*, 72(2000) 1483-1492.
- R.J. Forster. Microelectrodes: new dimensions in electrochemistry. *Chem. Soc. Rev.* 1994, pp.289-297.
- C.G. Zoski. Ultramicroelectrodes: design, fabrication and characterization. *Electroanalysis* 14 (2002) 1041-1051.
- J. Heinze. Ultramicroelectrodes in electrochemistry. *Angew. Chem. Int. Ed. Engl.,* 32 (1993) 1268-1288.
- M.V. Mirkin et al. Nanometer-sized electrochemical sensors. *Anal. Chem.,* 69 (1997) 1627-1634.
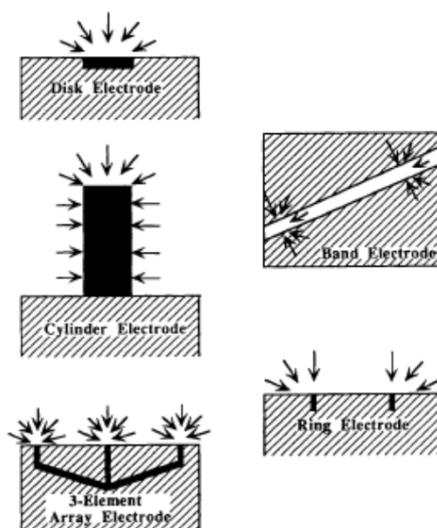
Figure 1 Illustrations of the most common microelectrode geometries, and their diffusion fields.

Microelectrode Gallery
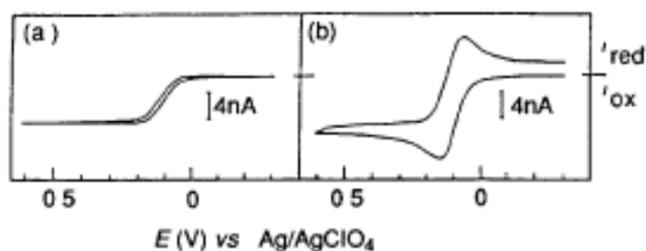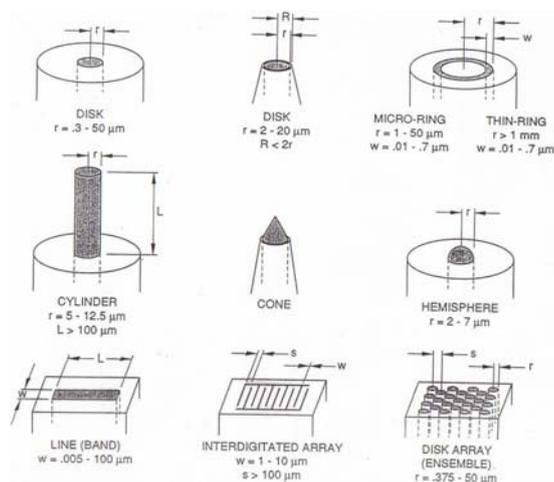
Figure 3 Cyclic voltammetric response at slow scan rates for the oxidation of 1 0 mM ferrocene at a gold disk microelectrode ($r = 6 5$ μm) Supporting electrolyte is 0 1 M tetrabutyl ammonium perchlorate in acetonitrile (a) Scan rate is 0 1 V s ^{1} (b) scan rate is 10 V s ^{1}
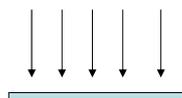
Sigmoidal shape: characteristic of radial diffusion.
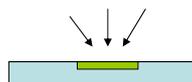
Peak Shape : characteristic of Planar diffusion.

