



# Electrochemistry

CHEM 5390

# Introduction

## Conduction in a cell

### Charge is conducted by:

- The electrodes and leads – involves electrons
- The solution – involves migration of cations and anions
- The interface – involves oxidation and reduction

# Electrochemical Cells

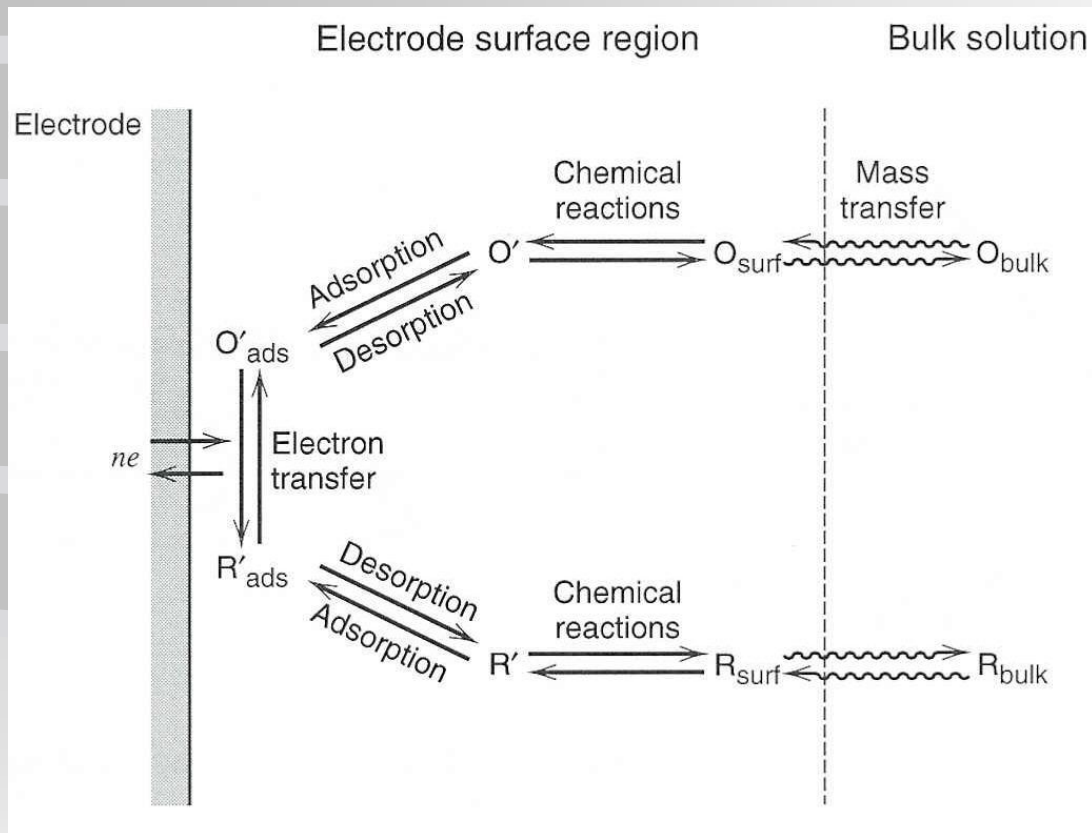
Consider an overall electrode reaction



The current (or electrode reaction rate) is governed by:

- 1) mass transfer**
- 2) electron transfer
- 3) chemical reactions before or after the electron transfer (i.e. homogenous process – protonation or dimerization or heterogeneous process – catalytic decomposition at electrode surface)

# Electrical Double Layer



**Figure 1.3.6** Pathway of a general electrode reaction.

# Mass Transfer

If we assume that an electrochemical experiment has fast electron transfer and rapid chemical reactions, then net rate of the electrode reaction,  $v_{\text{rxn}}$ , is governed by the rate at which the electroactive species is brought to the surface by mass transfer,  $v_{\text{mt}}$ .

$$v_{\text{rxn}} = v_{\text{mt}} = i/nFA$$

These types of reactions are called reversible or Nernstian, because the principle species obey thermodynamics at the electrode surface.

# Introduction

## Faradaic and Nonfaradaic currents

Faradaic processes – direct transfer of electrons by an oxidation or reduction reaction.

Obeys Faradays law – the amount of chemical reactant at an electrode is proportional to the current. (faradaic current).

Nonfaradaic current – background current.

# Introduction

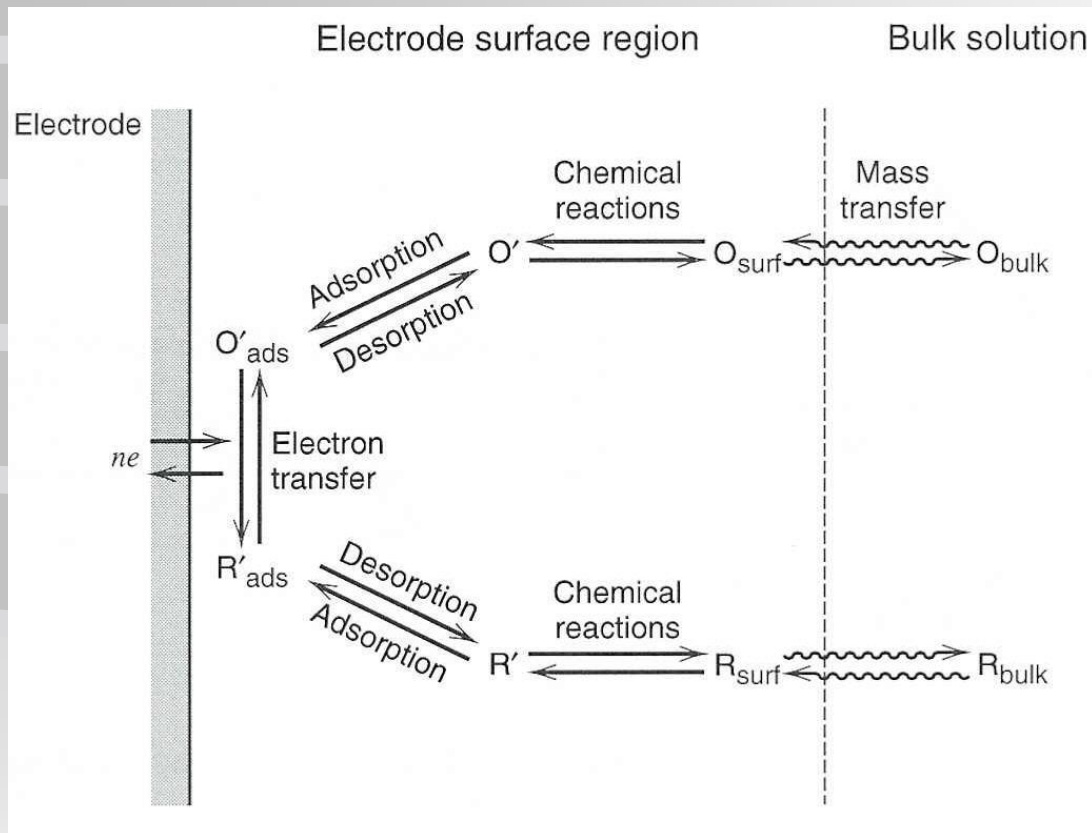
## Mass Transfer

For faradaic current to continue the species must be continuously transferred from the bulk of the solution to the electrode surface.

This occurs by:

- **Convection** – mechanical motion of the solution; stirring or hydrodynamic transport.  
Natural convection – caused by density gradients.  
Forced convection – stagnant, laminar, turbulent flow.
- **Migration** – movement of ions by electrostatic attraction; movement of charged body under the influence of an electric field (electrical potential gradient).
- **Diffusion** – motion of species due to a concentration gradient.

# Electrical Double Layer



**Figure 1.3.6** Pathway of a general electrode reaction.

# Mass Transfer

Experiments which are carried out in unstirred solutions containing a large excess of a base electrolyte are governed by diffusion.

Experiments which are carried out using stirring or rotating are governed by convection, although diffusion will still occur in the layer adjacent to the electrode.

# Mass Transfer

Mass transfer to an electrode is governed by the Nernst-Planck equation.

