

Electrochemical Cells

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References on Electrochemistry: Many books published or edited by Allen J. Bard (of University of Austin, TX)

Interfacial Electrochemistry J. Lyklema. 1991. Fundamentals of Interface and Colloid Science. vol 1 and 2. (references on Thermodynamics)

Electrochemical Cells

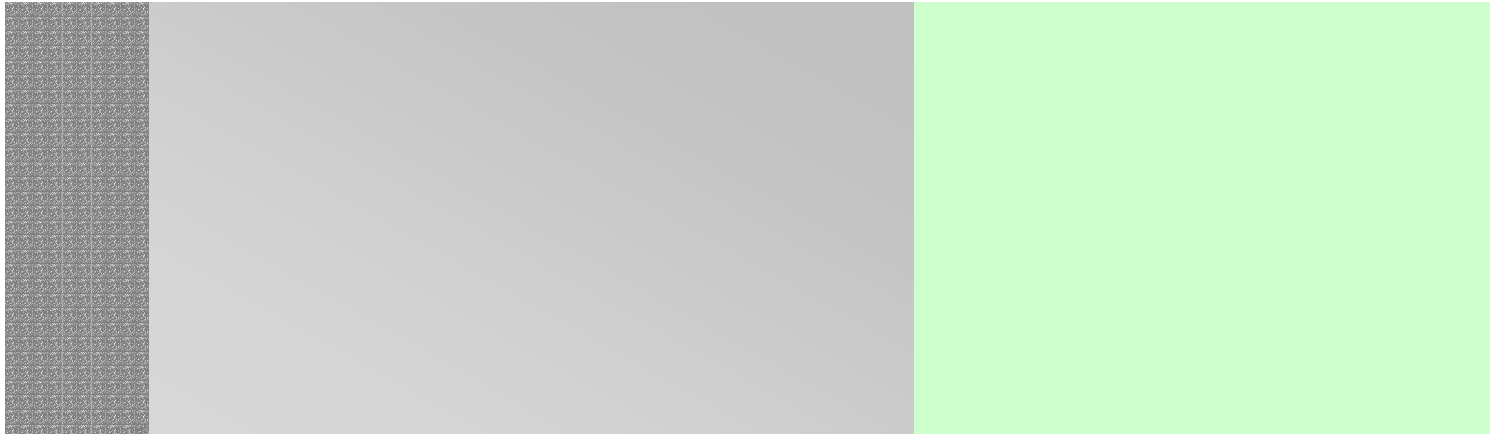
- In electrochemistry we are interested in the processes that affect the transport of charge at interfaces usually between a conductor (electrode) and an ionic conductor (electrolyte).
- Electrode charge is carried by electrons e.g. electrodes include solid metals (Pt, Au), liquid metals (Hg), carbon (graphite) and semiconductors. Electrolyte charge is carried by ions e.g. H^+ , Cl^- in water or ions in non-aqueous solutions.
- An electrochemical cell consists of at least of two electrodes in contact with an electrolyte.
- The electrolyte and the electrodes are the electrode compartment. If the electrolytes are different the two compartments can be joined by a salt bridge which is a concentrated electrolyte solution (KNO_3) that completes the circuit.

Many events occur at and near electrodes

Electrode

Interfacial region (0.5-100 nm)

Bulk Solution



Faradic
electron
transfer at
electrode
surface



Non-Faradic
Ionic concentrations
different from the bulk
solution because of
polarization effects
and production of a
double layer
This affects currents
and cell potentials

