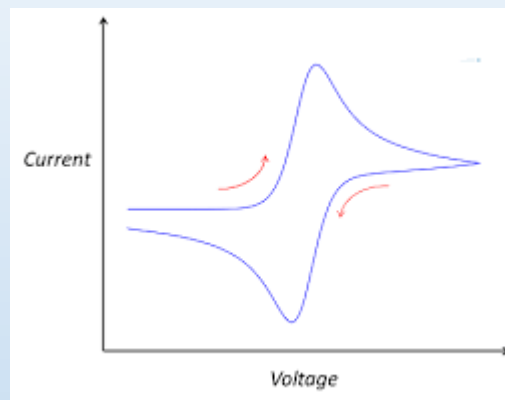


Fundamentals of Electrochemistry



Course: CSO 203

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PIONEERS OF ELECTROCHEMISTRY

- Humphry Davy: British Chemist (1778-1829)



Worked on production of electricity in an electrolytic cell resulted from chemical reactions between electrolyte and metal

- Michael Faraday: British Chemist (1791-1867)



Electrical force exerted on molecules to cause them dissociate.

Amount of materials decomposition related directly to the amount of electricity passing through the solution

- Hermann Von Helmholtz: German Physicist (1821-1894)



Made significant contribution in fluid dynamics, including Helmholtz's theorems

Formation of Electrical Double Layer

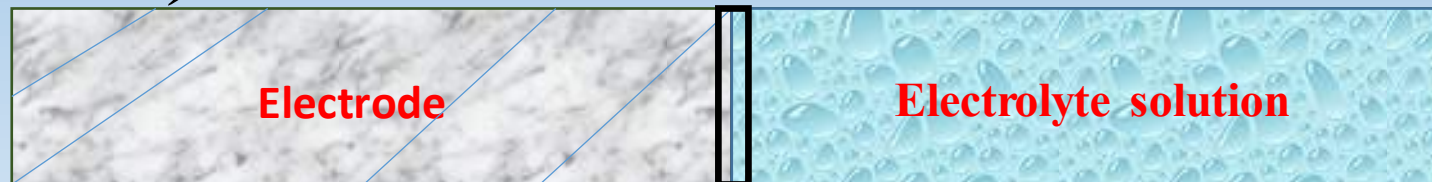
When an electrode (macroscopic object) is brought in contact with liquid ionic conductor (electrolyte), interactions of ions assist to develop interfacial region at the electrode surface, which is termed as electrical double layer

The first layer, the surface charge (either positive or negative). The second layer is composed of ions attracted to the surface charge via the Coulomb force, electrically screening the first layer.

Closely contact of two phases. Two layers of opposite polarity formed at the interface between electrode and electrolyte.

Difference of electric potential accompanied by charge separation.

*Interface region has different scenario (**electronic property, structure, electric field**) compared to the bulk)*



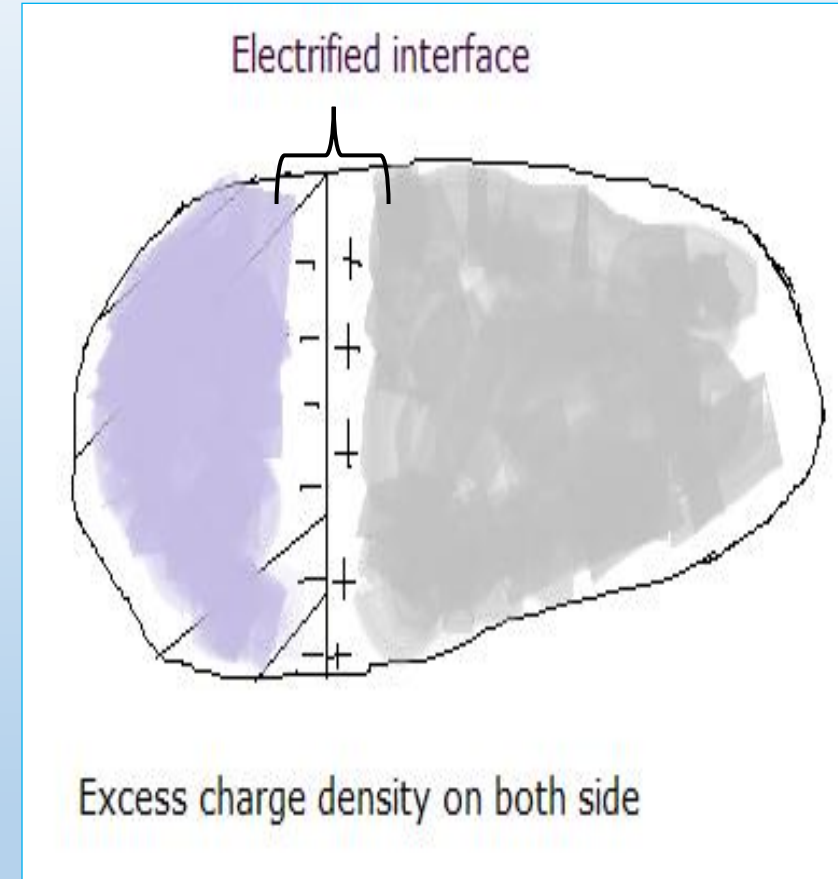
Important aspects of electrical double layer

Generation of induced charge depending on direction of electric field

Separation of charge across the electrode–electrolyte interface

Interface region as a whole electrically neutral

Arrangement of charges and oriented dipoles constitute the interface architecture



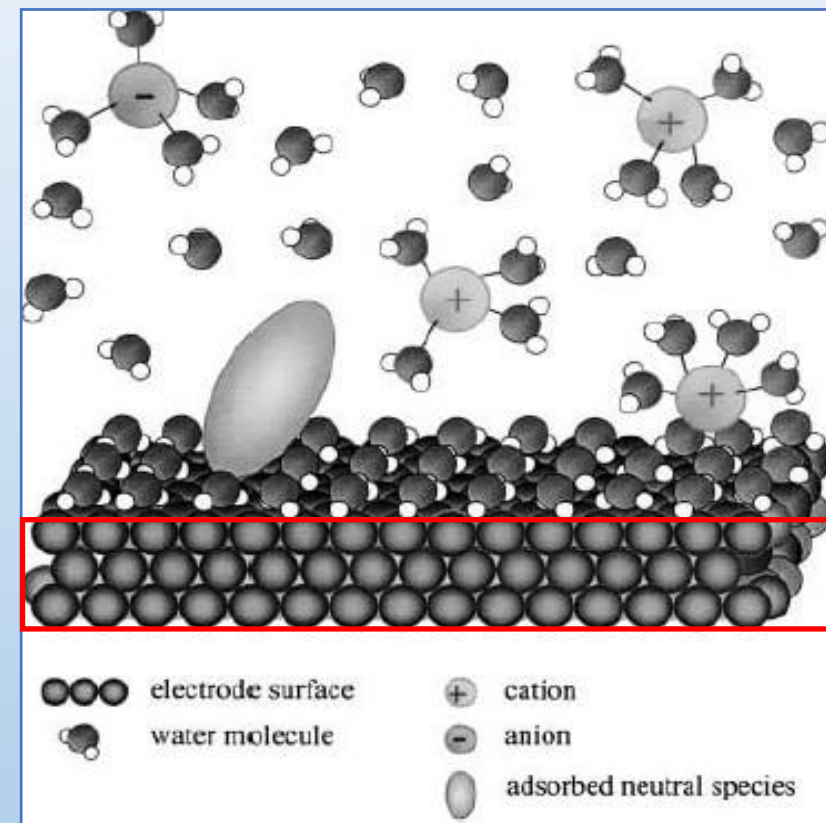
A Bird view into an Electrified Interface

Layer of adsorbed water molecule on electrode surface

Hydrogen atoms of adsorbed water molecules are oriented towards negative metal surface

In case of excess positive charge at the metal surface dipoles of water will have different orientation

By removing some water large neutral molecule can be specifically adsorbed



Bockris, J. M.; Reddy, A. K. *Modern Electrochemistry 2A*; NY, 2000

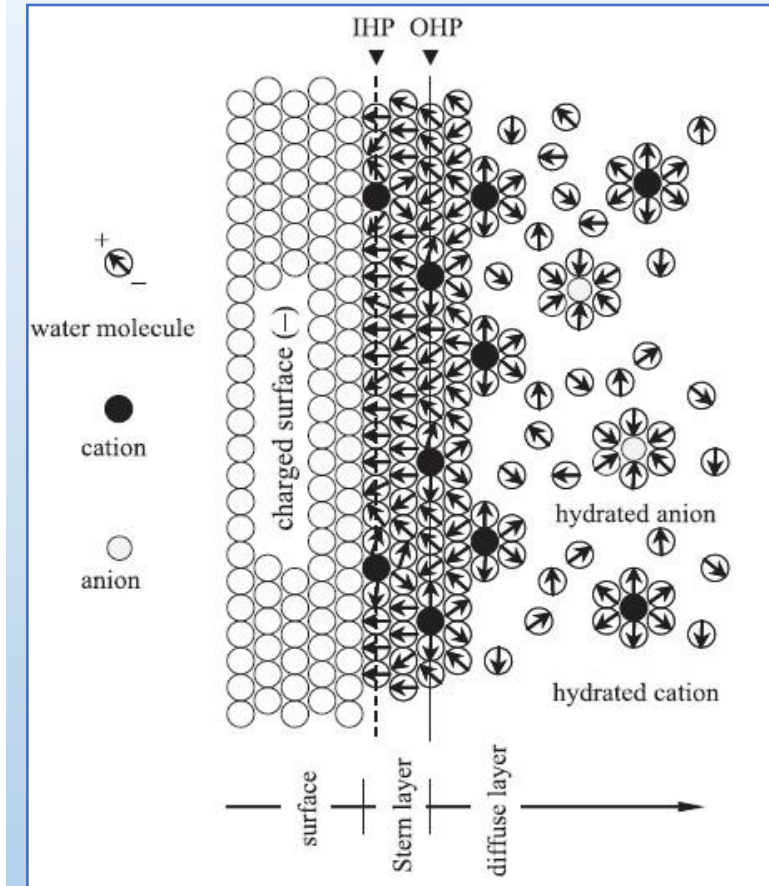
Electrical Double Layer Models

*Existence of double layer at the electrode surface as a parallel plate compact layer was first proposed by Helmholtz. The inner layer is also called the **compact, Helmholtz, or Stern layer**. In 1853 he showed that an electrical double layer (DL) is essentially a **molecular dielectric** and stores charge electrostatically.*

Below the electrolyte's decomposition voltage, the stored charge is linearly dependent on the voltage applied

*In 1910 Gouy-Chapman stated about **diffuse double layer** of accumulation of ions due to extent of Boltzmann distribution at a certain distance from metal surface*

In 1924 Stern suggested that interface includes both rigid layer and diffuse layer



Inner Helmholtz Plane & Outer Helmholtz Plane

Inner Helmholtz Plane (IHP) is the locus of the centre of specifically adsorbed dehydrated ions (anions for example) at a distance x_1 .