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

$J_i(x)$  – flux of species  $i$  (mol/s cm<sup>2</sup>) at distance  $x$  from surface

$D_i$  – diffusion coefficient (cm<sup>2</sup>/s)

$dC_i(x)/dx$  – concentration gradient at distance  $x$

$d\phi(x)/dx$  – potential gradient

$z_i$  and  $C_i$  – charge (dimensionless) and concentration (mol/cm<sup>3</sup>) of species  $i$

$v(x)$  – velocity (cm/s)

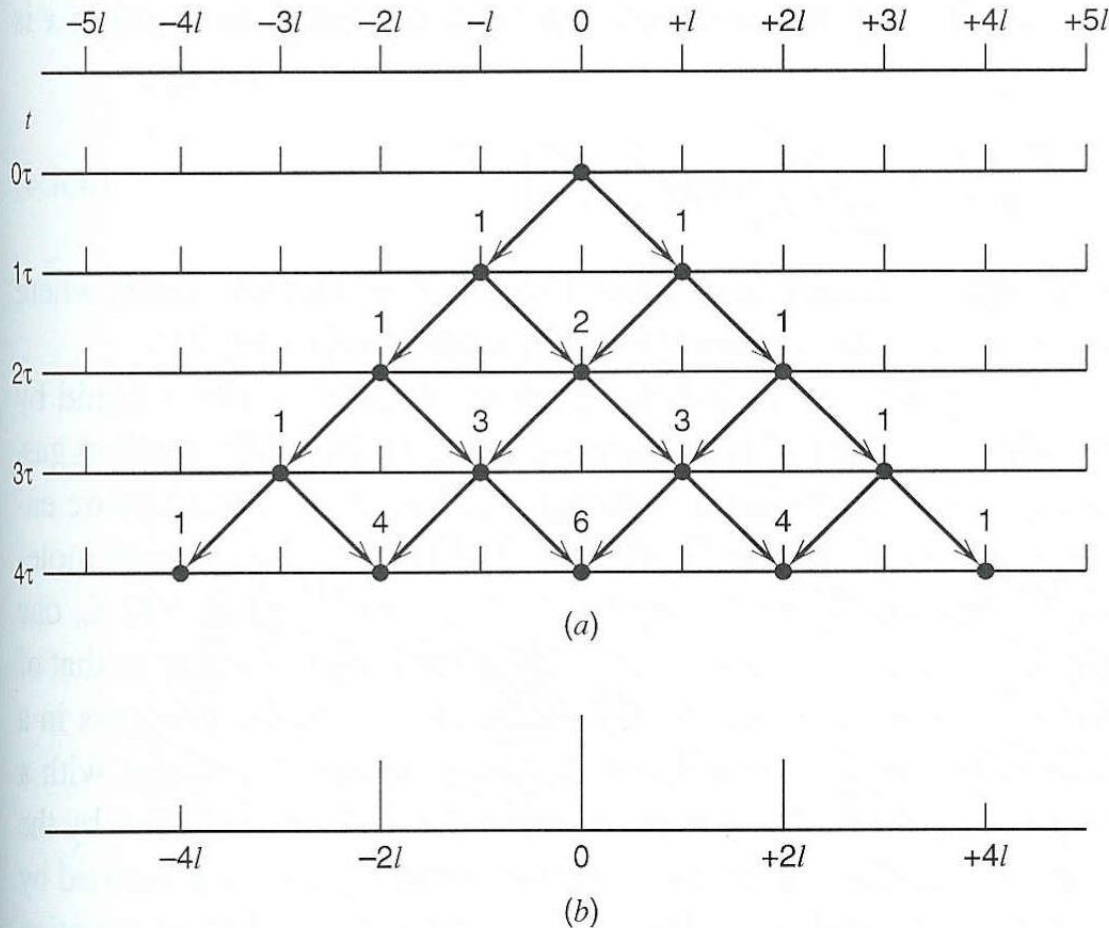
# Mass Transfer

## Diffusion

With migration decreased by supporting electrolyte and no convection in quiescent solution – mass transfer of an electroactive species near the electrode is restricted to diffusion.

Diffusion occurs by random walk process where the step size is  $l$  and one step every  $\tau$  seconds.

# Mass Transfer



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

# Mass Transfer

## Diffusion

Mean square displacement of the molecule –  $\bar{\Delta}^2$

total possibilities –  $2m$

$$m = t/\tau$$

$$\bar{\Delta}^2 = ml^2 = t/\tau l^2 = 2Dt$$

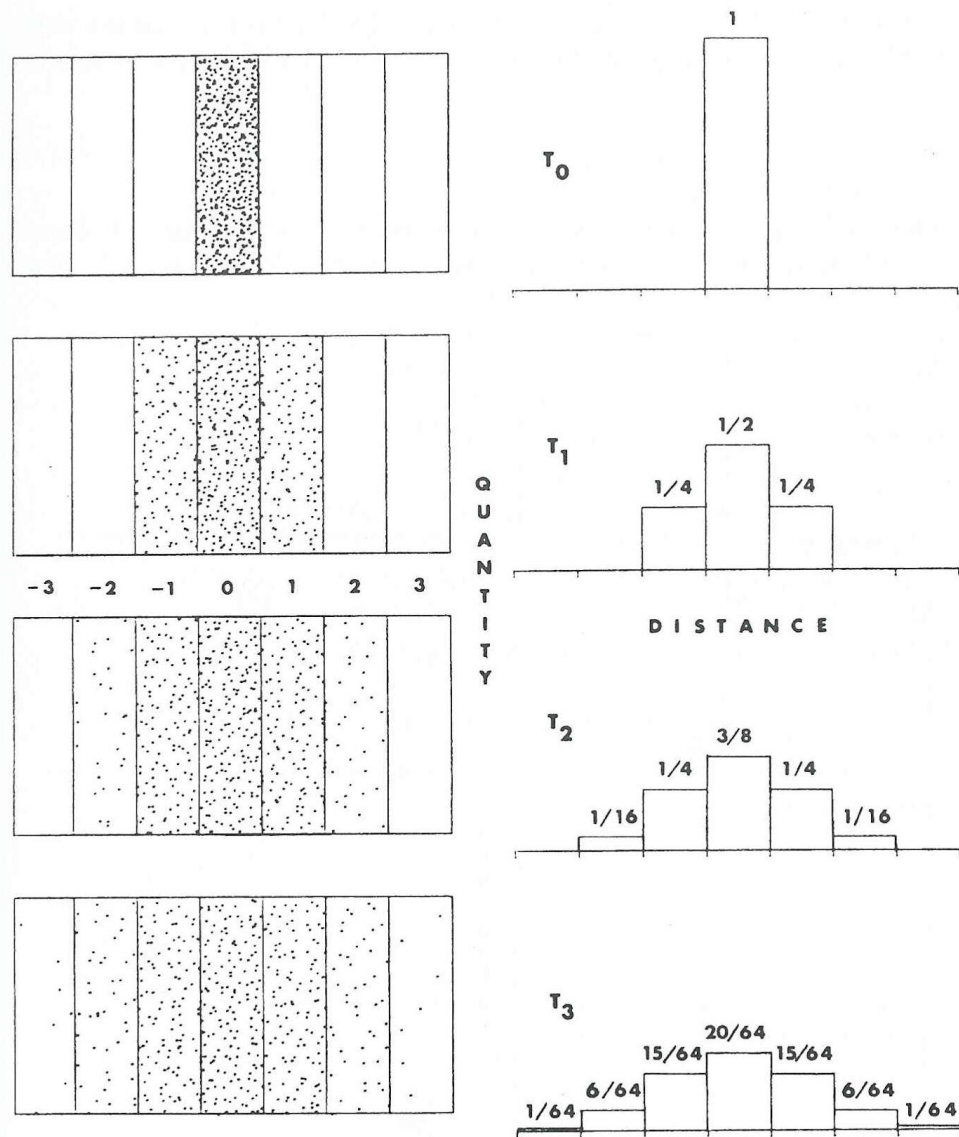
$D$  – diffusion coefficient

$l^2/2\tau$  – related to step size and step frequency

$$\bar{\Delta} = (2Dt)^{1/2}$$

For  $N_0$  molecules located at origin at  $t = 0$ , a gaussian curve describes the distribution with time.