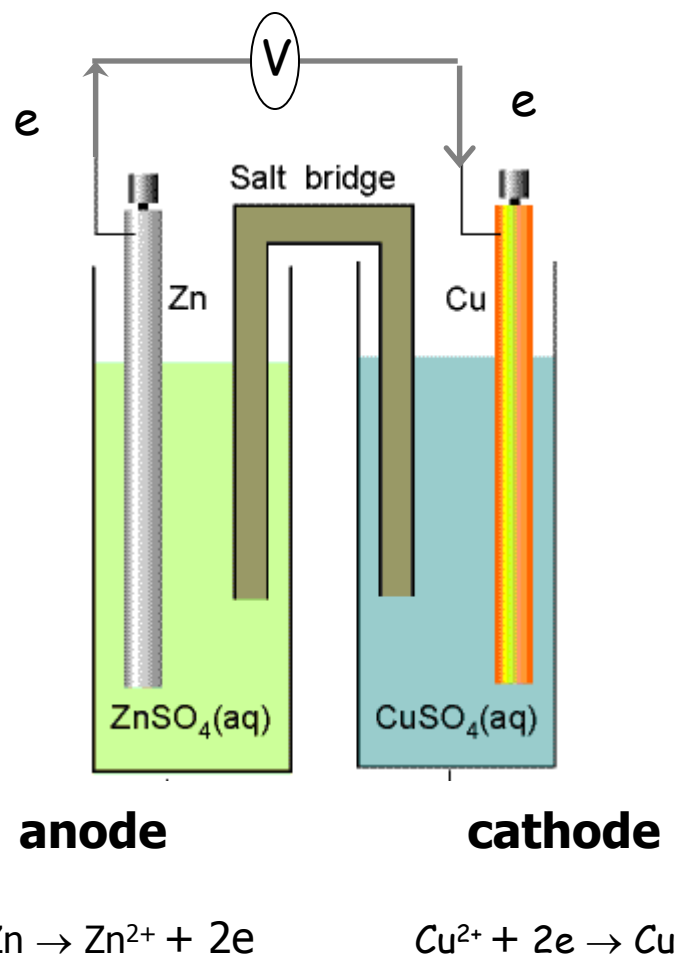


mass transfer from bulk
solution to electrode.

Kinetics governed by
diffusion and convection

Redox reactions and half-cells

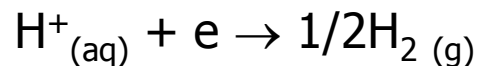
- A reaction in which there is a transfer of electron(s) from one species to another is called a redox reaction
- Any redox reaction can be represented as the difference of two half-reactions
- Write the overall chemical reaction taking place in a cell in terms of two half-reactions, which describe the chemical changes that occur at the two electrodes
- Each half reaction responds to the interfacial potential difference at the corresponding electrode
- Oxidation occurs at the anode and reduction occurs at the cathode



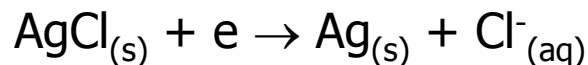
Example

➤ By convention one writes each half reaction as a reduction.

➤ Anode



➤ Cathode



➤ Potential of cell is

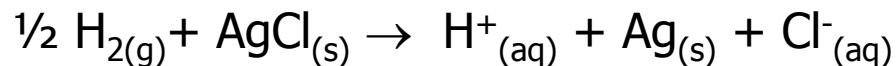
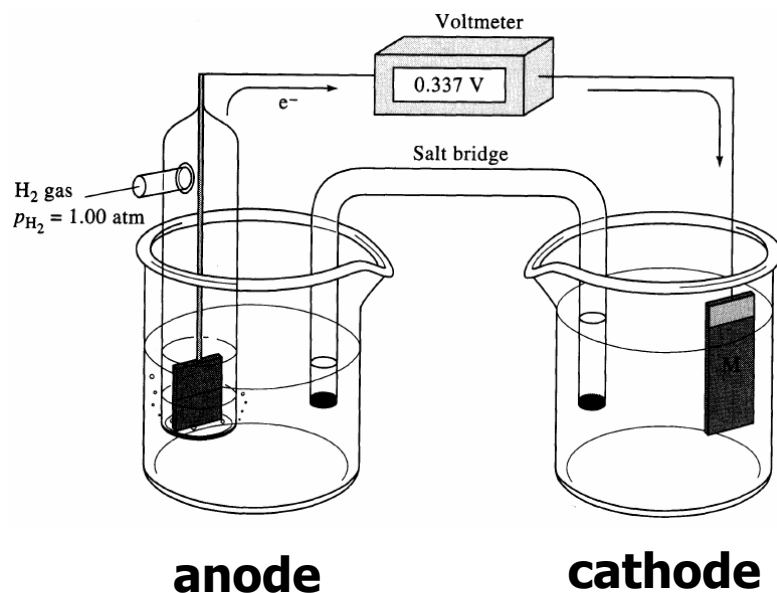
$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