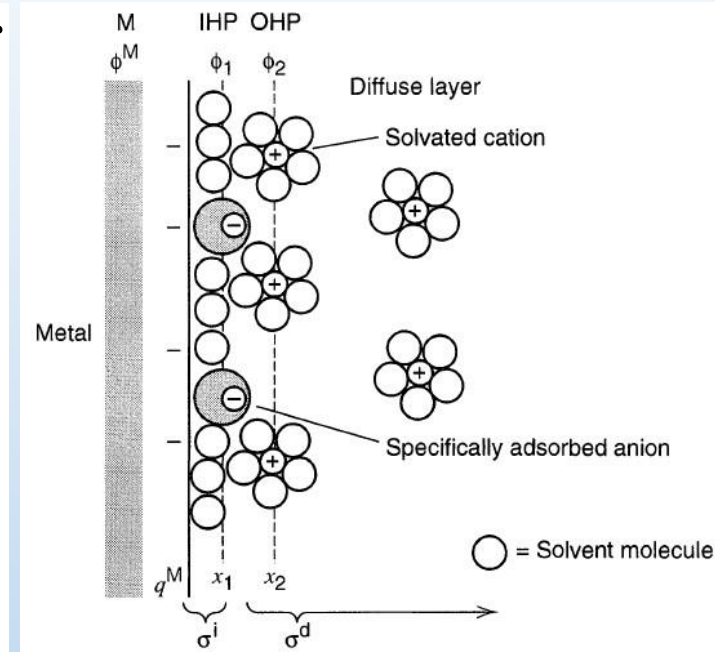
The total charge density from specifically adsorbed ions in this inner layer is σ^i ($\mu\text{C}/\text{cm}^2$).

Solvated ions can approach the metal only to a distance x_2 .

The interaction of the solvated ions with the charged metal involves only long-range electrostatic forces

Outer Helmholtz Plane (OHP) is the plane of just nearby approach of hydrated/solvated counter ions or locus of solvated ion

A diffused layer is formed after the OHP which extends from the OHP into the bulk of the solution



Inner Helmholtz Plane & Outer Helmholtz Plane

Because of thermal agitation in the solution, the nonspecifically adsorbed ions are distributed in a three-dimensional diffuse layer

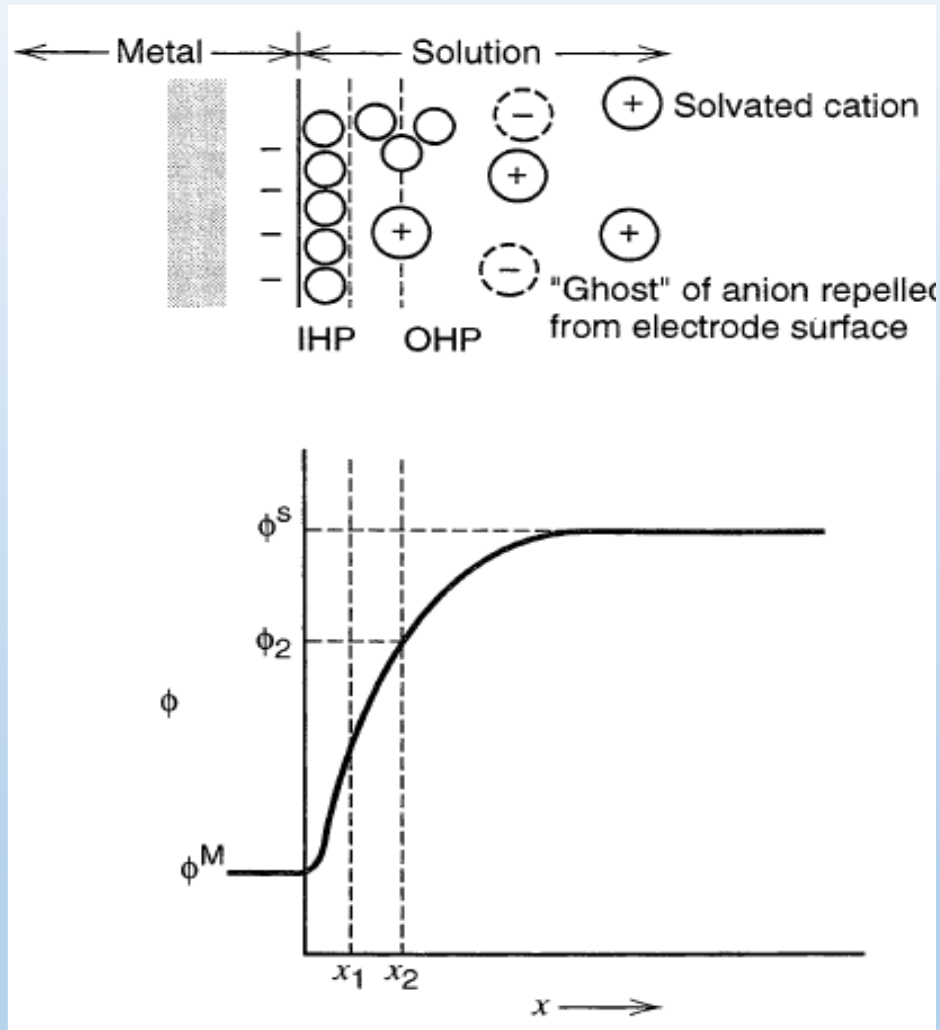
The excess charge density in the diffuse layer is σ^d , hence the total excess charge density on the solution side of the double layer, σ^s , is given by $\sigma^s = \sigma^i + \sigma^d = -\sigma^M$

The thickness of the diffuse layer depends on the total ionic concentration in the solution; for concentrations greater than 10^{-2} M, the thickness is less than $\sim 100 \text{ \AA}$

The structure of the double layer affect the rates of electrochemical processes

One of course cannot neglect the existence of the double-layer capacitance or the presence of a charging current in electrochemical experiments

Potential profile across the double-layer region

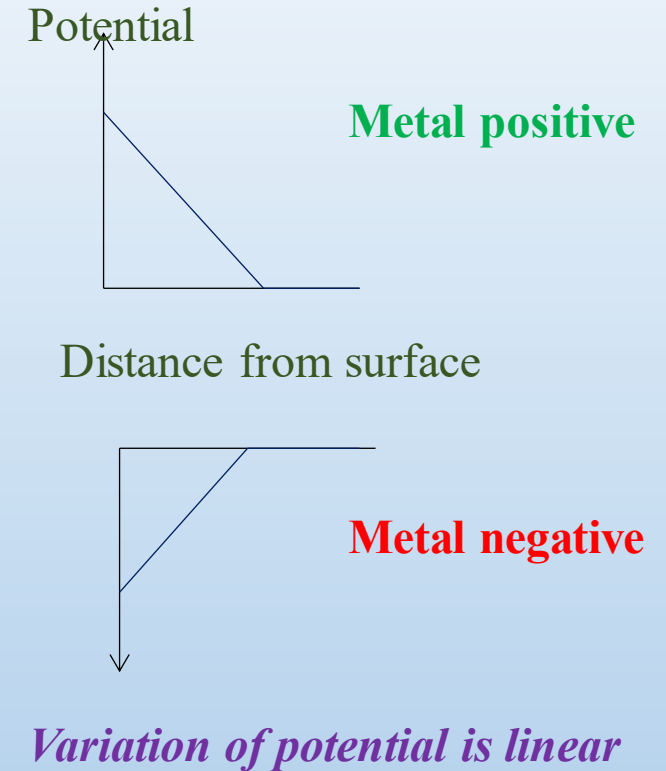


Consider an electroactive species that is not specifically adsorbed. This species can approach the electrode only to the OHP, and the total potential it experiences is less.

Potential profile across the double-layer region in the absence of specific adsorption of ions. The variable ϕ , called the inner potential.

Helmholtz-Perrin Parallel-Plate Model

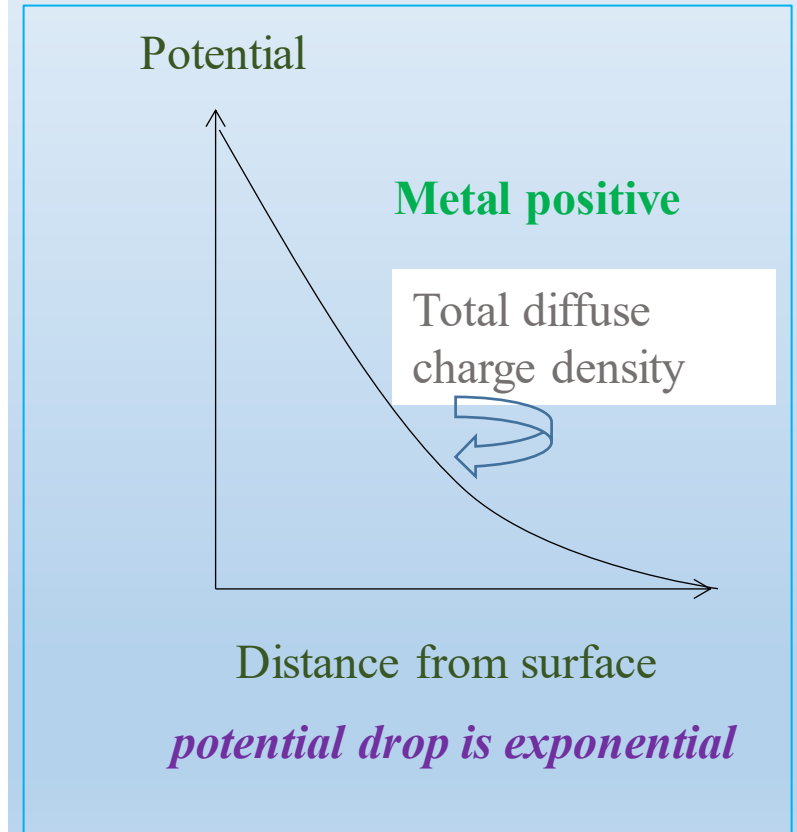
- Charge densities on the two sheets are equal in magnitude but opposite in sign
- Composed of charged at fixed distance
- In concentrated solution reasonably successful model
- Constant differential capacities