# Mass Transfer



**Figure 2.1** Schematic representation of the diffusion process.

# Mass Transfer

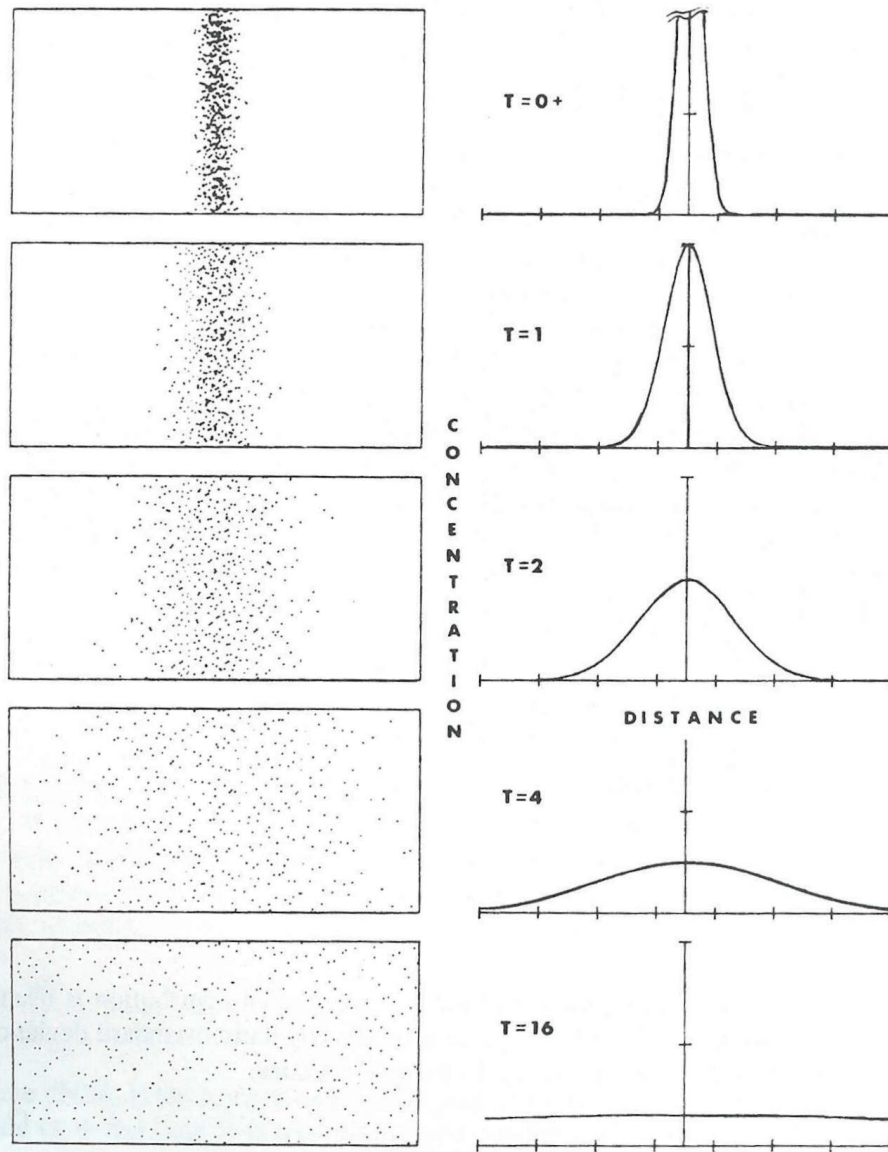
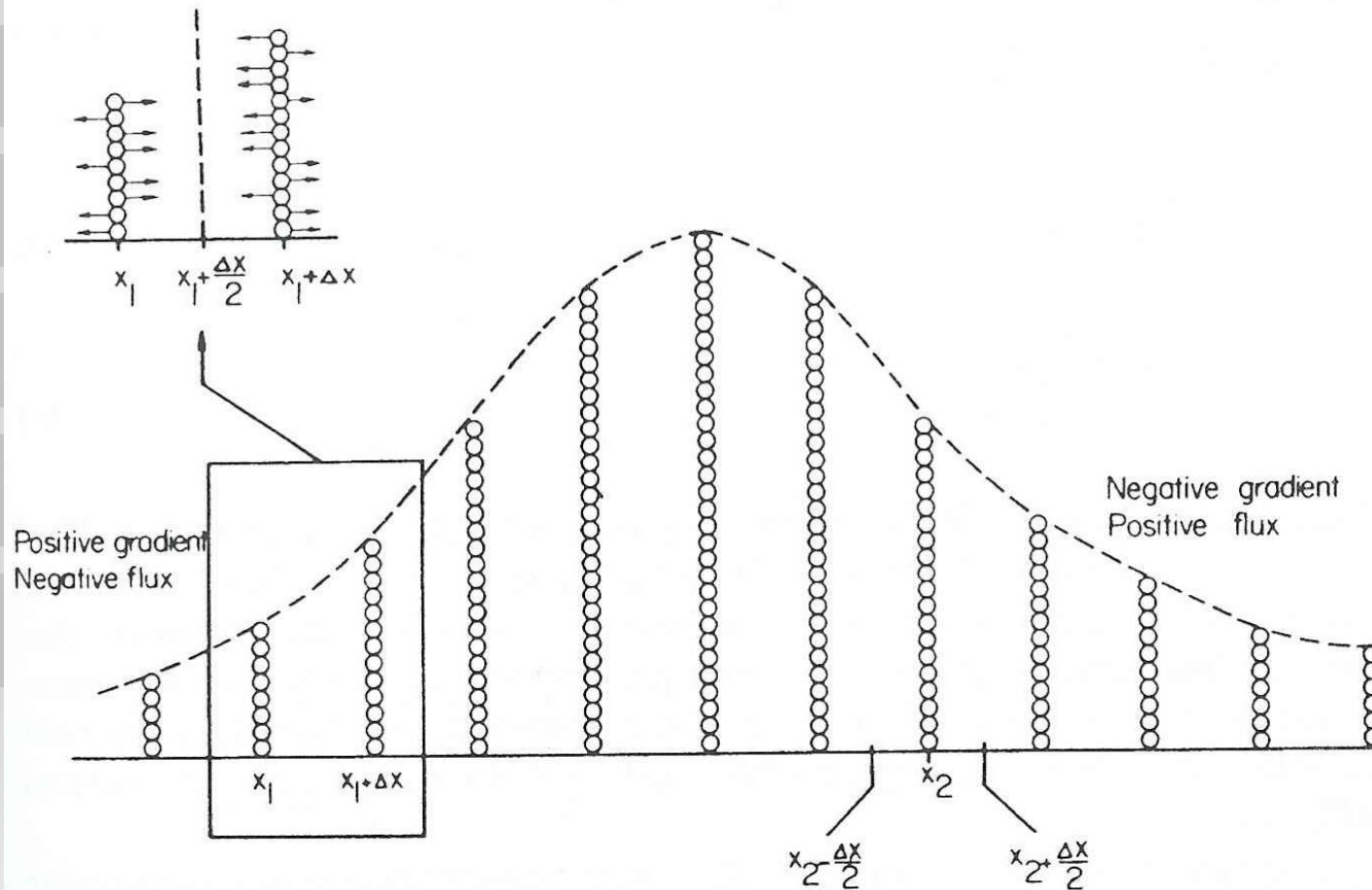


Figure 2.2 Spreading of an impulse of molecules at various times after creation.

# Mass Transfer



**Figure 2.3** Schematic representation of a Gaussian concentration profile by closely spaced spikes (or impulses) of molecules.

# Mass Transfer

## Diffusion

Number of molecules,  $N_{(x,t)}$  in a segment  $\Delta x$  wide centered on position  $x$  is:

$$N_{(x,t)}/N_o = \Delta x/2(\pi Dt)^{1/2} \exp (-x^2/4Dt)$$

# Mass Transfer

A simple model can be used to describe diffusion. Assume linear diffusion to a plane electrode where differences in concentration only arise perpendicular to the electrode surface.

Diffusion is quantitatively described by Fick's law where the rate of diffusion is known as flux in moles  $\text{m}^{-2} \text{s}^{-1}$ .