➤ Sometimes written as

$$E_{\text{cell}} = E_{\text{Right}} - E_{\text{Left}}$$

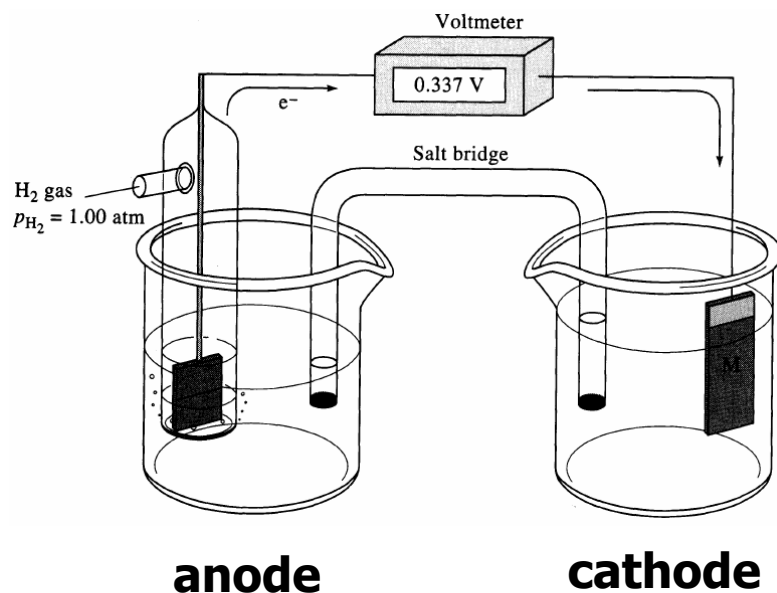
➤ At standard state

$$E^{\circ} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$$



At standard state $E^{\circ}_{\text{cathode}}$ is determined relative to the Standard Hydrogen Electrode (SHE)

- Hydrogen ions at unit activity in equilibrium with hydrogen gas at 1 atmosphere)
- The equilibrium potential is detected with a platinum electrode that is coated with platinum black (finely divided platinum) to enlarge the effective surface area.
- At all temperatures
- Potentials of electrodes are compared to SHE, where SHE is at the anode and second electrode is at cathode.



Standard state for all other species in solution, solid or in a gas is when they have an activity, $a = 1$.

- Standard state of a component considered as a **solvent** is taken to be the pure liquid or pure solid at one atmosphere pressure and at the temperature in question.
- Standard state of a component considered to be a **solute**. It is a hypothetical state in which the solute would exist at unit molality (mol/kg) or (molarity) (mol/liter) and one atmosphere, but would still have the environment typical of a dilute ideal solution

Standard cell potential, E° of Ag/AgCl is + 0.2223 V

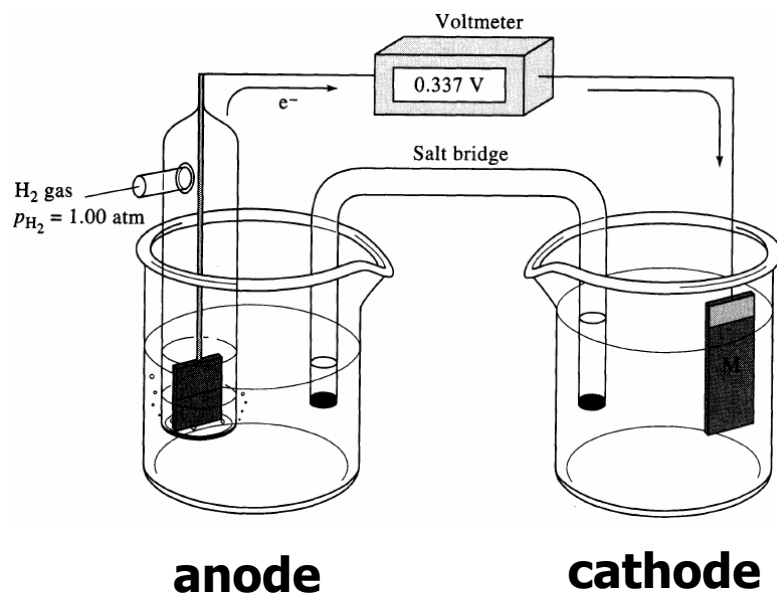
➤ $E_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$

$$E^\circ_{\text{anode}} = E_{\text{SHE}} = 0.0 \text{ V}$$

➤ Therefore

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} = +0.2223 \text{ V}$$

➤ We find that the standard cell potential (E°) is positive.



What does a positive, standard cell potential, E° imply?