Gouy-Chapman Diffuse Charge Model

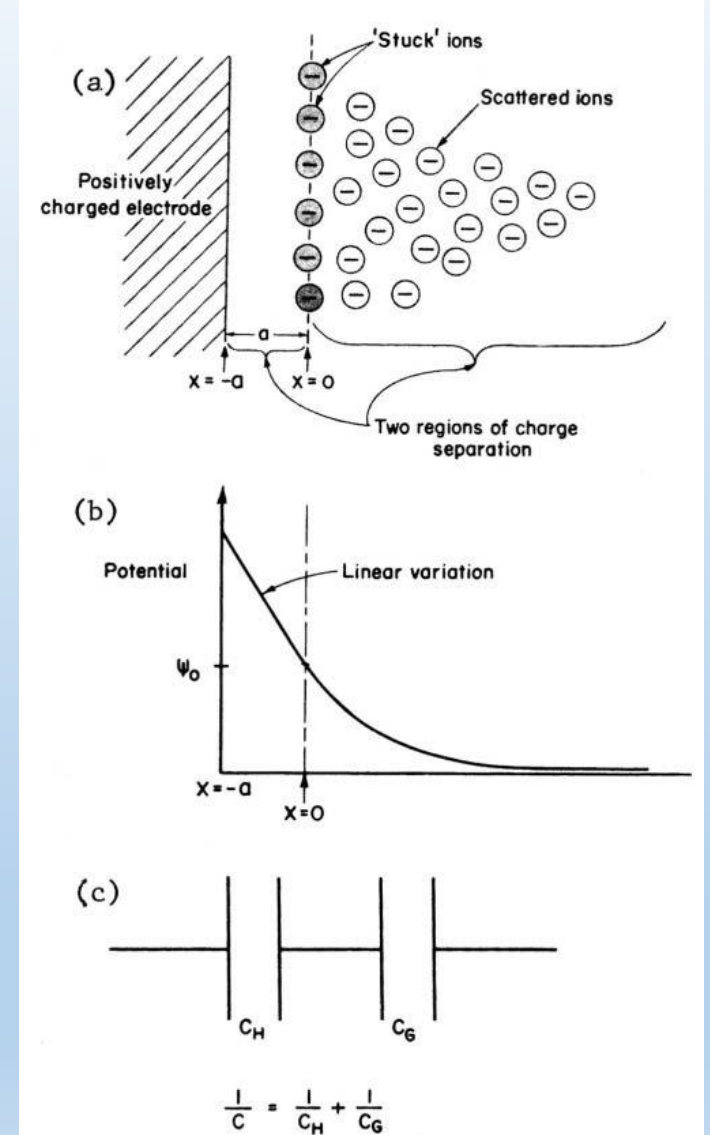
Thermal agitation beyond OHP !!!

- **Excess charge density on the OHP is not equivalent to that on metal surfaces**
- **Ions are considered as point charges, ion-ion interaction is not considered**
- **Few solvated ion leave the second row and randomly walk in solution**
- **Differential capacities have the shape of inverted parabolas**



Stern Model

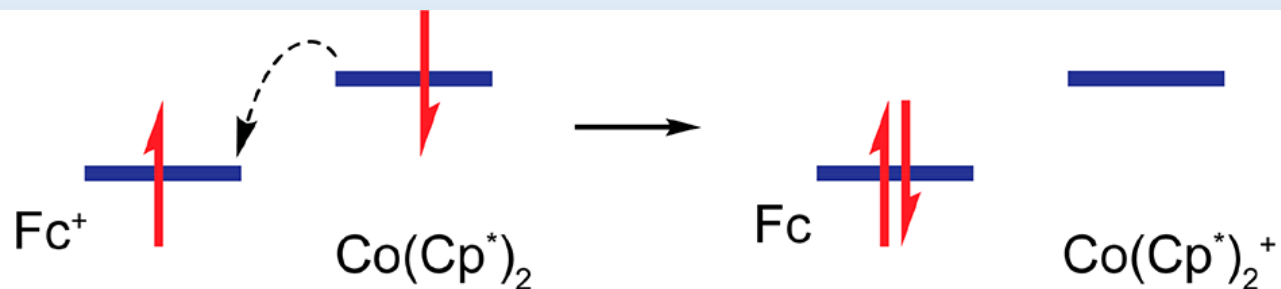
- *Considers both fixed and Diffuse layer*
- *Ions are under the combined influence of electrical ordering and thermal disordering forces*
- *Eliminating the point charge approximation*
- *Decreasing Concentration , solution charge is free to move under electrical and thermal forces*
- *Increasing Concentration, solution charge is squeezed into OHP*
- *Small amount of charge is scattered diffusely into solution*



Driving force of Electrochemistry !!!

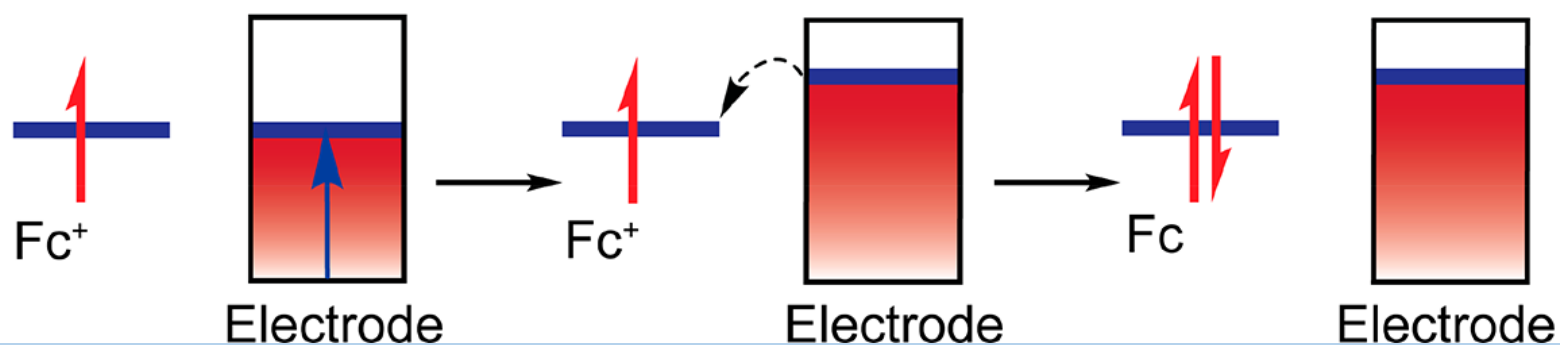
A

Homogeneous
Electron Transfer
using a chemical reductant



Heterogeneous
Electron Transfer
using an electrode

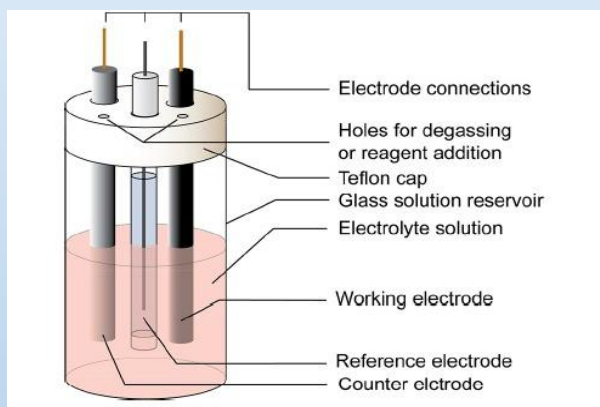
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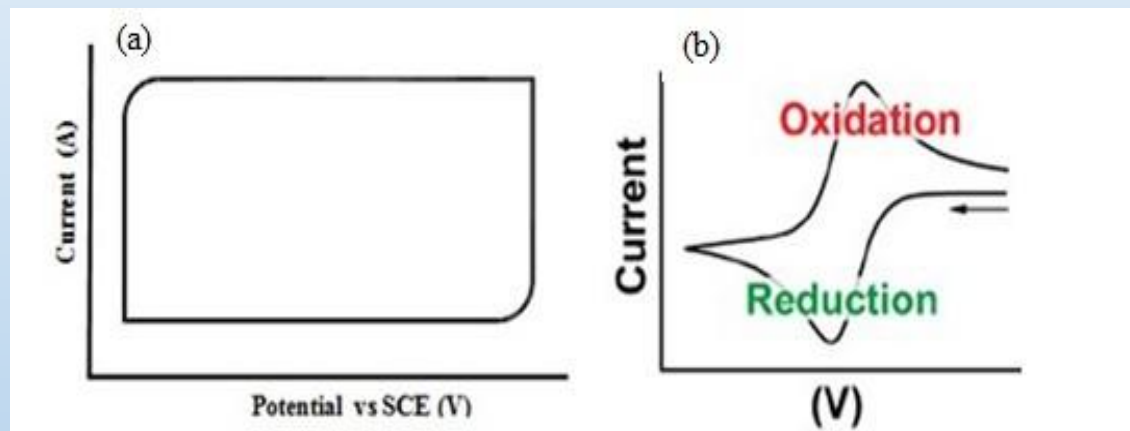
Basics of Cyclic voltammetry (CV)

CV is a widely used electroanalytical technique for investigating the electron transfer process

Electrochemical Cell



Representation of CV



- a) Rectangular shape CV is indicative of non-Faradaic nature
- b) If redox species is present in the electrolyte solution, CV with peak currents is indicative of Faradaic process

Faradaic and Nonfaradaic Processes

Two types of electrochemical reactions occur at electrode surfaces: Faradaic and Nonfaradaic

*Charges are transferred across the metal-solution interface causes oxidation or reduction to occur. Since such reactions are governed by Faraday's law (i.e., the amount of chemical reaction caused by the flow of current is proportional to the amount of electricity passed), they are called **faradaic** processes*