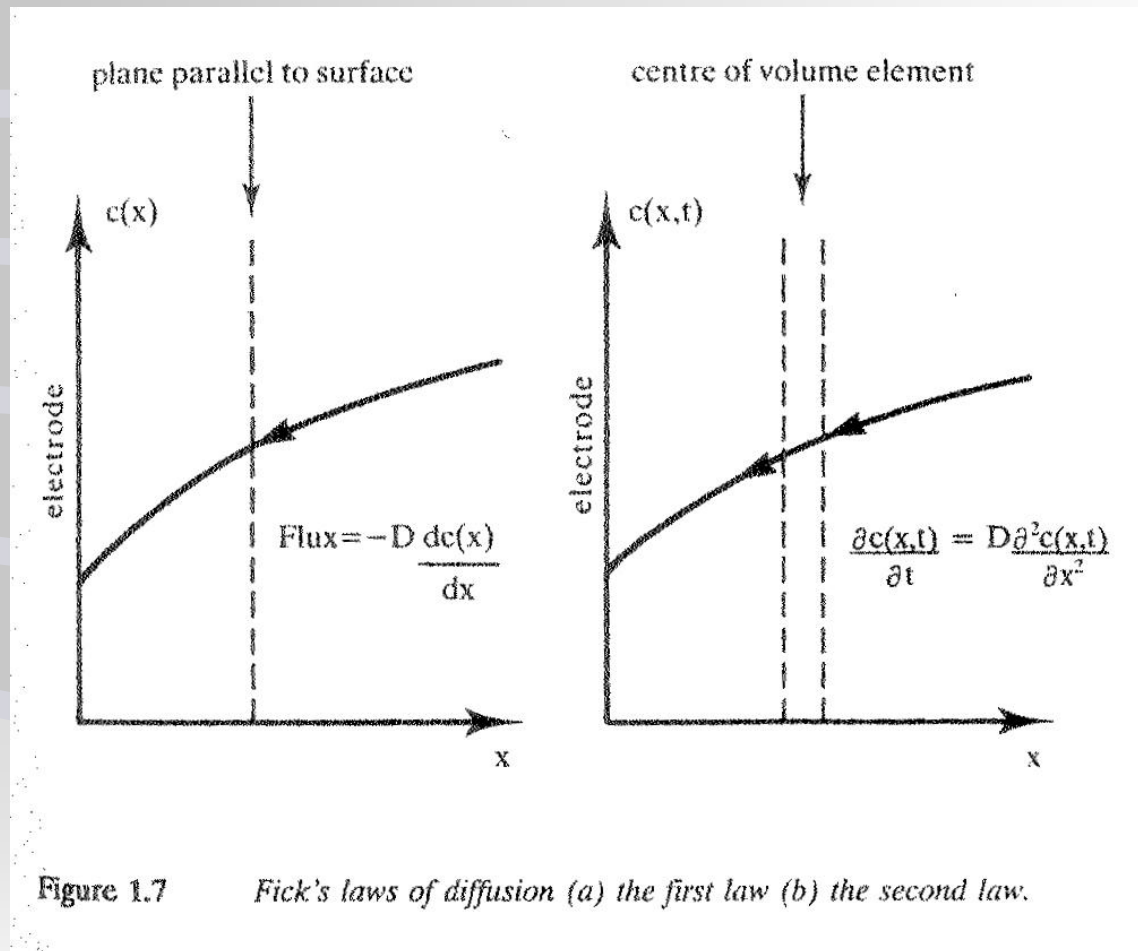
# Mass Transfer

Fick's first law:

$$Flux = -D \frac{dc(x)}{dx}$$

Where  $dc(x)/dx$  is the concentration gradient  
and  $D$  is the diffusion coefficient,  $m^2s^{-1}$ .

# Mass Transfer



# Mass Transfer

The second law describes the change with time of the concentration at the center of a volume element bounded by two planes parallel to the surface.

Fick's second law:

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

# Mass Transfer

## Fick's Law of Diffusion

Fick's second law pertains to the change in concentration of O with time.

$$\partial C_o / \partial t = D_o \nabla^2 C_o$$

$\nabla^2$  – Laplacian operation – varies with electrode geometries.

# Mass Transfer

**TABLE 4.4.2** Forms of the Laplacian Operator for Different Geometries<sup>a</sup>

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

<sup>a</sup>See also J. Crank, "The Mathematics of Diffusion," Clarendon, Oxford, 1976.

<sup>b</sup> $r$  = radial distance measured from the center of the disk;  $z$  = distance normal to the disk surface.

<sup>c</sup> $x$  = distance in the plane of the band;  $z$  = distance normal to the band surface.

# Mass Transfer

With the solution of the equations using Laplace transformations, the Cottrell equation is obtained. (potential step under diffusion control)

$$j = \frac{nFD^{\frac{1}{2}}c_o}{\pi^{\frac{1}{2}}t^{\frac{1}{2}}} \quad i = \frac{nFAD^{\frac{1}{2}}c_o}{\pi^{\frac{1}{2}}t^{\frac{1}{2}}}$$

# Mass Transfer

When a potential step is carried out in an unstirred solution, the  $j - t$  response can be analyzed:

- by plotting  $j$  vs  $t^{-1/2}$ , the plot will be linear and pass through the origin,  $D$  is equal to the slope.

# Mass Transfer

Experiments which are carried out in unstirred solutions containing a large excess of a base electrolyte are governed by diffusion.

Experiments which are carried out using stirring or rotating are governed by convection, although diffusion will still occur in the layer adjacent to the electrode.

# Solution

The electrochemical cell contains the electrodes and a solvent and supporting electrolyte.

How do you choose the best solution for the experiment?

Must consider the electrochemical as well as chemical reactions.

# Solution

## Ideal Solvent System Properties

- Electrochemically Inert (stable over a wide range of potentials)
- High electrical conductivity
- Good solvent power
- Chemical Inertness
- Available in pure form
- Low cost

# Solution

## Electrochemically Inertness

For a solvent system to be stable over a wide range of potentials – it cannot undergo any electrochemical reaction during oxidation or reduction of the analyte.

## Solvent (solution) Breakdown Potential

Potential of an electrochemical reaction of the solvent system.

Examples: Water, Tetrabutylammonium hexafluorophosphate in ACN (+3.4 - -2.9 V vs SCE), Nitrobenzene (hard to oxidize easy to reduce)

# Solution

## High electrical conductivity

Solvent system must support the passage of an electric current – have low electrical resistance and high dielectric constant ( $>10$ ).

Examples: Water 80.1

for organic electrochemistry – DMF (36.7, ACN 37.5, DMSO 46.7)

# Solution

## Good solvent power

Able to dissolve a wide range of substances at acceptable concentrations ( $\sim 0.1\text{M}$  for electrolytes and  $0.1\text{-}1\text{ mM}$  for analytes)

Example of salts which dissolve well in organic solvents:  
hexafluorophosphates, tetrafluoroborates,  
ethyltributylammonium tetrafluoroborate, tetrabutylammonium  
hexafluorophosphate.

# Solvent

Good solvent power

Viscosity is also important.

Low viscosity is better so that mass transport by diffusional control can last up to 40-50 sec for techniques like chronopotentiometry.

Viscosity is affected by temperature where low temperatures could essentially stop mass transport.

# Supporting Electrolyte

## Possible Roles of the Supporting Electrolyte (inert)

- Regulates cell resistance and mass transport by electrical migration
- Control or “buffer” the level of hydronium ion activity in solution
- Associate with the electroactive analyte (i.e. complexing of ions with metals, EDTA)
- Form ion-pair or micellar aggregates with the electroactive analyte (ionic liquids)
- Determines the structure of the double layer
- Impose positive or negative voltage limits because of redox properties

# Supporting Electrolyte

## Control of Cell Resistance

Primary function of the supporting electrolyte is to provide a conducting medium which will minimize  $iR$  drop and ohmic heating of the solution (i.e. when  $i$  is large).

To have mass transport controlled only by diffusion need to use 50-100 times the concentration of supporting electrolyte to electroactive analyte (suppresses electrical migration).

# Supporting Electrolyte

TABLE 7.7 Limiting Ionic Conductivities of Ions  $\lambda_i^\circ$  in Selected Solvents<sup>a</sup>

Ion	Water <sup>b</sup>	Acetone	Acetonitrile	Propylene Carbonate	Nitro-methane	Nitro-benzene	Dimethyl formamide	Dimethyl Sulfoxide	Sulfolane (40°C)
H(sol) <sup>+</sup>	349.8	90	100		63		35	16	
Li(sol) <sup>+</sup>	38.7	72.8	69.3	7.3	55		25.0	11.4	4.3
Na(sol) <sup>+</sup>	50.1	78.4	76.9		58	16.3	29.9	13.5	3.6
K(sol) <sup>+</sup>	73.5	80.6	83.6	12.0	60	17.8	30.8	13.9	4.0
Me <sub>4</sub> N <sup>+</sup>	44.9	97.7	94.5		54.5	17.1	38.9	18.6 <sup>c</sup>	4.3
Et <sub>4</sub> N <sup>+</sup>	32.7	89.0	84.8	13.3	47.6	16.4	35.6	17.1	4.0
<i>n</i> -Bu <sub>4</sub> N <sup>+</sup>	19.5	67.3	64.1	9.3	34 <sup>c</sup>	11.9	25.9	11.6	2.8
Cl <sup>-</sup>	76.4	105.2	98.4	20.2	62.5	22.2	55.1	24.2	9.3
Br <sup>-</sup>	78.1	115.9	100.7	19.4	62.9	21.6	53.6	24.3	8.9
I <sup>-</sup>	76.8	113.0	102.4	18.8	62	20.4	52.3	24.0	7.2
NO <sub>3</sub> <sup>-</sup>	71.5	120.1	106.4		64	22.6	57.3	27.0	
BF <sub>4</sub> <sup>-</sup>			108.5						
PF <sub>6</sub> <sup>-</sup>			104.2						6.0
ClO <sub>4</sub> <sup>-</sup>	67.3	115.3	103.7	18.8	64	20.9	52.4	24.7	6.7

<sup>a</sup>All values at 25°C unless otherwise indicated; data from Ref. 48 unless otherwise indicated.