UME's Radial vs. Planar Diffusion

Radial Diffusion

- Redox wave:
  - sigmoidal shape
- $I_{ss} = 4nFrD_oC_o^*$
  - I_{ss} scan rate independent $\propto D_oC_o^*$

Planar Diffusion

- Redox wave:
  - normal shape
- $I_p \propto v^{1/2} \propto D_o^{1/2} C$

2 mV/s

1 nA

30 V/s

20 nA

600 500 400 300 200 100

E, mV
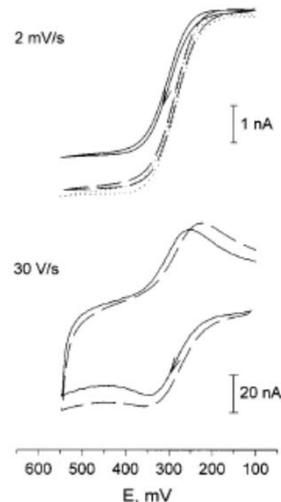
Figure 4. Cyclic voltammograms of gel-encapsulated FcCOO⁻ (initially 3 mM) acquired 1 (dotted line), 2 (solid line), and 26 (dashed line) days after gelation.

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.

Diffusion

$d = \sqrt{2Dt}$

d = Distance
D = Diffusion Coefficient
t = Time

Planar Diffusion

t_2
t_1

Non-Planar Diffusion

t_1 t_2

BAS

Spherical/Hemispherical electrode
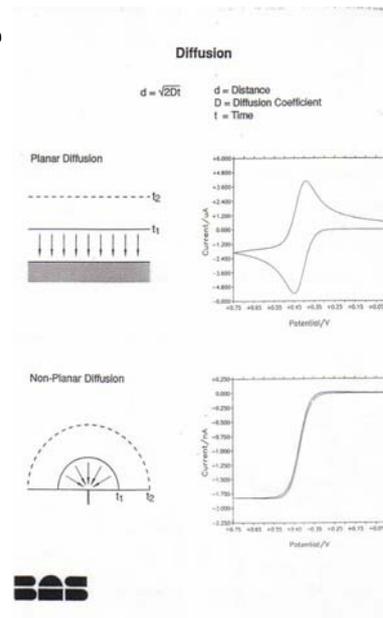
Microelectrode geometries: Some quantitative results.

$$\frac{\partial c}{\partial t} = D\left\{\frac{\partial^2 c}{\partial r^2} + \frac{2}{r}\frac{\partial c}{\partial r}\right\}$$

$i_D = 4\pi\, nFDc^\infty a$ Sphere

$i_D = 2\pi\, nFDc^\infty a$ Hemisphere

Inlaid Disc electrode

$$\frac{\partial c}{\partial t} = D\left\{\frac{\partial^2 c}{\partial r^2} + \frac{1}{r}\frac{\partial c}{\partial r} + \frac{\partial^2 c}{\partial z^2}\right\}$$

Steady state diffusion Limited current

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

Surface diameter

$$i_D = 2nFDc^\infty d_S$$

$d_S = 2\pi a$ Sphere

$= \pi a$ Hemisphere

$= 2a$ Inlaid Disc

$$i_D \propto a$$

SS current proportional to electrode radius a.

Typical geometries are spherical and inlaid disc. Spherical easy to analyze mathematically. Inlaid disc easy to fabricate, but difficult to treat mathematically.

Microelectrode experiments produce sigmoidal voltammograms characteristic of steady state conditions

Diffusion layer thickness $\delta = r_{hs}$

Diffusion limited current

$$I_d = 2\pi\, nFD\, c\, r_{hs}$$

Microdisc & Microhemisphere Electrodes
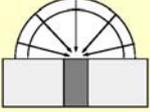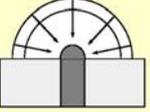
Diffusion layer thickness $\delta = \frac{\pi r_d}{4}$

Diffusion limited current $I_d = 4\,nFD\,c\,r_d$
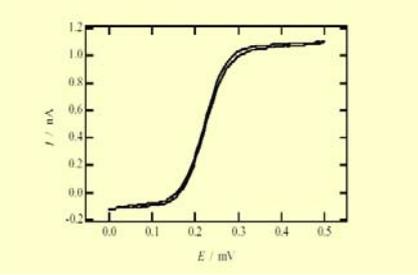
Experiments using ultramicroelectrodes very good for performing accurate kinetic measurements.
Disadvantages include low currents and difficult theory !