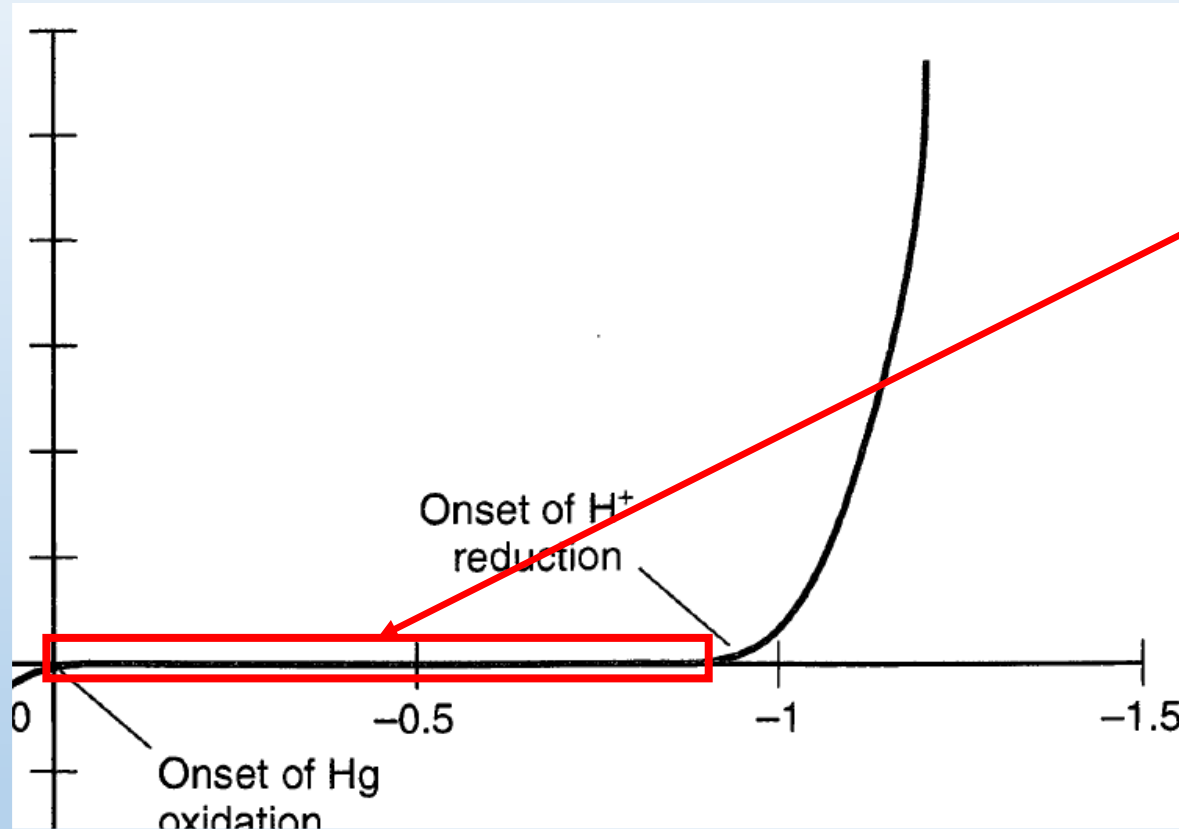
*Electrodes at which faradaic processes occur are sometimes called **charge transfer electrodes***

At a range of potentials, a given electrode-solution interface will show no charge-transfer reactions occur because such reactions are thermodynamically or kinetically unfavorable

*However, processes such as adsorption and desorption can occur, and the structure of the electrode-solution interface (electrical double layer) can change with changing either applied potential or solution composition. These processes are called **nonfaradaic processes***

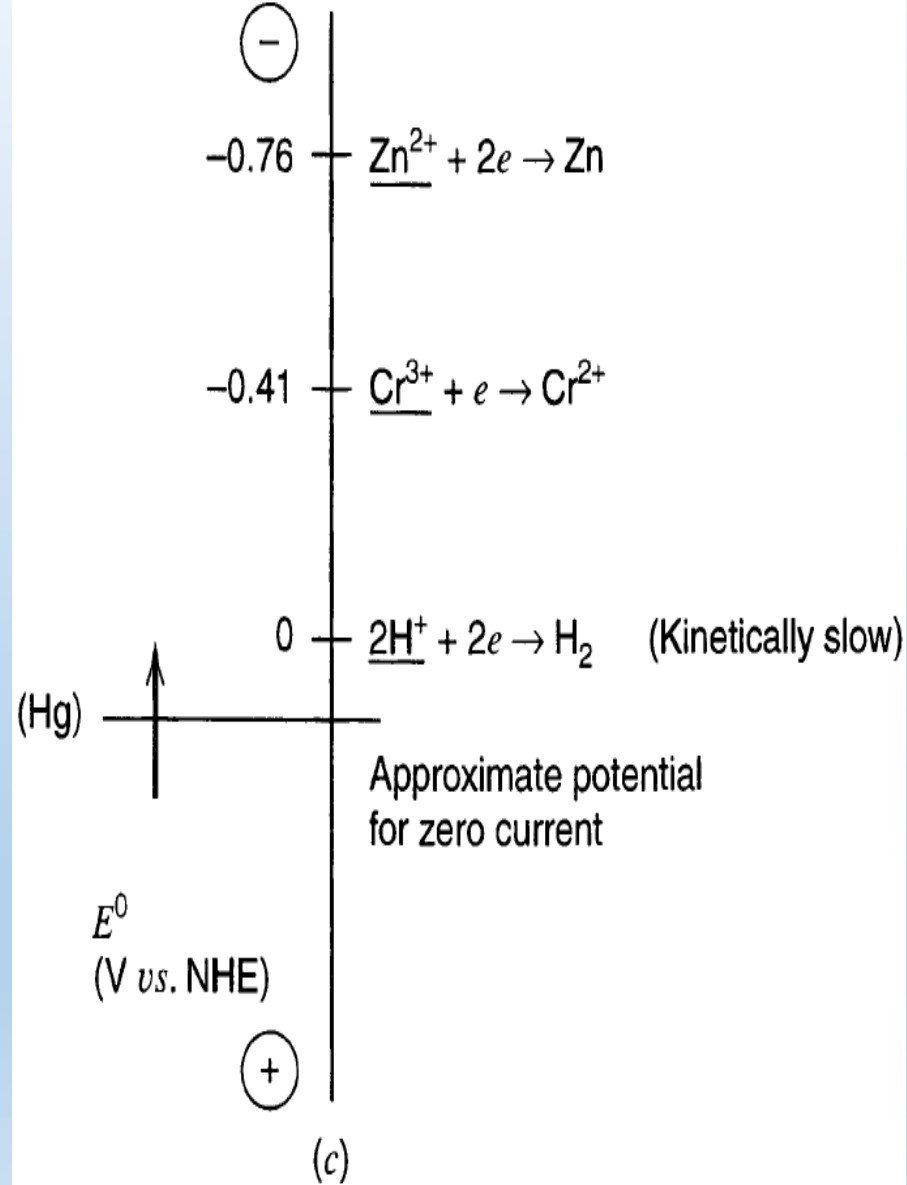
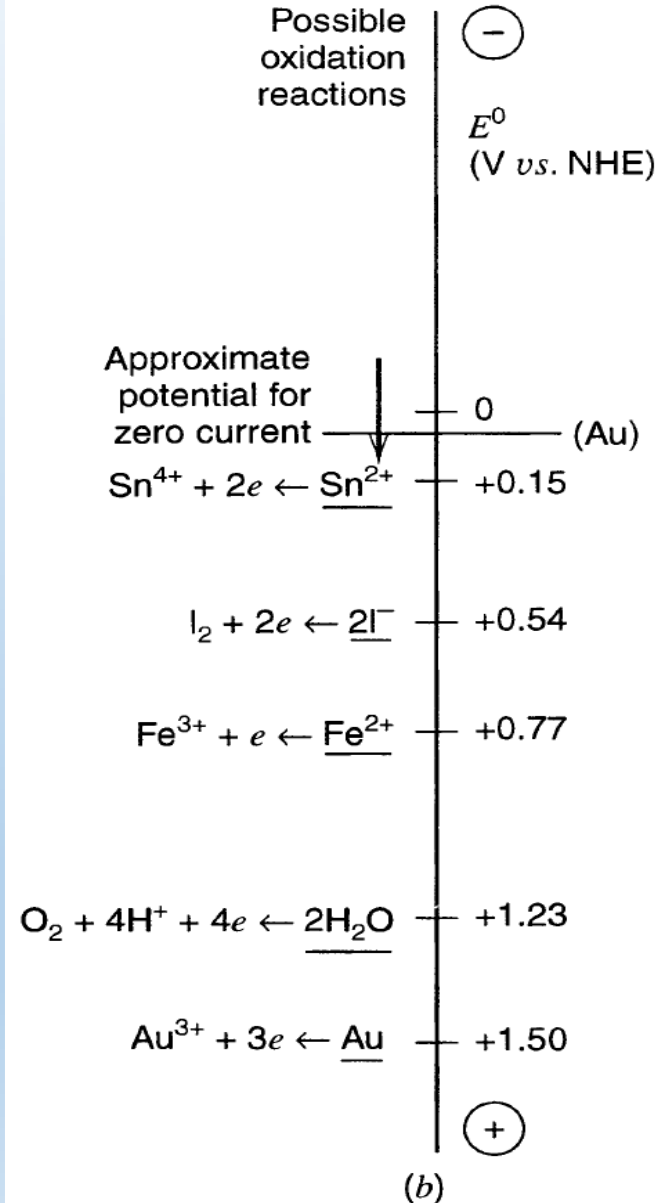
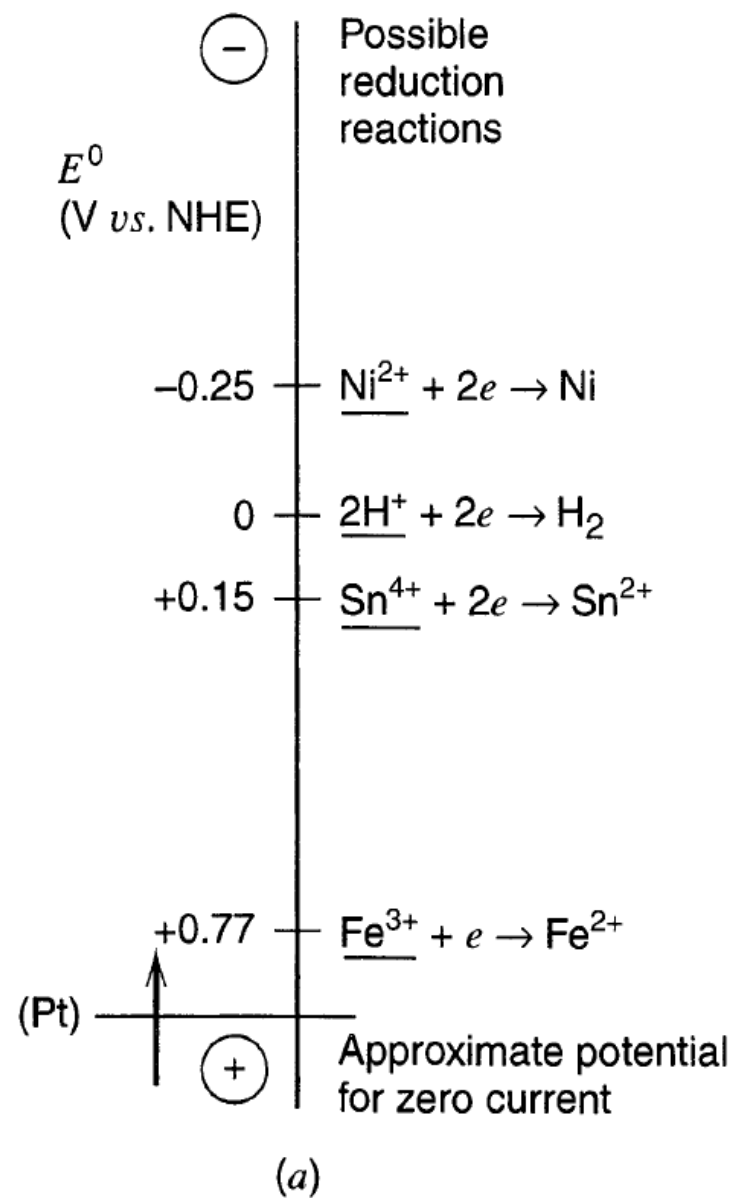
Faradaic and Nonfaradaic Processes

*The region in below Figure between 0 and -0.8 V vs. (NHE) is **nonfaradaic processes***



Although electron does not cross the interface, external currents can flow (at least transiently) when the potential, electrode area, or solution composition changes

Standard Oxidation/Reduction Potentials at Various Electrode



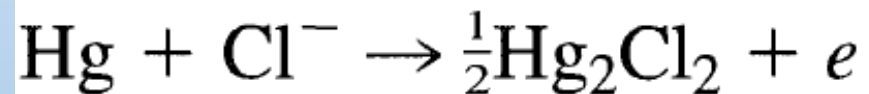
Ideal Polarized Electrode

An electrode at which no charge transfer process occur across the metal-solution interface, regardless of the potential imposed by an outside source of voltage, is called an ideal polarized (or ideal polarizable) electrode (IPE).