<sup>b</sup>Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*, Butterworths Scientific Publications, London, 1955, p. 452.

<sup>c</sup>Janz, G. J.; Tomkins, R. P. T., eds., *Nonaqueous Electrolytes Handbook*, Academic Press, New York, 1972.

# Supporting Electrolyte

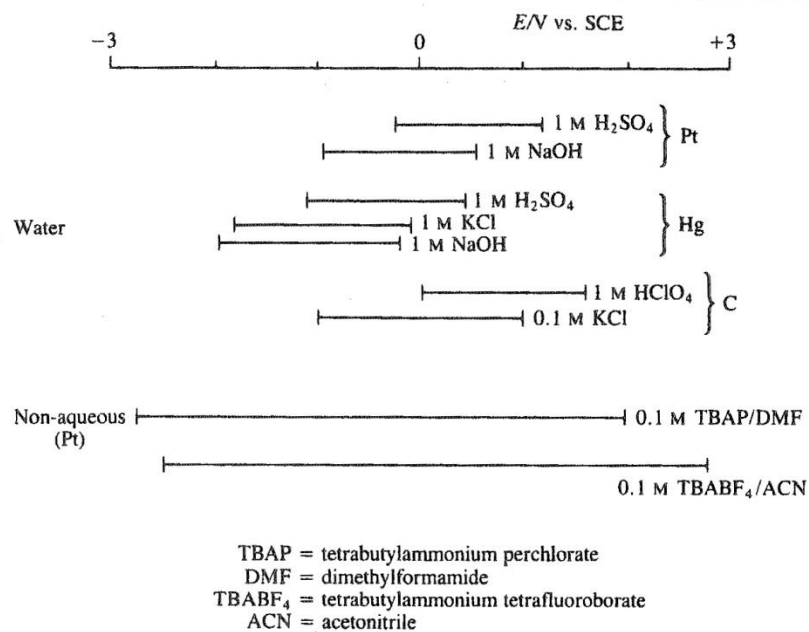
TABLE 7.6 Solubilities of Tetraalkylammonium Salt Electrolytes and Specific Resistances of the Solutions at 25°C

	Acetonitrile		1,2-Dimethoxyethane		Tetrahydrofuran		Dimethylformamide	
	Solubility (g 100 mL <sup>-1</sup> of Solution (conc., M)	Specific Resistance (Ω-cm) (conc., M)	Solubility (g 100 mL <sup>-1</sup> of Solution (conc., M)	Specific Resistance (Ω-cm) (conc., M)	Solubility (g 100 mL <sup>-1</sup> of Solution (conc., M)	Specific Resistance (Ω-cm) (conc., M)	Solubility (g 100 mL <sup>-1</sup> of Solution (conc., M)	Specific Resistance (Ω-cm) (conc., M)
Et <sub>4</sub> NClO <sub>4</sub>	26(1.13)	26(0.60)	(<0.01)		(<0.01)		23(1.00)	52(0.60)
<i>n</i> -Bu <sub>4</sub> NClO <sub>4</sub>	70(2.05)	37(0.60)	31(1.10)	312(1.0)	50(1.48)	368(1.0)	79(2.29)	77(0.60)
Et <sub>4</sub> NBF <sub>4</sub>	37(1.69)	18(1.0)	(<0.01)		(<0.01)		27(1.24)	38(1.0)
<i>n</i> -Bu <sub>4</sub> NBF <sub>4</sub>	71(2.21)	31(1.0)	53(1.70)	228(1.0)	65(2.02)	373(1.0)	75(2.34)	69(1.0)
Et <sub>4</sub> NBr	7.8(0.37)		(<0.01)		(<0.01)		4.1(0.19)	
<i>n</i> -Bu <sub>4</sub> NBr	66(1.99)	48(0.60)	(<0.01)		4.8(0.14)		52(1.57)	106(0.60)

Source: Ref. 35.

# Solution

**Table 7.2.** Some supporting electrolytes and their approximate potential ranges in water and other solvents for platinum, mercury, and carbon



Chemical Inertness  
Available in pure form  
Low cost

# Supporting Electrolyte

## Advantages:

- eliminates the contribution of migration to mass transfer for the electroactive species
- decreases resistance of the cell
- establishes the solution composition (i.e. pH, ionic strength, ligand concentration)
- reduces electrical power dissipated in the cell leading to simpler instruments
- eliminates sample matrix effects
- helps keep double layer thin with respect to diffusion layer
- established uniform ionic strength throughout the solution, while ions are being produced or consumed at the electrodes

# Supporting Electrolyte

## Disadvantages:

- large concentrations can bring impurities and interferences
- can give own faradic response
- can react with products of electrode process
- can adsorb on electrode surface and alter kinetics

# Mass Transfer

## Migration

In bulk solution, concentration gradients are small and the total current is carried by migration:

For a species,  $j$ , the mobility of the species is given by the Einstein-Smoluchowski equation:

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

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

# Mass Transfer

## Mix Mechanisms near Electrode

Flux of species at electrode surface controls the rate of reaction.

Electroactive substance transported by both migration and diffusion.

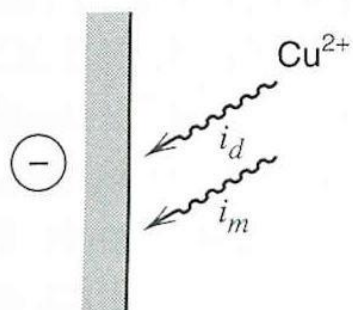
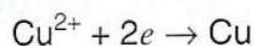
$$i = i_d + i_m$$

Best to minimize contribution from migration for experiments.

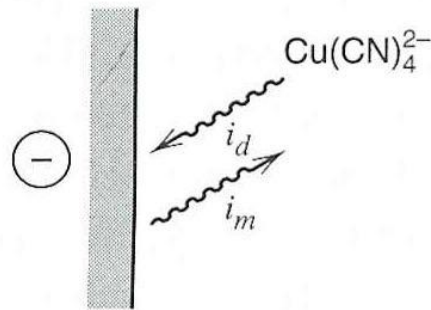
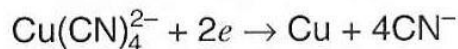
# Mass Transfer

## Mix Mechanisms near Electrode

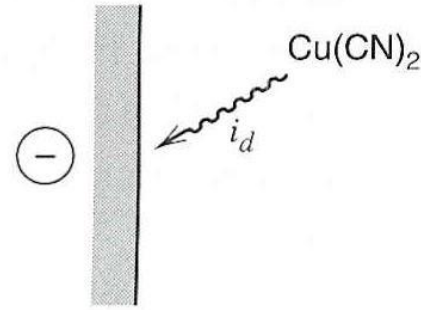
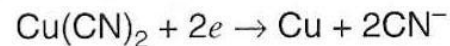
$i_d$  and  $i_m$  can be in the same or in opposite directions.



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



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



$$(c) i = i_d$$

**Figure 4.3.1** Examples of reduction processes with different contributions of the migration current: (a) positively charged reactant, (b) negatively charged reactant, (c) uncharged reactant.