- Use mathematics and language of reversible thermodynamics to illustrate what a positive E° implies
- By thermodynamically reversible. We imply that the reaction can respond to an infinitesimal small driving force and reverse its direction
- Lets consider a reversible redox reaction that is closed to its surroundings. The change in energy, dU can be expressed in terms of work and heat

$$dU = dq + dw = dq - \underset{\substack{\uparrow \\ \text{mechanical}}}{pdV} - \underset{\substack{\uparrow \\ \text{electrical}}}{zFE} \quad \text{E.1}$$

U : internal energy	q : heat
w : work	p : pressure
V : volume	z : valence or # charges
F : Faraday constant	E : Potential
S : entropy	H : enthalpy
G : Gibb's energy	μ : chemical potential
n_i : moles of i	

From second Law, S the entropy is

$$dS = \frac{dq}{T} \quad \text{E.2}$$

For the reversible process E.1 becomes

$$dU = TdS - pdV - zFE \quad \text{E.3}$$

$E^0 > 0 \rightarrow dG^0 < 0 \rightarrow$ spontaneous reaction

$$dU = TdS - pdV - zFE \quad \text{E.3}$$

In terms of Gibb's energy, G (also called free enthalpy or Gibb's free energy) E.3 becomes

$$G \equiv H - TS \equiv U + pV - TS$$

$$dG = dU + pdV + VdP - TdS - SdT \quad \text{E.4}$$

Substitute E.3 into E.4

$$dG = TdS - pdV - zFE + pdV + VdP - TdS - SdT$$

$$dG = -nFE + VdP - SdT$$

$$dG = -zFE_{P,T} \quad \text{E.5}$$

In an open system Gibb's energy at constant P and T

$$dG = -zFE + \sum_i \mu_i dn_i \quad \text{E.6}$$

When n is constant

$$dG = -(zFE)_{P,T,n_i} \quad \text{E.7}$$

When n is constant with activity of one and measurements are at standard state then

$$dG^0 = -(zFE^0)_{P,T,n_i} \quad \text{E.8}$$

$E^0 > 0 \rightarrow dG^0 < 0$ spontaneous reaction

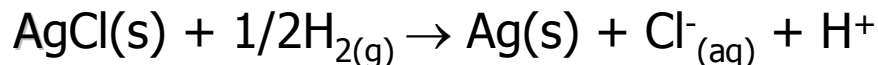
$E^0 < 0 \rightarrow dG^0 > 0$ energy is required to drive the reaction

E^0 is often called the electromotive force or EMF of the cell.

Positive E° implies the reaction is favorable thermodynamically
Negative E° implies the reaction requires energy to proceed

➤ E° positive

e.g.,



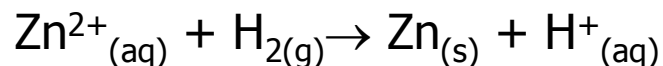
reaction will proceed spontaneously

AgCl can readily be reduced by H_2 to form Ag

AgCl it is a good electron acceptor or oxidizing agent relative to SHE

➤ E° negative

e.g.,



is not favorable

Zn^{2+} cannot be readily reduced by H_2 to form Zn.

Zn^{2+} is a better electron donor or reducing agent.

Electrochemistry Series of Metals

Least Active do not want to lose electrons good oxidizing agents

Gold	(Au)	stable metals
Platinum	(Pt)	
Silver	(Ag)	
Mercury	(Hg)	
Copper	(Cu)	
(Hydrogen)	(H)	
Lead	(Pb)	
Tin	(Sn)	
Nickel	(Ni)	
Iron	(Fe)	
Zinc	(Zn)	
Chromium	(Cr)	
Aluminium	(Al)	
Magnesium	(Mg)	
Sodium	(Na)	
Calcium	(Ca)	unstable metals
Potassium	(K)	
Lithium	(Li)	