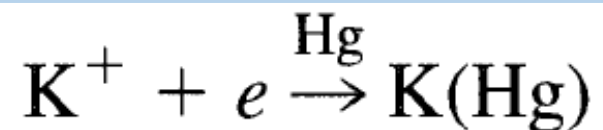
Ideally, no real electrode available that can behave as an IPE over the whole potential range in a solution

Some electrode-solution systems can approach ideal polarizability over limited potential ranges

For example, a mercury electrode in contact with a deoxygenated potassium chloride solution approaches the behavior of an IPE over a potential range about 2 V wide



At very negative potentials K^+ can be reduced at the electrode surface



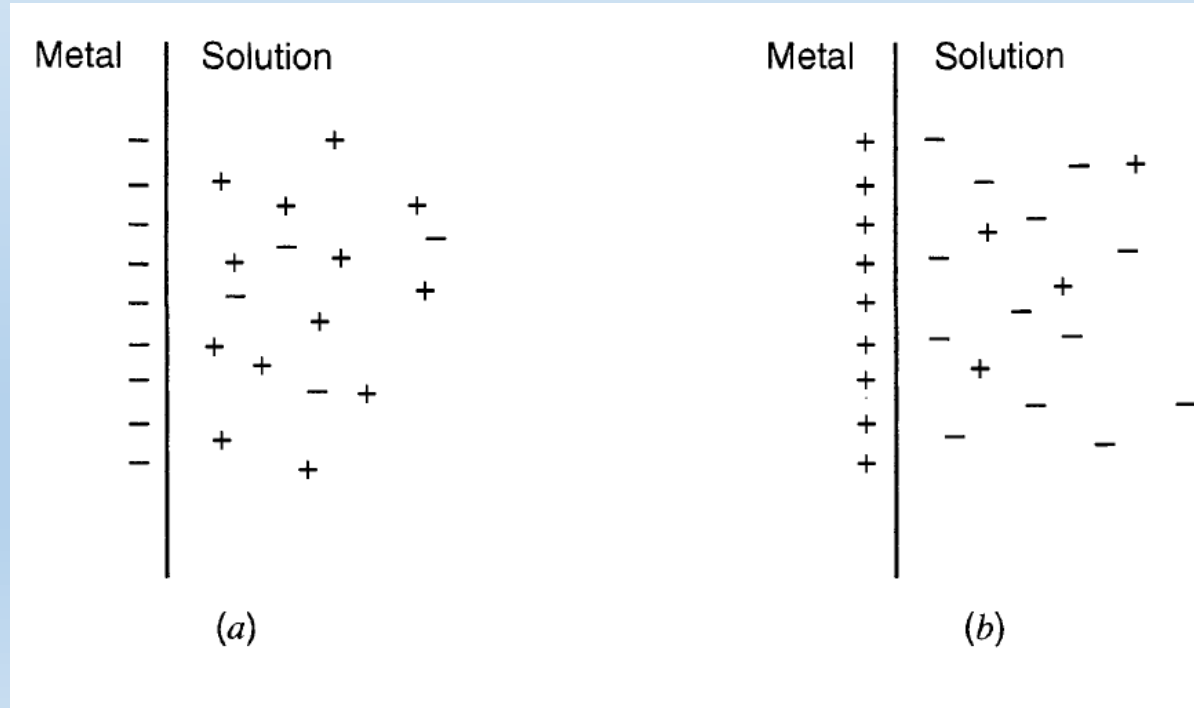
Metal (Electrode)-solution interface as a capacitor

At an applied potential ranges, the metal-solution interface acts as a capacitor with a charge on the metal, q^M , (a) negative and (b) positive

The charges that will develop in the solution, q^s

Nature of the electrical charges on the metal (either negative or positive) with respect to the solution, depends on the applied potential and solution composition

At all times, however, $q^M = -q^s$



Metal (Electrode)-solution interface as a capacitor

*In an actual experimental arrangement, **two metal electrodes**, and thus two interfaces, would have to be considered*

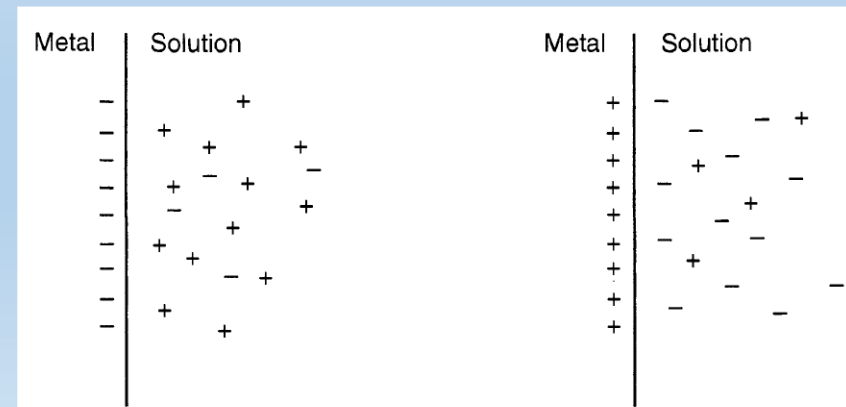
The charge on the metal, q^M , represents either an excess or deficiency of electrons and resides in a very thin layer ($<0.1 \text{ \AA}$) on the metal surface

The charge in solution, q^S , is made up of an excess of either cations or anions in the vicinity of the electrode surface

The charges q^M and q^S are often divided by the electrode area and expressed as charge densities, such as, ($\sigma^M = q^M/A$, usually given in $\mu\text{C}/\text{cm}^2$).

At a given potential, the electrode- solution interface is characterized by a double-layer capacitance, C_{dl} , typically in the range of 10 to 40 $\mu\text{F}/\text{cm}^2$.

However, unlike real capacitors, whose capacitances are independent of the voltage across them, Q is often a function of potential.



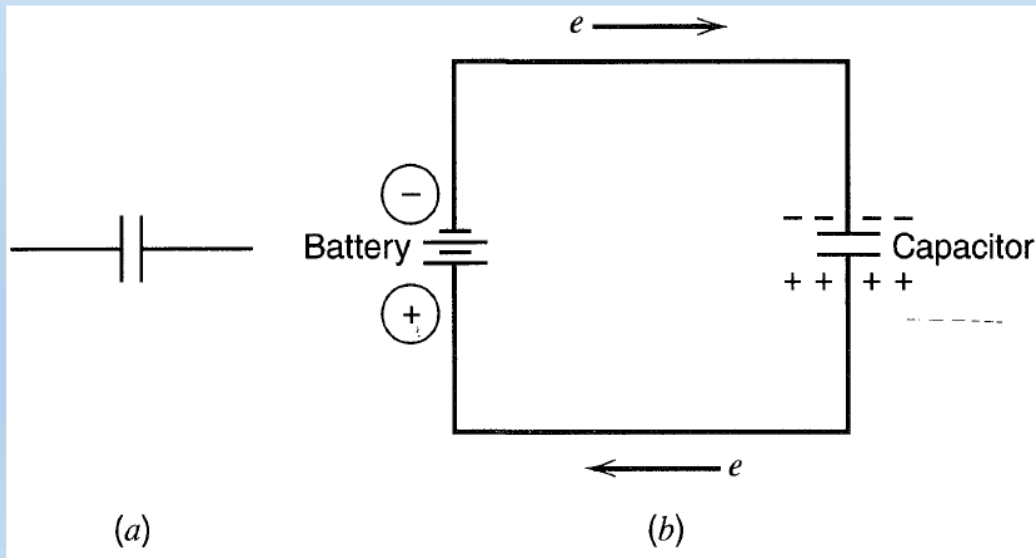
Charging a capacitor with a battery

*Since charge cannot cross the IPE interface when the potential across it is changed, the behavior of the electrode-solution interface is analogous to that of a **capacitor***

A capacitor is an electrical circuit element composed of two metal sheets separated by a dielectric material and its behavior is governed by the equation

$$\frac{q}{E} = C$$

E is the potential across the capacitor (in volts, V), and C is the capacitance (in farads, F). When a potential is applied across a capacitor, charges, q will accumulate on its metal plates



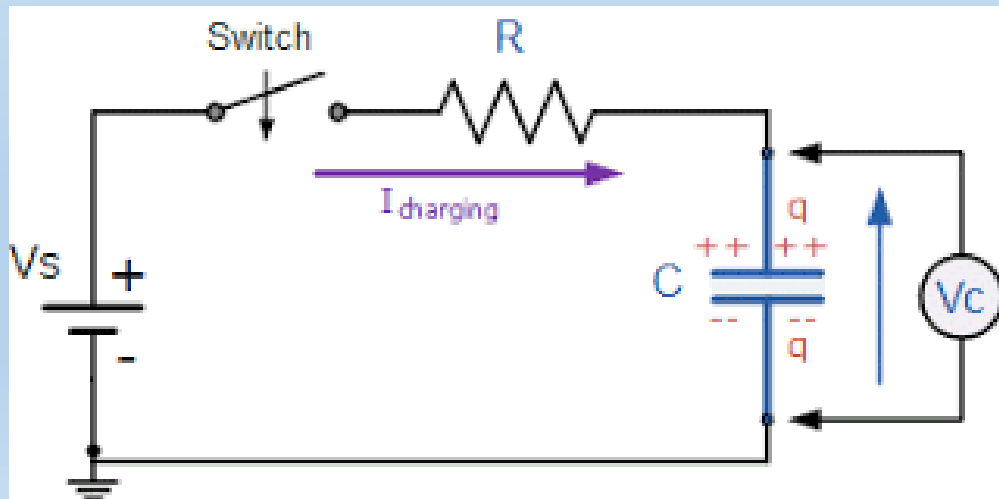
Charging Current or Capacitor Current

During this charging process for a discharged capacitor, a current (called the charging current/capacitor current) will flow in the circuit