# Mass Transfer

For quiescent conditions, convection is zero, so:

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

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

where  $i_{d,j}$  – diffusion current of species  $j$

$i_{m,j}$  – migration current of species  $j$

(in Chapter 4, subscript  $j$  is used to represent the species instead of subscript  $i$  as in Chapter 2)

# Mass Transfer

Total current,  $i$  is made up of all contributions from all species.

$$i = \sum_j i_j$$

$$i = \frac{F^2 A}{RT} \cdot \frac{\partial \phi}{\partial x} \sum_j z_j^2 D_j C_j + FA \sum_j z_j D_j \frac{\partial C_j}{\partial x}$$

↑  
migration

↑  
diffusion

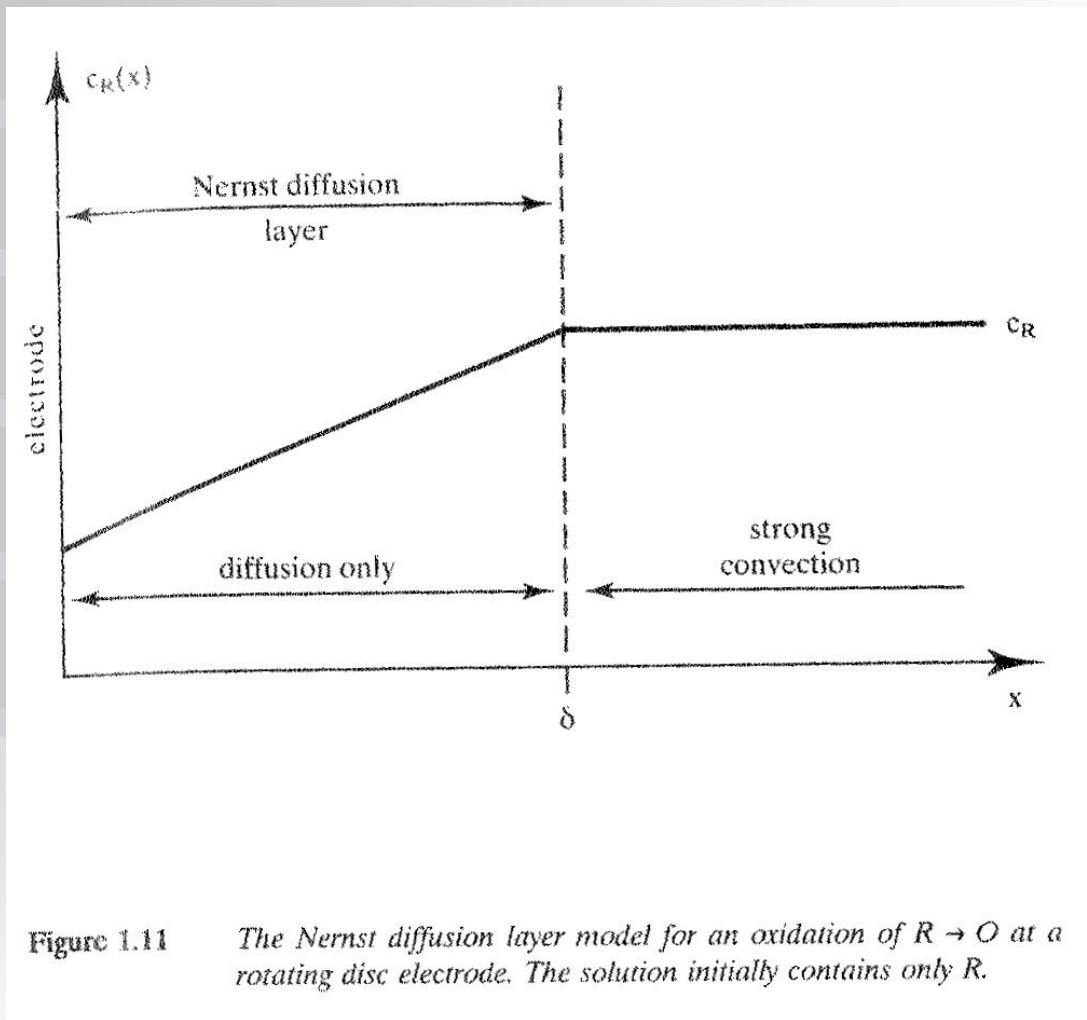
# Mass Transfer

For convection-diffusion experiments:  
i.e. rotating disk experiments

The electrolyte is divided into two zones:

- A stagnant layer next to the surface (diffusion only) with thickness,  $\delta$  and
- Outside this layer convection dominates

# Mass Transfer



# Mass Transfer

The equation for the rotating disk experiment is:

$$j_L = 0.62 n F D^{0.66} \nu^{-0.166} c_o \omega^{0.5}$$

# Introduction

## Conduction in a cell

### Charge is conducted by:

- The electrodes and leads – involves electrons
- The solution – involves migration of cations and anions
- **The interface – involves oxidation and reduction**

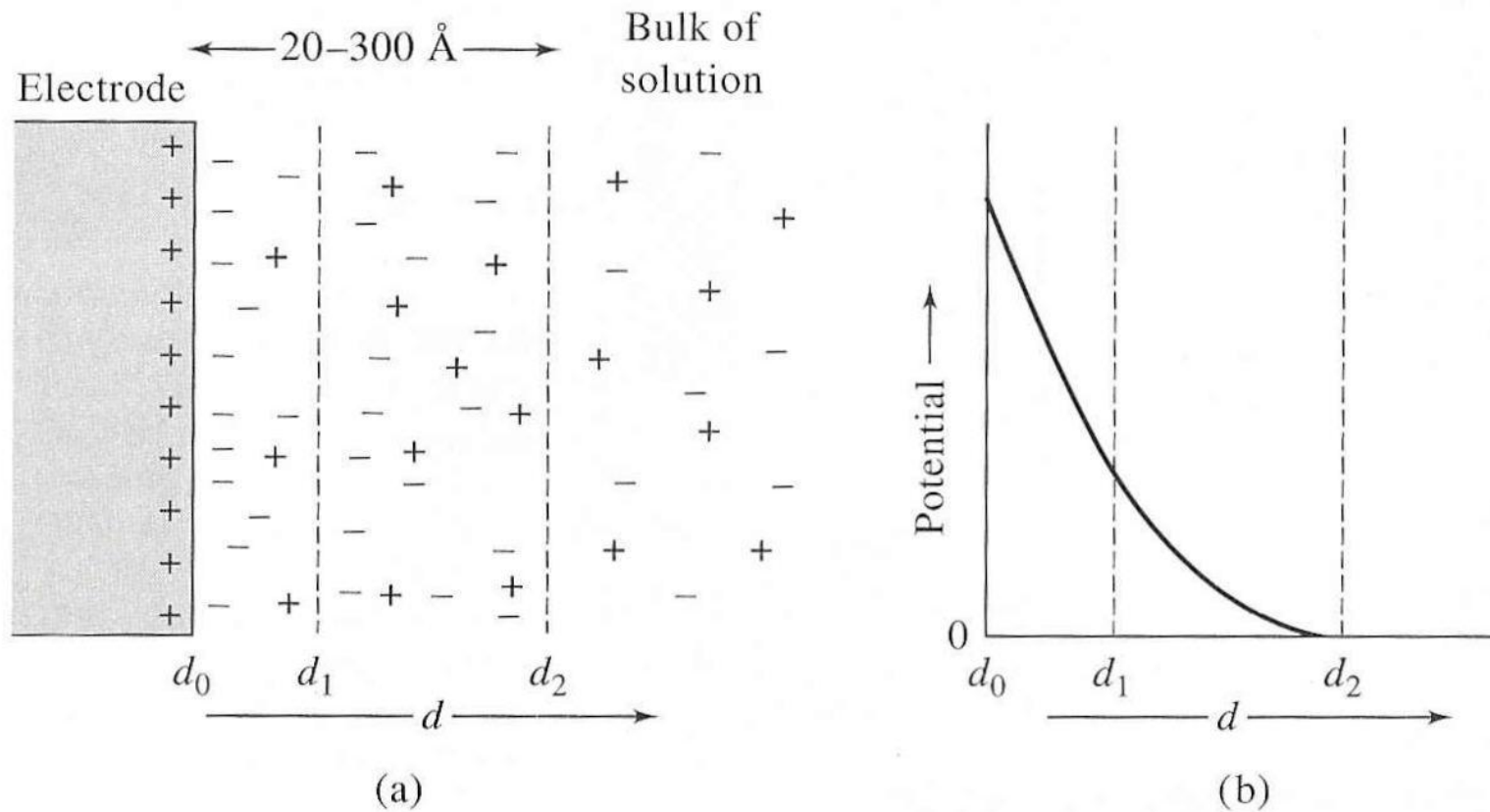
# Introduction

## Solution structure

The double layer consist of

- Compact Inner layer where potential decreases linearly with distance from the electrode surface
- A diffuse layer where potential decreases exponentially

# Introduction



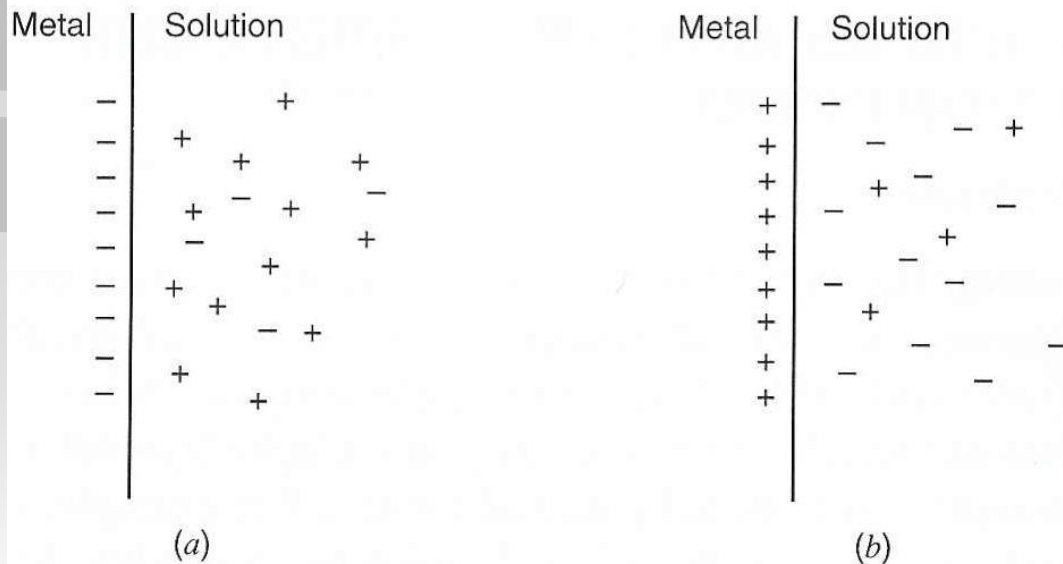
**Figure 22-2** Electrical double layer formed at electrode surface as a result of an applied potential.