Most active easily lose electrons good reducing agents

Standard Electrode (Half) Potentials at 25°C vs SHE

Li^+	+ e^-	$\rightarrow \text{Li}$	-3.05 V
K^+	+ e^-	$\rightarrow \text{K}$	-2.92 V
Ca^{2+}	+ 2 e^-	$\rightarrow \text{Ca}$	-2.76 V
Na^+	+ e^-	$\rightarrow \text{Na}$	-2.71 V
Ti^{4+}	+ 4 e^-	$\rightarrow \text{Ti}$	-1.63 V
H_2O	+ 2 e^-	$\rightarrow \text{H}_2 + \text{OH}^-$	-0.83 V
Zn^{2+}	+ 2 e^-	$\rightarrow \text{Zn}$	-0.763 V
Cr^{3+}	+ 3 e^-	$\rightarrow \text{Cr}$	-0.744 V
Fe^{2+}	+ 2 e^-	$\rightarrow \text{Fe}$	-0.409 V
Cd^{2+}	+ 2 e^-	$\rightarrow \text{Cd}$	-0.401 V
Ni^{2+}	+ 2 e^-	$\rightarrow \text{Ni}$	-0.230 V
Pb^{2+}	+ 2 e^-	$\rightarrow \text{Pb}$	-0.126 V
H^+	+ 2 e^-	$\rightarrow \text{H}_2$	0.00 V
AgCl	+ e^-	$\rightarrow \text{Ag} + \text{Cl}^-$	+0.223 V
Hg_2Cl_2	+ 2 e^-	$\rightarrow 2\text{Hg} + 2\text{Cl}^-$	+0.268 V
Cu^{2+}	+ 2 e^-	$\rightarrow \text{Cu}$	+0.340 V
$\text{I}_{2(\text{g})}$	+ 2 e^-	$\rightarrow 2\text{I}^-$	+0.536 V
Ag^+	+ e^-	$\rightarrow \text{Ag}$	+0.799 V
Pt^{2+}	+ 2 e^-	$\rightarrow \text{Pt}$	+1.188 V
$\text{Cl}_{2(\text{g})}$	+ 2 e^-	$\rightarrow 2\text{Cl}^-$	+1.358 V
Au^+	+ e^-	$\rightarrow \text{Au}$	+1.680 V