❏ Using Ultramicroelectrodes Allows Decreasing Ohmic Drop and Cell Time Constant

$I_{tot} = I_F + I_C$
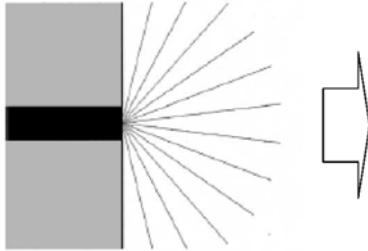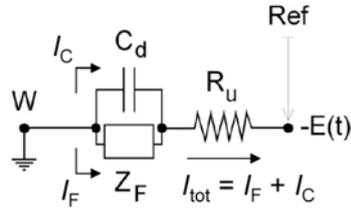
o *In Planar Diffusion only:*

$$R_u \, I_{tot} \propto r_0 \to 0$$

o *For Any Diffusional Regime:*

$$\tau_{cell} = R_u \, C_d \propto r_0 \to 0$$

We make an approximate calculation of the i_F/i_C ratio for an inlaid microdisc electrode of radius a under steady state conditions.

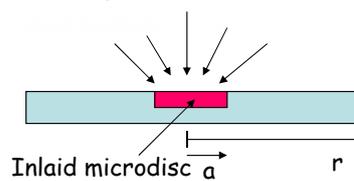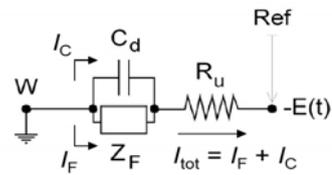$$i_C \cong \upsilon C_{DL} = \upsilon \frac{\varepsilon \pi}{X_H} a^2$$

Helmholtz layer thickness

$$C_{DL} \cong \frac{\varepsilon \, A}{X_H} = \frac{\varepsilon}{X_H} \pi \, a^2$$

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

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

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

$I_{tot} = I_F + I_C$

Inlaid microdisc

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.

Chen & Kucernak, Electrochem. Commun. 4 (2002) 80-85
Chen & Kucernak, J. Phys. Chem.B. 106 (2002) 9396-9404

Electrophoretic paint

$a \cong 0.9nm$

$a \cong 38nm$
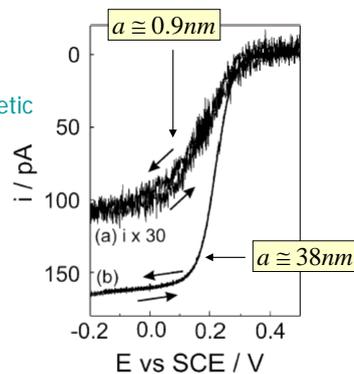
(a) i x 30
(b)
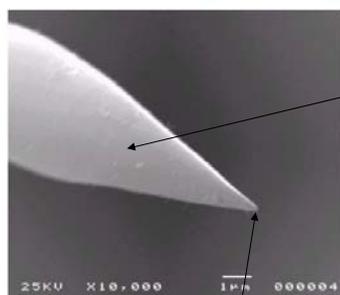
Nanoelectrode

Fig. 1. SEM image of an etched carbon fiber.

Fig. 3. The steady-state voltammograms (both forward and reverse scans) of reduction of 0.01 mol dm^{-3} K$_3$Fe(CN)$_6$ in 0.5 mol dm^{-3} KCl. Both electrodes were fabricated using three repeated EDP coating/heating cycles. The effective radii are calculated from the diffusion limited currents as 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