# Electrical Double Layer

There is a charge on the metal electrode,  $q^M$  and a charge in the solution,  $q^S$ .

This is the electrical double layer.

The charge density,  $\sigma - (\mu\text{C}/\text{cm}^2)$



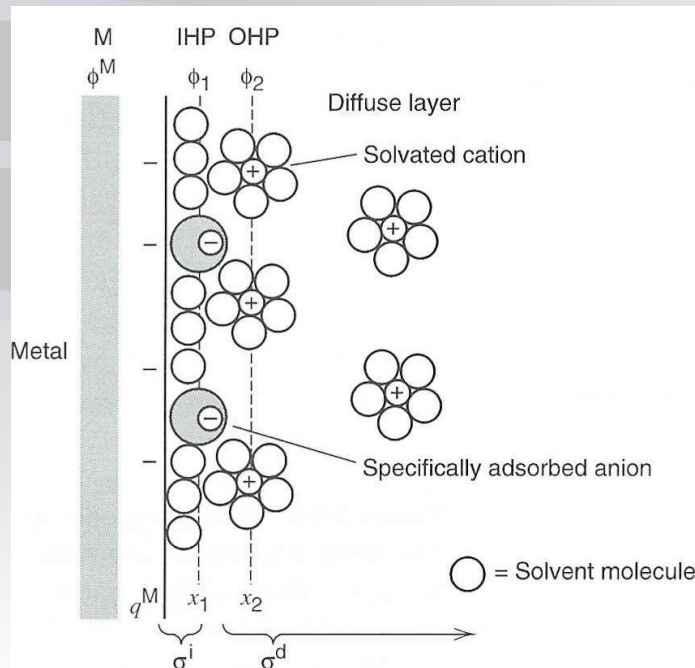
**Figure 1.2.2** The metal–solution interface as a capacitor with a charge on the metal,  $q^M$ , (a) negative and (b) positive.

# Electrical Double Layer

Inner Layer – solution closest to electrode, adsorbed ions.

Also called the compact, Helmholtz, or Stern Layer

$$\sigma^S = \sigma^i + \sigma^d = -\sigma^M$$



**Figure 1.2.3** Proposed model of the double-layer region under conditions where anions are specifically adsorbed.

# Electrical Double Layer

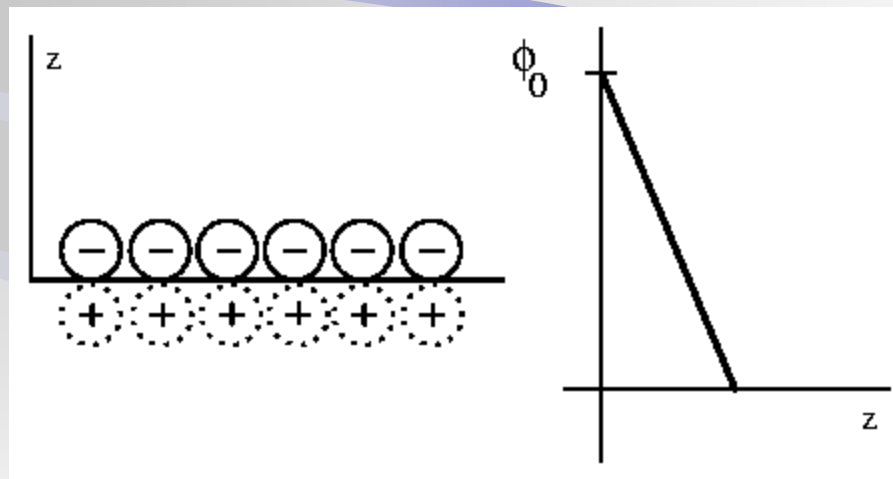
## Models for the Double Layer

- Helmholtz
- Gouy-Chapman
- Stern
- Grahame
- Bockris, Muller

# Electrical Double Layer

## Helmholtz Model

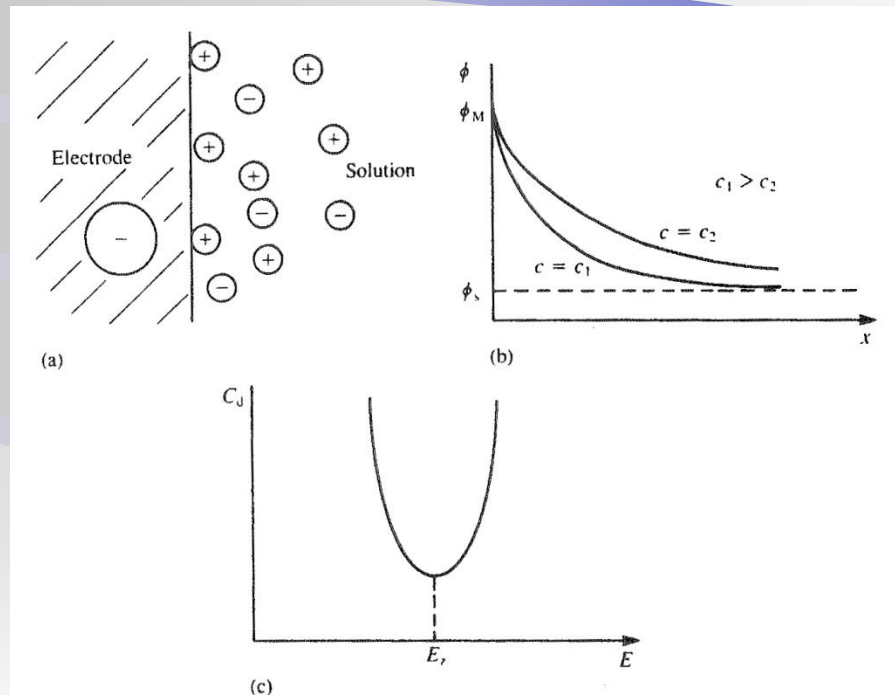
First double layer model – considers the ordering of positive and negative charges on two sides of an interface. Compact layer does not stretch into the solution (capacitor).



# Electrical Double Layer

## Gouy-Chapman Model

Considers the applied potential and electrolyte concentration influence the value of the double layer capacity. So the double layer would have variable thickness (diffuse double layer).

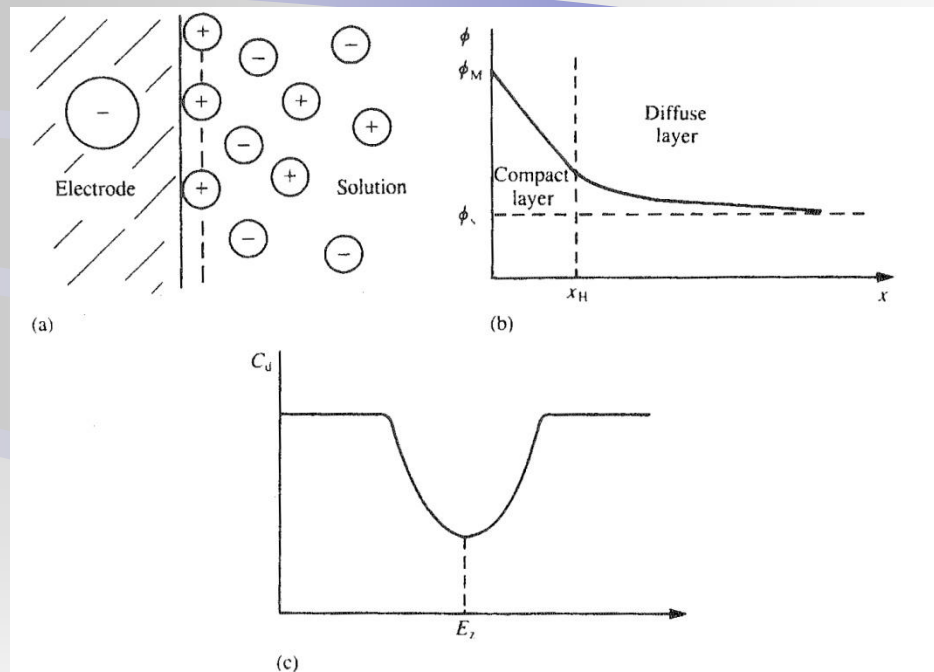


**Fig. 3.6** The Gouy-Chapman model of the double layer. (a) Arrangement of the ions in a diffuse way; (b) Variation of the electrostatic potential,  $\phi$ , with distance,  $x$ , from the electrode, showing effect of ion concentration,  $c$ . (c) Variation of  $C_d$  with potential, showing the minimum at the point of zero charge  $E_z$ .