The charge on the capacitor consists of an excess of electrons on one plate and a deficiency of electrons on the other plate and dielectric is in the middle

For example, if a 2 V battery is placed across a 10 μF capacitor, current will flow until 20 μC has accumulated on the capacitor plates following the equation, $\frac{q}{E} = C$

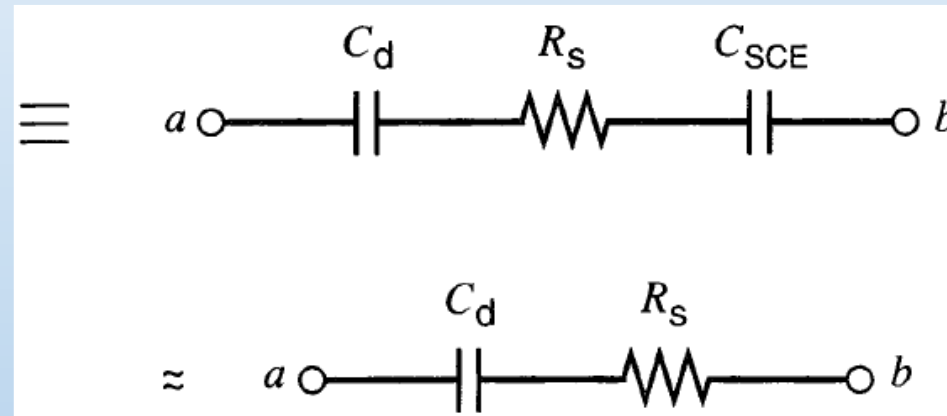
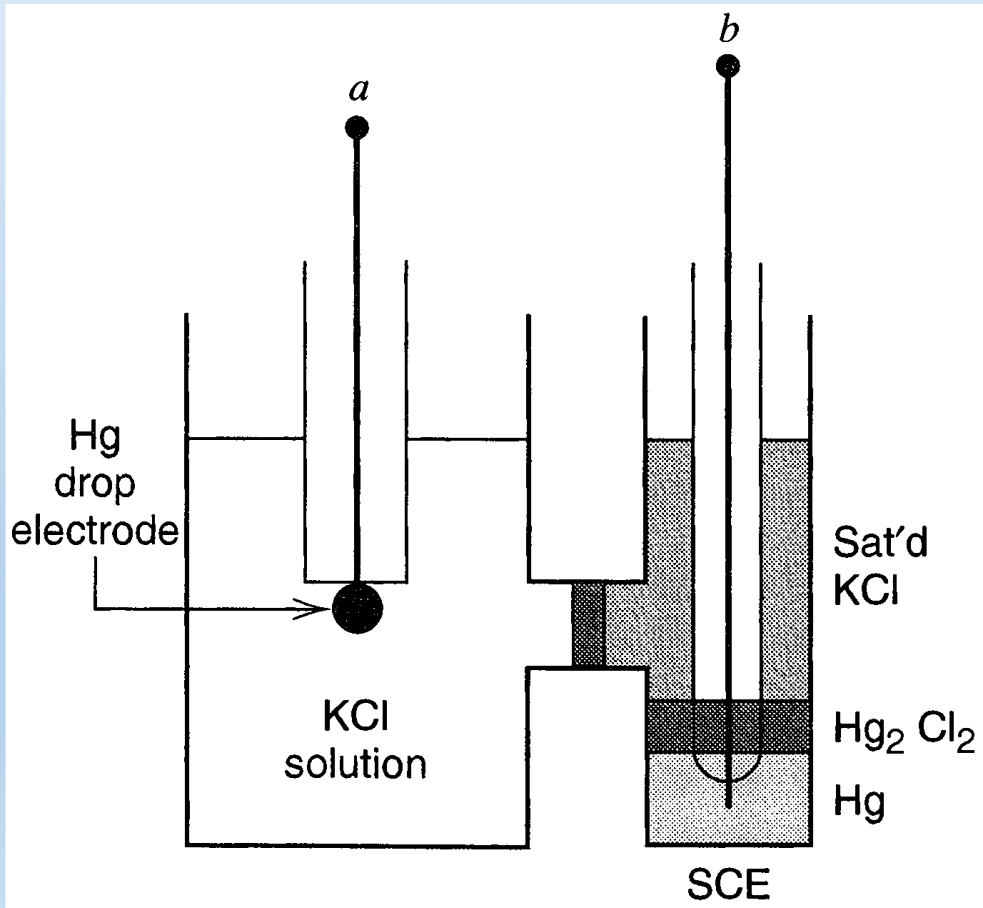
The magnitude of the current depends on the resistance in the circuit



Note that during electrode reactions involving very low concentrations of electroactive species, the charging current can be even much larger than the faradaic current for the reduction or oxidation reaction

Double-Layer Capacitance and Circuit Modelling

This cell, represented by Hg/K^+ , Cl^-/SCE , can be approximated by an electrical circuit with a resistor, R_s , representing the solution resistance and a capacitor, C_d , representing the double layer capacitance at the Hg/K^+ , Cl^- interface. The magnitude of the current depends on the resistance in the circuit.



Representation of the cell in terms of linear circuit elements

The capacitance of the SCE, C_{SCE} , should also be included. However, the series capacitance of C_d and C_{SCE} is $C_T = C_d C_{\text{SCE}} / (C_d + C_{\text{SCE}})$ and normally $C_{\text{SCE}} \gg C_d$ so that $C_T \sim C_d$. Thus, C_{SCE} can be neglected in the circuit.

Potential Steps for a RC Circuit

The result of a potential step to the IPE is the familiar RC circuit problem

The behavior of the current, i , with time, t , when applying a potential step of magnitude E , is

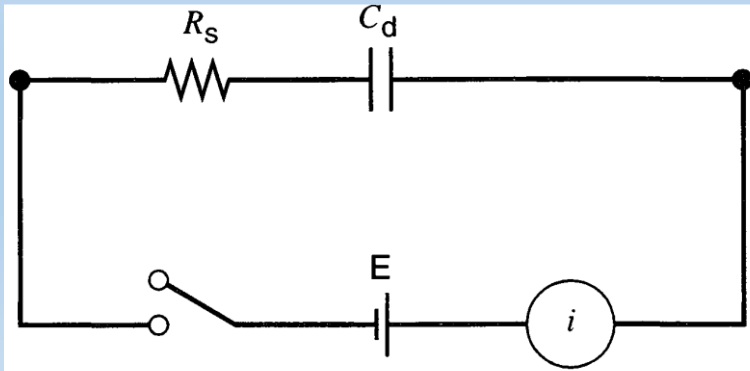
$$i = \frac{E}{R_s} e^{-t/R_s C_d}$$

A general equation for the charge, q , on a capacitor as a function of the voltage across E , is given by $q = C_d E_C$

What is i ? $i = dq/dt$

At any time, the sum of the voltages, E_R and E_C , across the resistor and the capacitor, respectively, must equal the applied voltage; hence

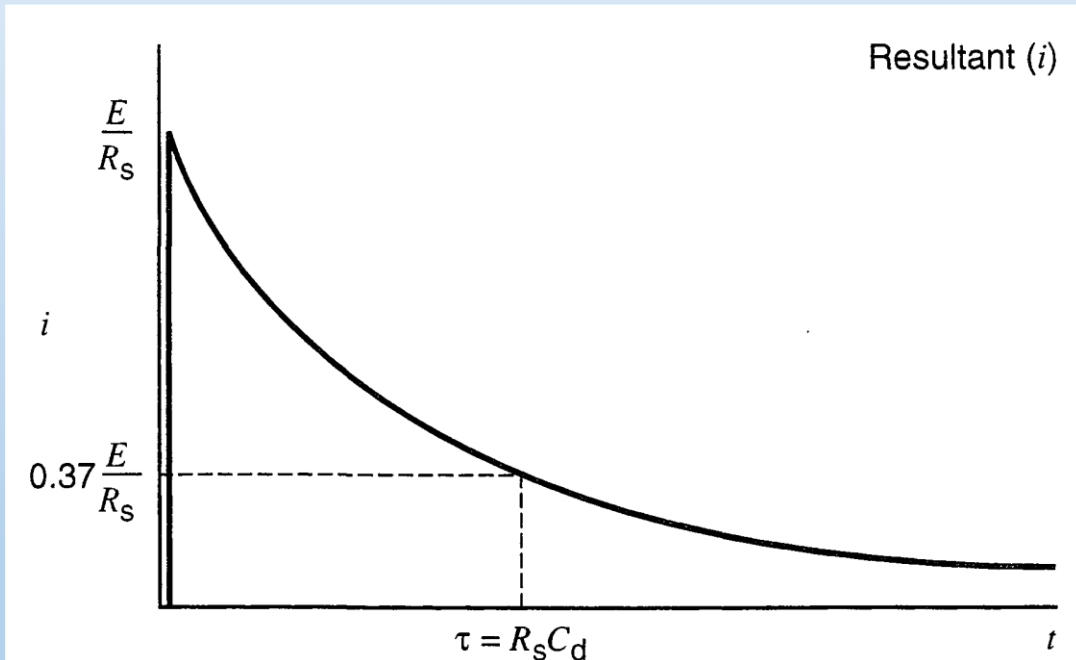
$$E = E_R + E_C = iR_s + \frac{q}{C_d}$$



$$\frac{dq}{dt} = \frac{-q}{R_s C_d} + \frac{E}{R_s}$$

Potential Steps for a RC Circuit

Hence, for a potential step input, there is an exponentially decaying current having a time constant, $\tau = R_s C_d$



The current for charging the double-layer capacitance drops to 37% of its initial value at $t = \tau$

The

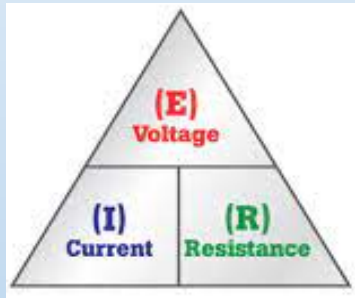
current for charging the double-layer capacitance drops to 37% of its initial value at $t = \tau$, and to 5% of its initial value at $t = 3 \tau$.