insulating paint

nanoelectrode

500 nm

insulating paint

nanoelectrode

100 nm

r_{el} = 70 nm
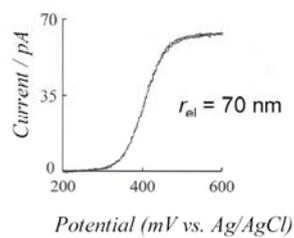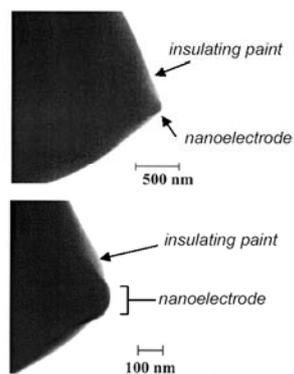
{Fc-CH$_2$-N(CH$_3$)$_3$$^+$,PF$_6$$^-$}, 2mM in 0.2 KCl

33

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.).
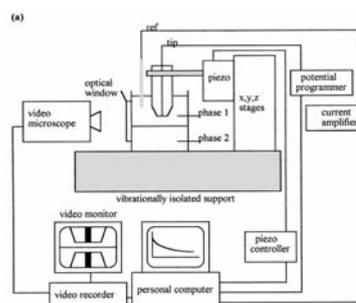

Scanning electrochemical microscopy (SECM)
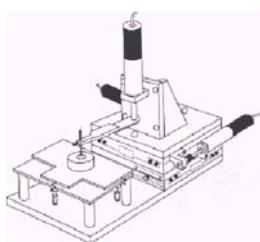
Diameter (typically 100 nm) of UME tip determines lateral resolution, hence Tip geometry important.

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 ubder 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.
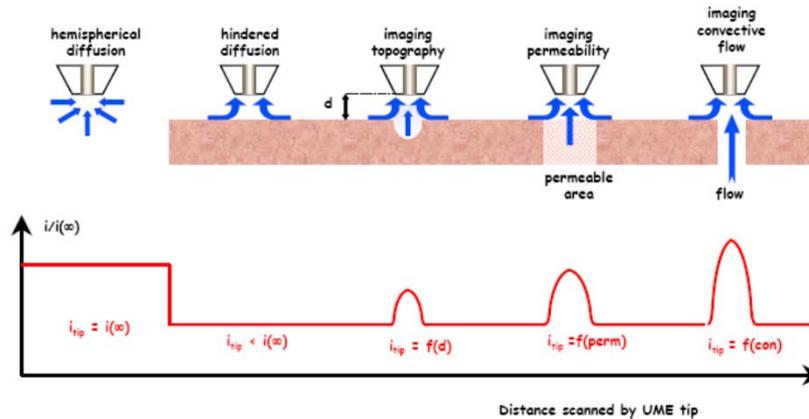