# Electrical Double Layer

## Stern Model

Combined the Helmholtz and G-C models – where the double layer was formed by a compact layer of ions next to the electrode and a diffuse layer extending into the bulk.

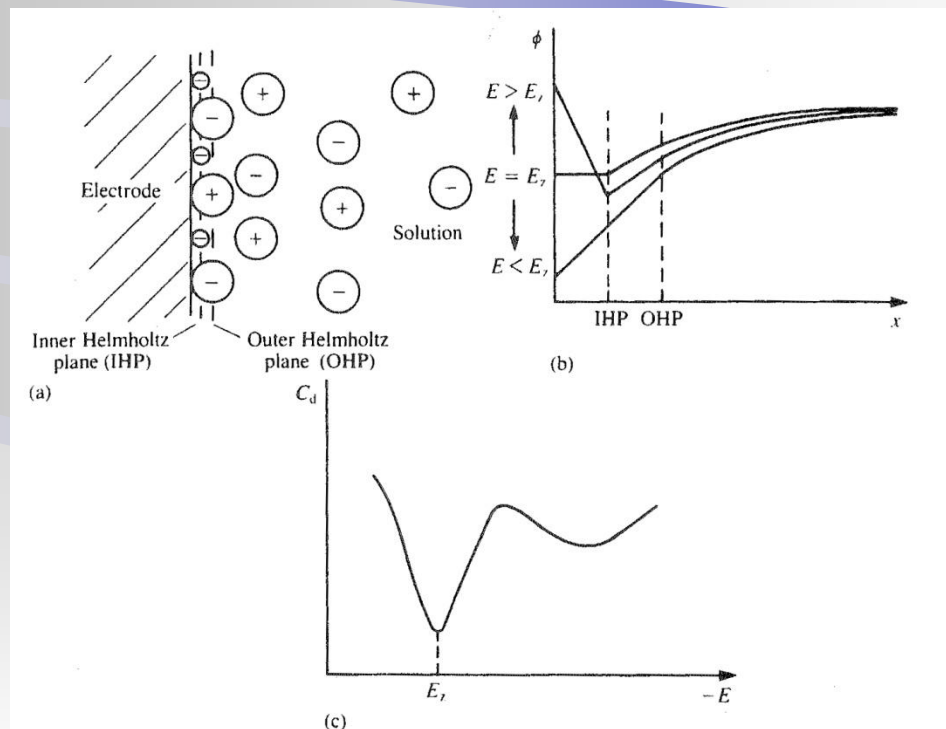


**Fig. 3.7** The Stern model of the double layer. (a) Arrangement of the ions in a compact and a diffuse layer; (b) Variation of the electrostatic potential,  $\phi$ , with distance,  $x$ , from the electrode; (c) Variation of  $C_d$  with potential.

# Electrical Double Layer

## Grahame Model

Added a third region to the Stern model. An adsorbed ion loses its solvation and bonding is strong. The IHP passes through the center of these ions. The OHP passes through the center of solvated ions, and the region outside the OHP is the diffuse region.

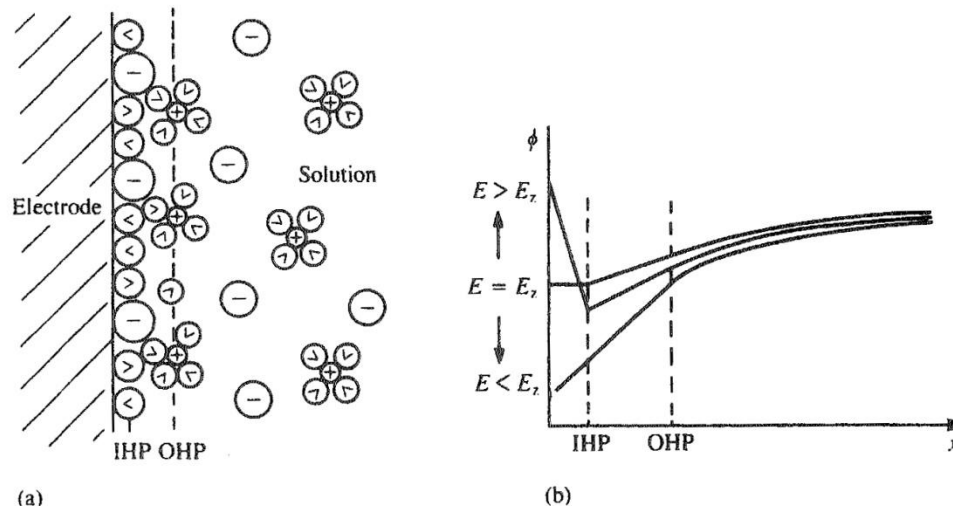


**Fig. 3.8** The Grahame model of the double layer, for the mercury electrode. (a) Arrangement of ions; (b) Variation of the electrostatic potential,  $\phi$ , with distance,  $x$ , from the electrode; (c) Variation of  $C_d$  with potential.

# Electrical Double Layer

## Bockris, Devanathan, and Muller Model

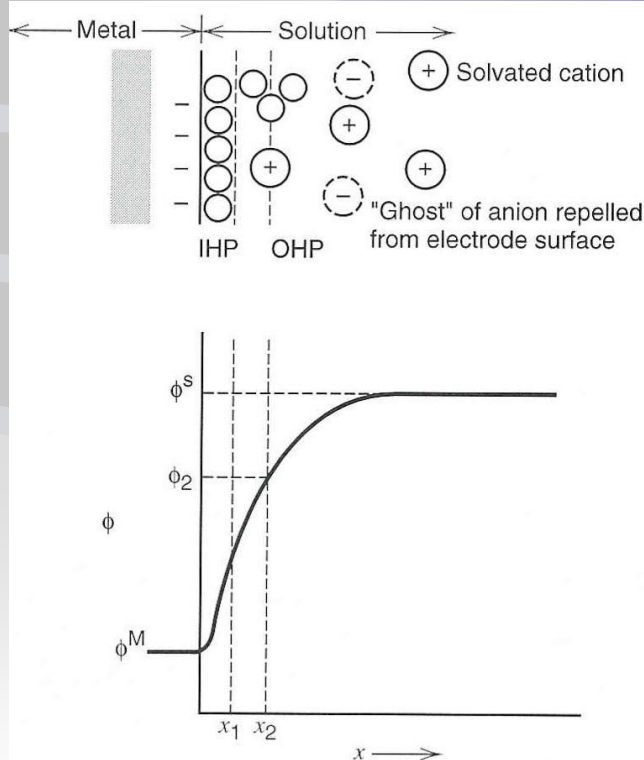
Takes into account the physical nature of the interfacial region, i.e. water also interacts with the electrode. Since solvent concentration is much higher than the solute, there must be predominately solvent molecules near the interface. Also introduced the shear plane – zeta potential.



**Fig. 3.9** The model of Bockris *et al.* of the double layer. (a) Arrangement of ions and solvent molecules;  $\odot$  represents a water molecule; (b) Variation of the electrostatic potential,  $\phi$ , with distance,  $x$ , from the electrode.

# Electrical Double Layer

Structure of double layer can effect the rate of electrode processes, since the potential varies throughout the layers.



**Figure 1.2.4** Potential profile across the double-layer region in the absence of specific adsorption of ions. The variable  $\phi$ , called the *inner potential*, is discussed in detail in Section 2.2. A more quantitative representation of this profile is shown in Figure 12.3.6.

# Class Assignment

- Research paper Topic
- Read Chapters 1, 4, and 13

“Electrochemical Methods” Bard