For example, if $R_s = 1 \text{ Ohm}$ and $C_d = 20 \mu F$, then calculate $\tau = 20 \mu s$ and double-layer charging is 95% complete in $60 \mu s$

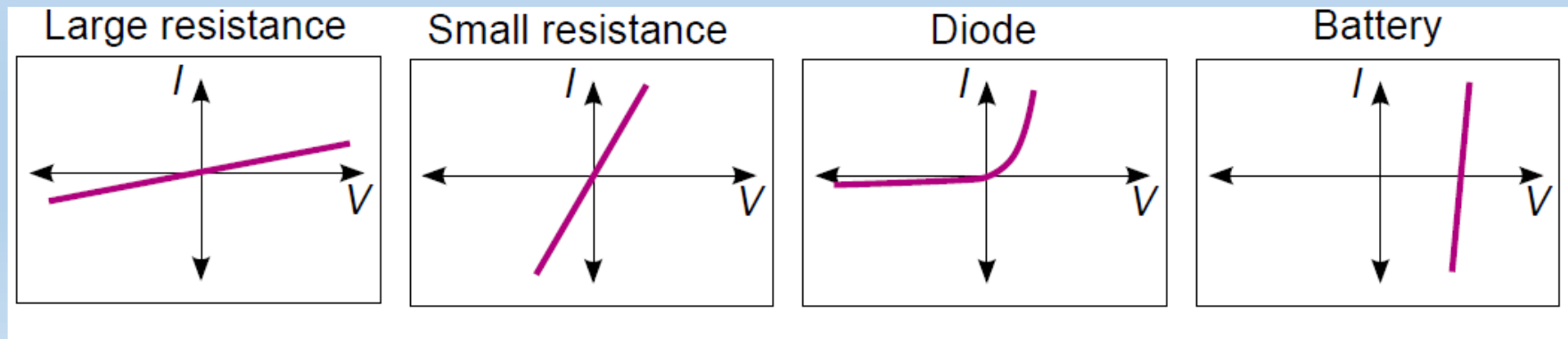
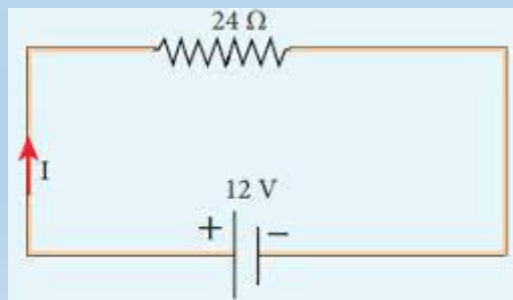
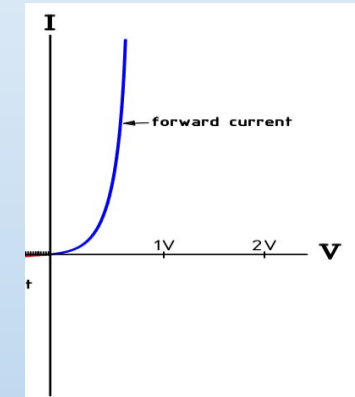
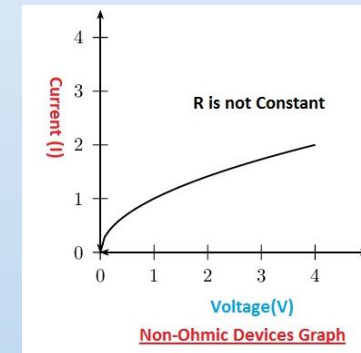
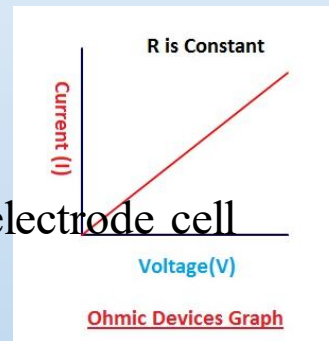
Ohm's Law and Its Limitation??

What is Ohm's Law?

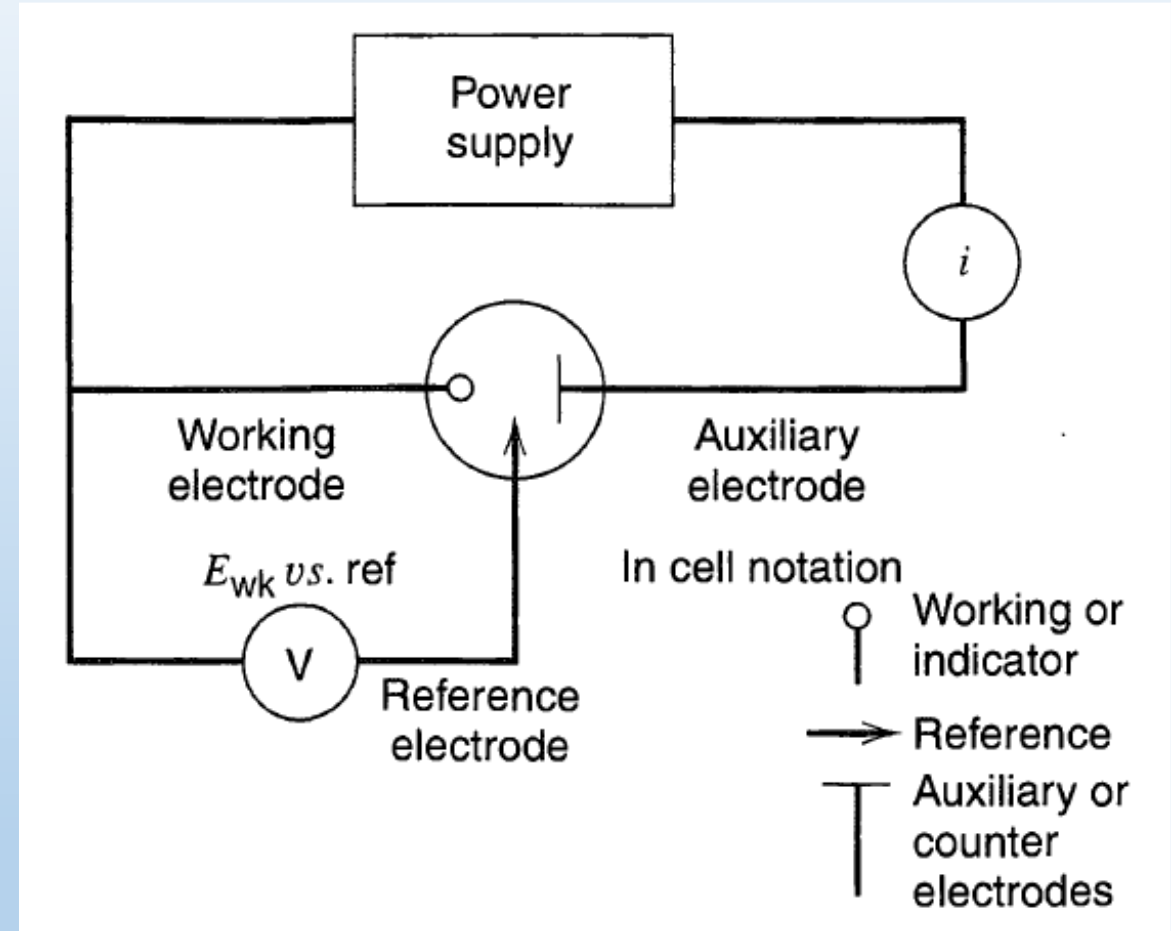
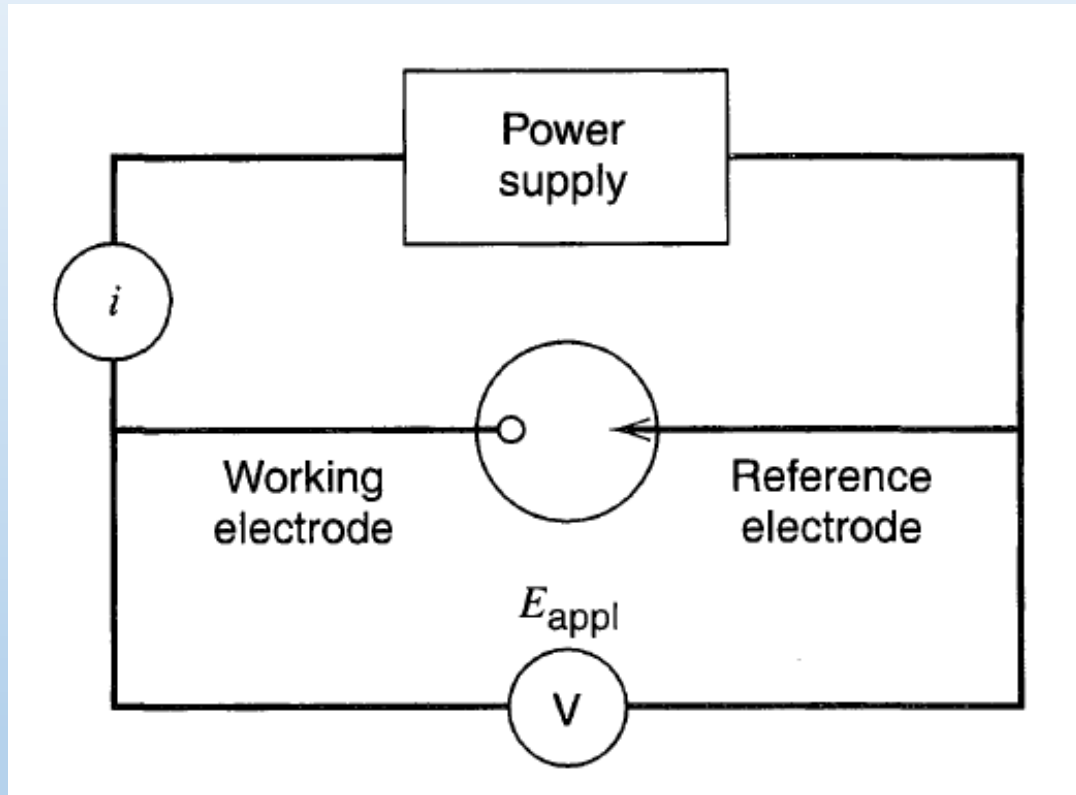
Ohm's law states that the current through a conductor between two points is directly proportional to the voltage applied across the two points