SECM set-up for imaging

Diagram of Scanning Electrochemical Microscope

Cell/Sample Holder
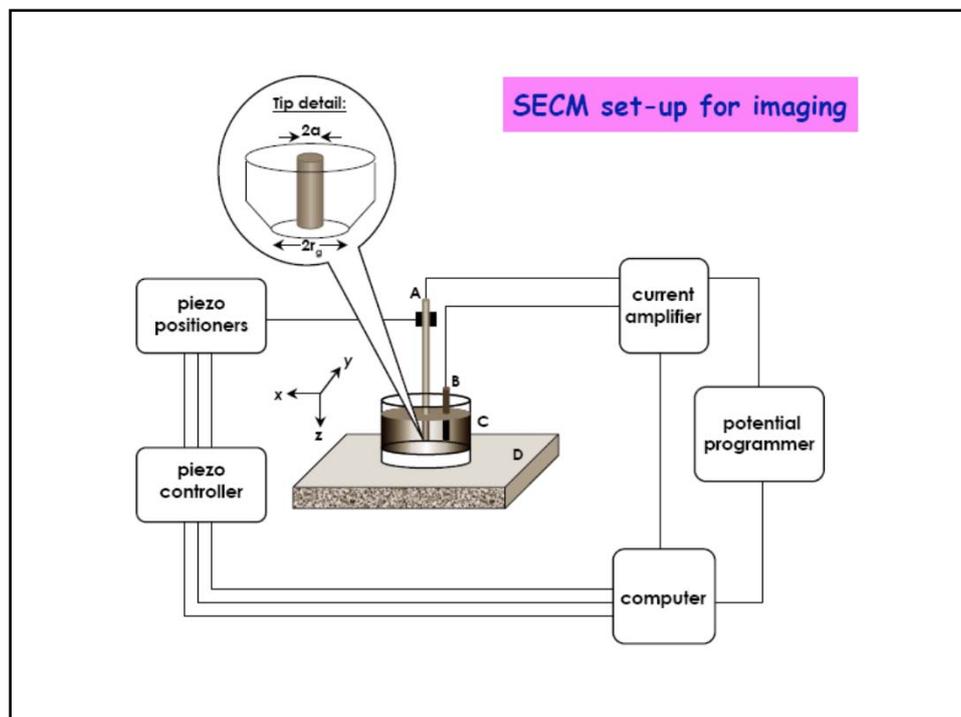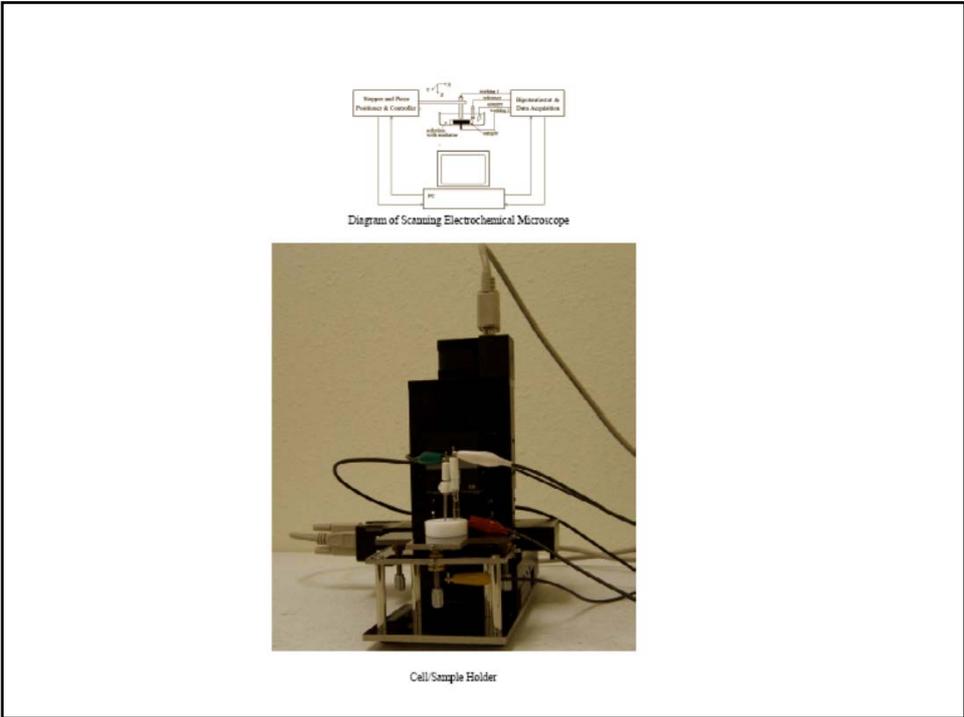
Imaging Applications

Principles

Tip positoned far from the substrate	Negative Feedback	Positive Feedback
$i(\infty) = 4\ naFDc^*$	$i < i(\infty) = i_{hin}$	$i > i(\infty) = i_{con}$

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 d 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 effected 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 occuring 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 $i_{T\infty}$ = 4nFDc$^\infty$a.
- 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 > $i_{T\infty}$. When this reaction is also diffusion limited the tip current reaches a maximum value.
- 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 ~ 0.1 cm/s,
  convective effects arising from tip motion (typically 10 μm/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.