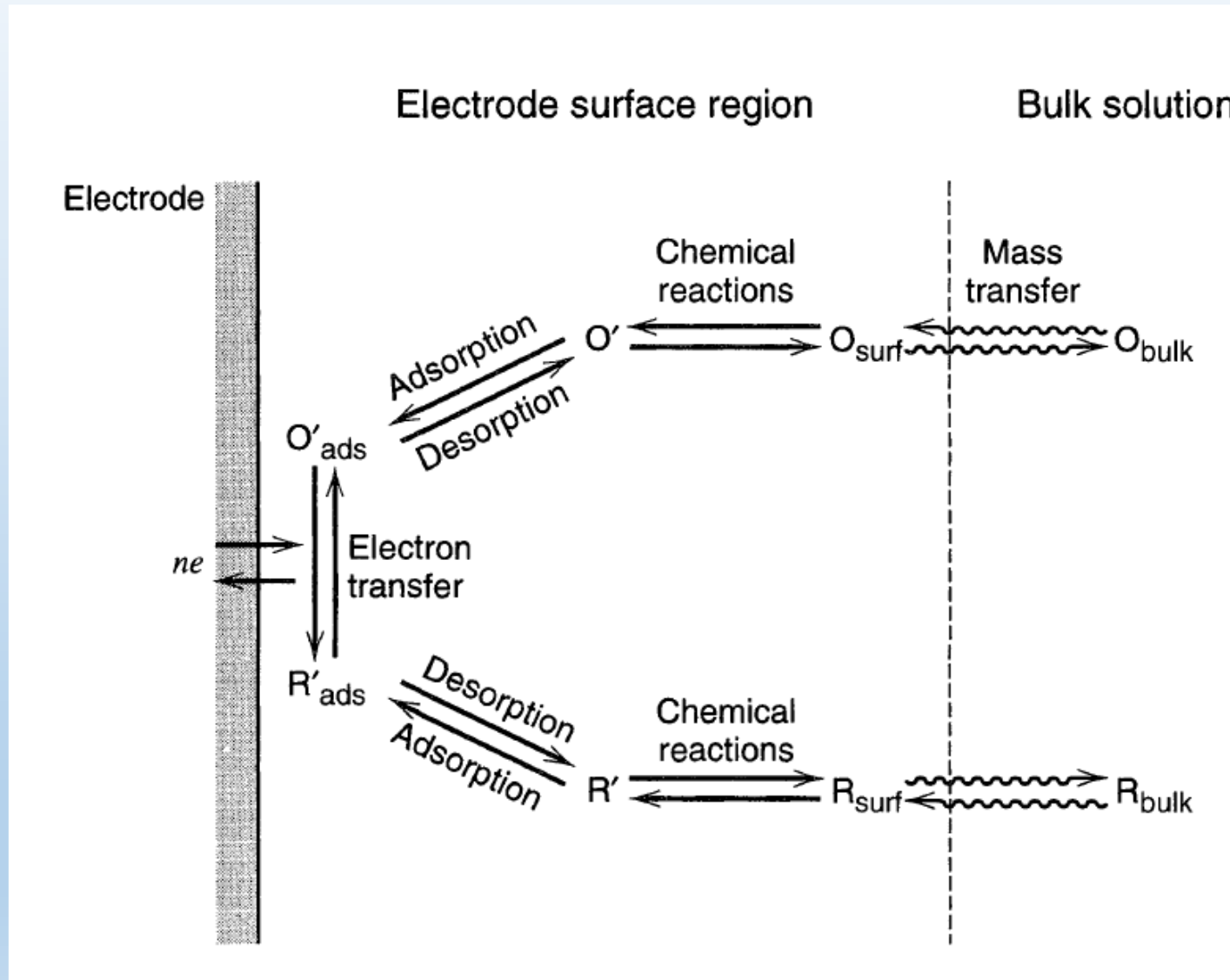
Three-electrode cell



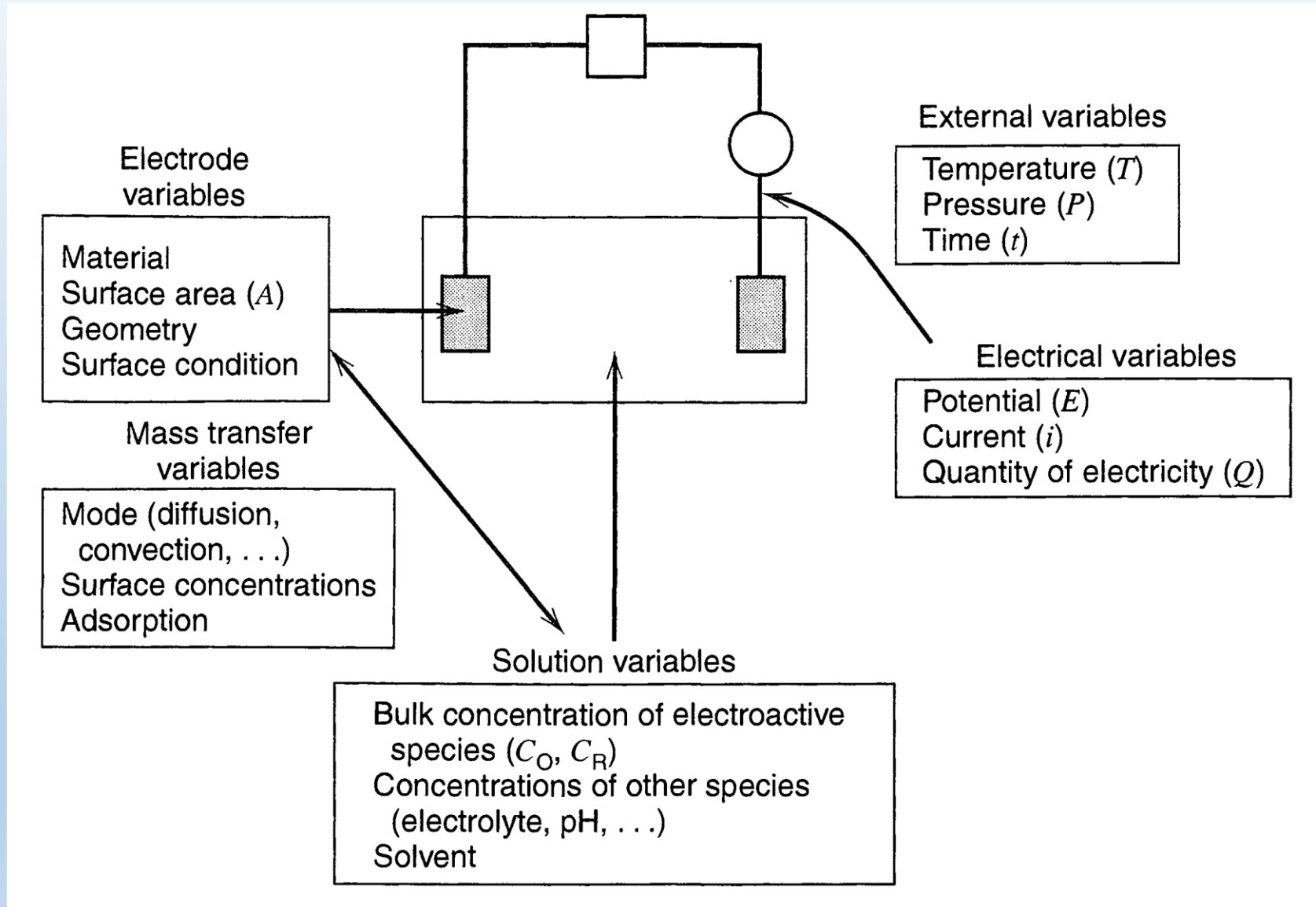
Two electrode vs Three-electrode cell



Pathway of a general electrochemical reaction



Factors Affecting the Electrochemical reactions



Electrochemical Cells—Types and Definitions

Electrochemical cells in which faradaic currents are flowing are classified as either *galvanic* or *electrolytic* cell

A galvanic cell is one in which reactions occur **spontaneously** at the electrodes when they are connected externally by a conductor

These cells are often employed in converting **chemical energy** into **electrical energy**

Galvanic cells of commercial importance include primary (non-rechargeable) cells, secondary (rechargeable) cells, and fuel cells

For discharging,

Negative plate reaction: $\text{Pb(s)} + \text{HSO}_4^-(\text{aq}) \rightarrow \text{PbSO}_4(\text{s}) + \text{H}^+(\text{aq}) + 2\text{e}^-$

Positive plate reaction: $\text{PbO}_2(\text{s}) + \text{HSO}_4^-(\text{aq}) + 3\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O(l)}$

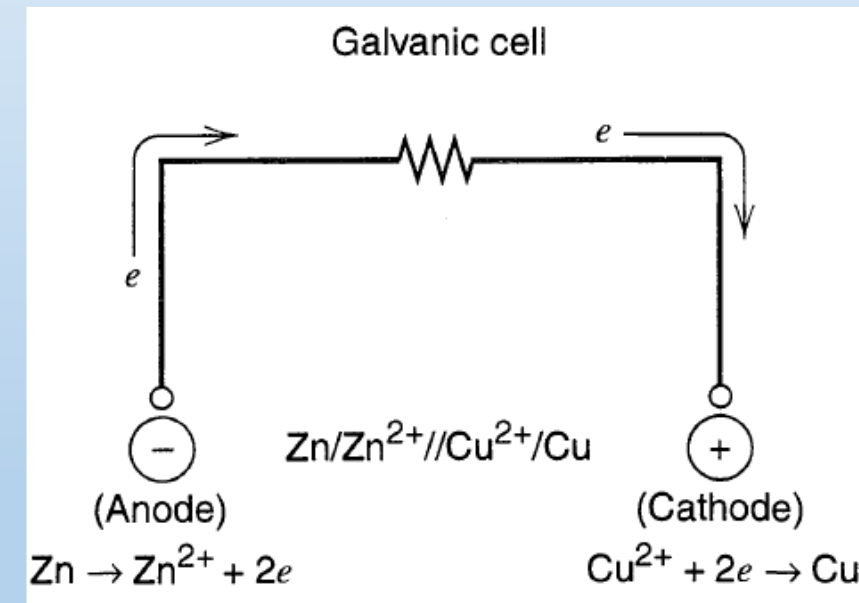
overall reaction:

$\text{Pb(s)} + \text{PbO}_2(\text{s}) + 2\text{H}^+(\text{aq}) + 2\text{HSO}_4^-(\text{aq}) \rightarrow 2\text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O(l)}$

For charging?



Lead-acid batteries



Electrochemical Cells—Types and Definitions

An **electrolytic cell** is one in which reactions are occurred by the imposition of an external voltage greater than the open-circuit potential of the cell

These cells are frequently employed to carry out desired chemical reactions by expending electrical energy

Commercial processes involving electrolytic cells include electrolytic syntheses (e.g., the production of chlorine and aluminum), electrorefining (e.g., copper), and electroplating (e.g., silver and gold)

Electrolysis can be defined broadly to include chemical changes accompanying faradaic reactions at electrodes in contact with electrolytes