$$i_{T,\infty} = 4nFDca$$

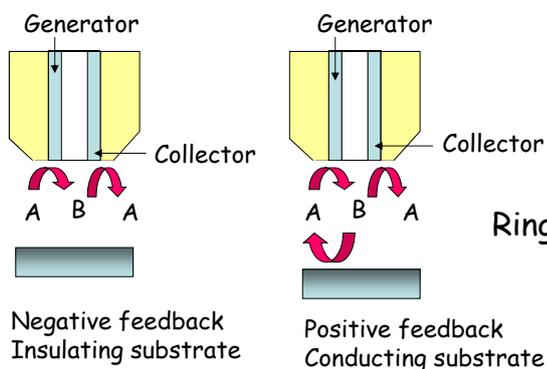Scanning electrochemical Microscopy (SECM) : Positive and negative feedback.
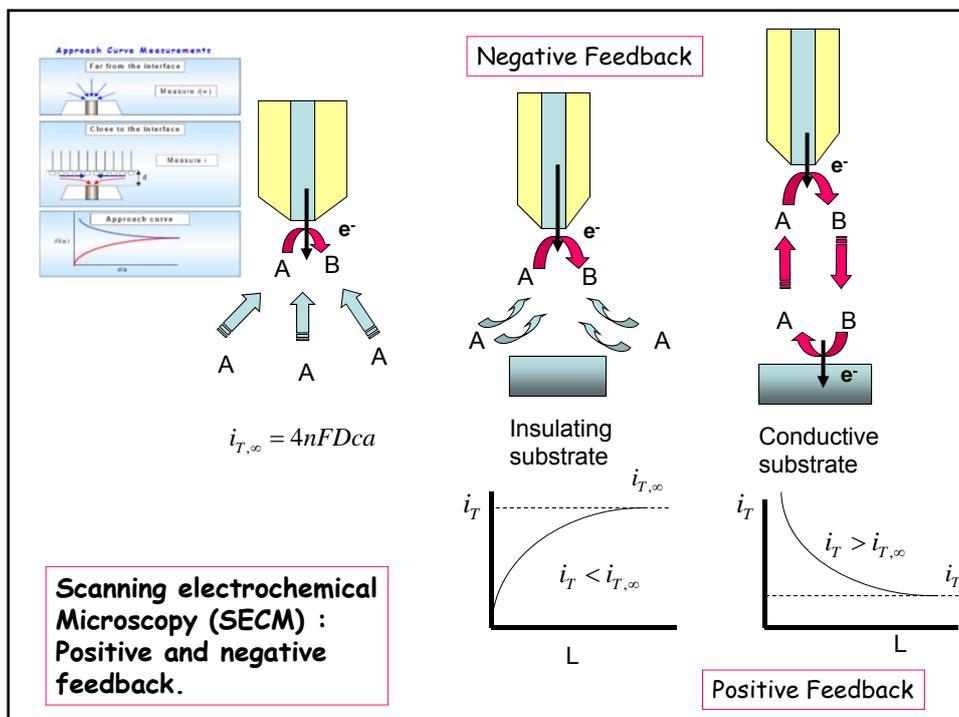
Generation/Collection Mode

- 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.

Quinn et al. Electrochem. Commun. 4(2002) 67-71.
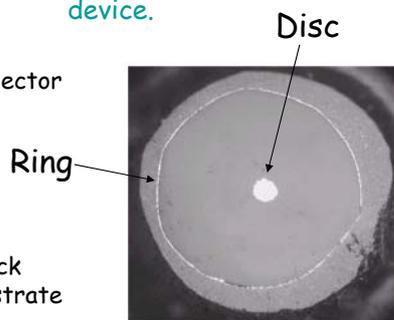
First attempt at ring/disc Generator collector device.

Fig. 3. A photograph of an RD electrode assembly. The diameter of the disk is 25 µm.

Generator

Collector

A   B   A

Negative feedback
Insulating substrate

Generator

Collector

A   B   A

Positive feedback
Conducting substrate

Behaviour of reaction intermediates probed.

Disc

Ring