Reducing
agents

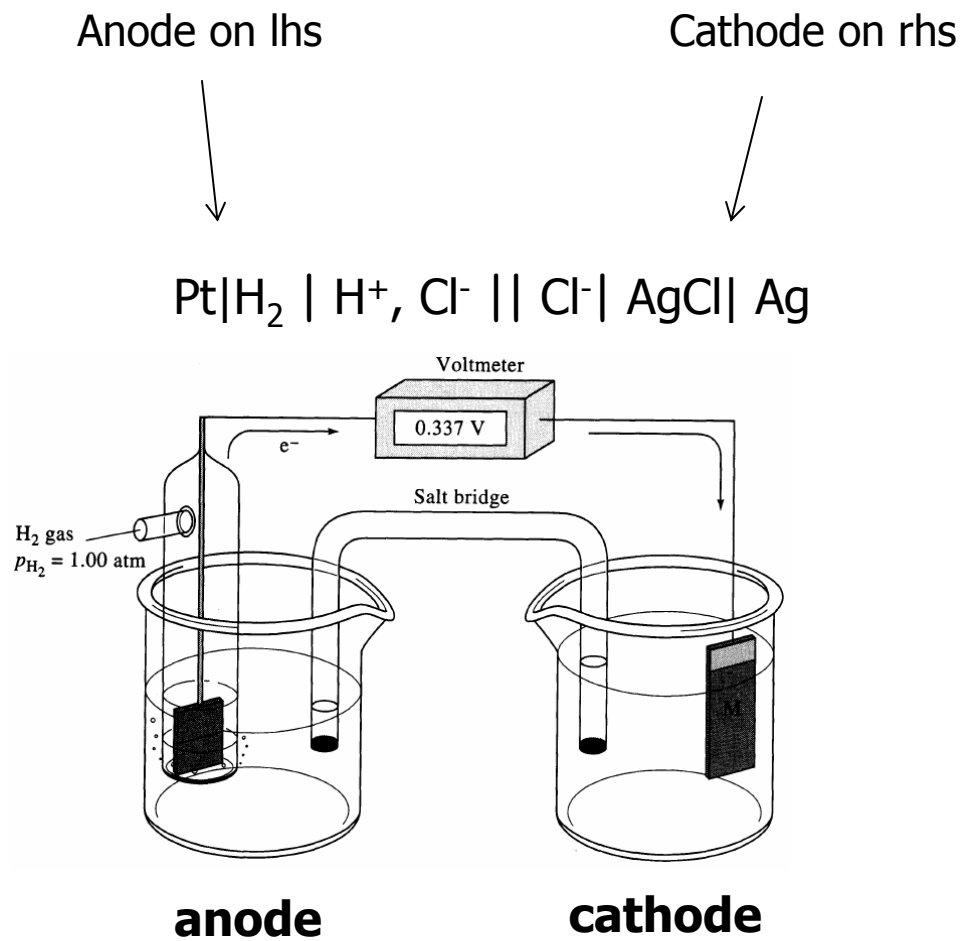


Oxidizing
agents

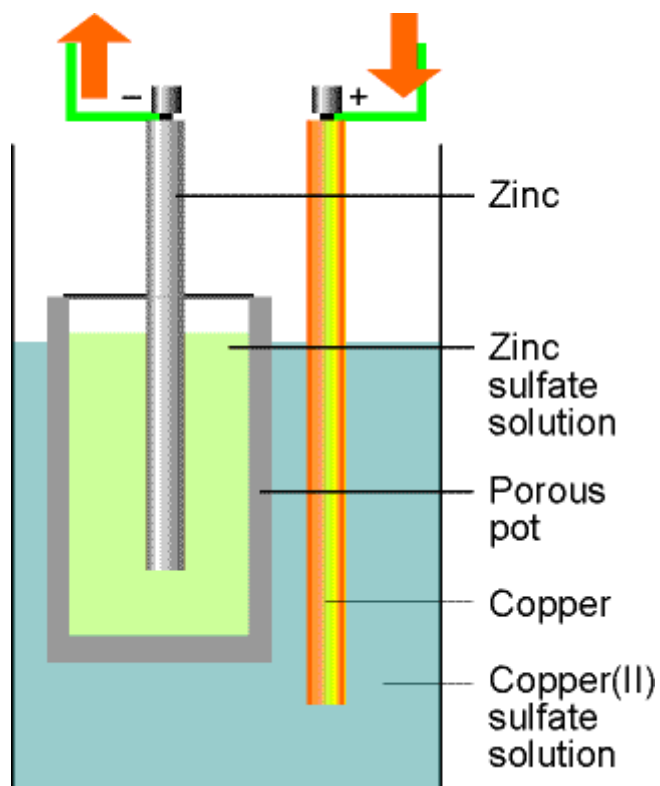
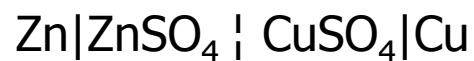


Notation to describe Electrochemical Cells

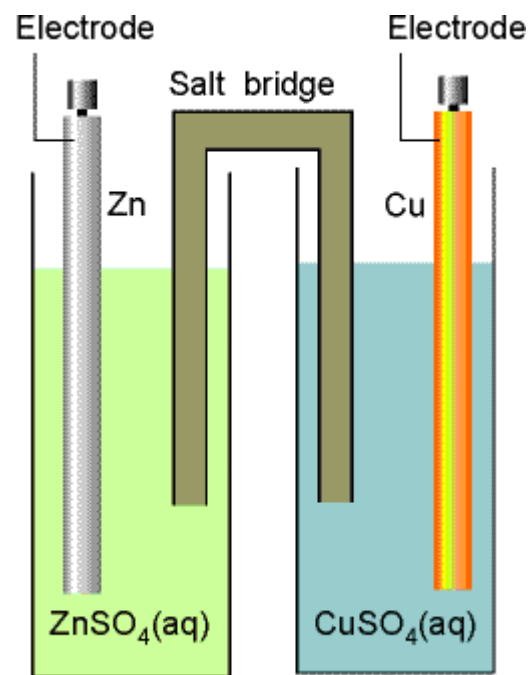
- | slash or vertical line indicates phase boundary
- , (comma) separates two components in the same phase
- || double vertical line or double slash indicates two phase boundaries (liquid-liquid junctions) designed not to add significant potential difference to overall cell potential.
- | dotted line indicates these liquid-liquid potentials are significant.



Notation Examples

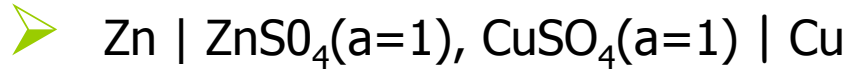


anode cathode

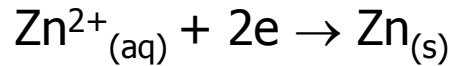


anode cathode

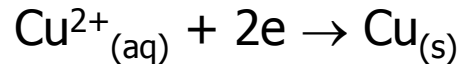
Example Calculate E° and dG° at standard state all activities =1



Anode



Cathode



Standard Potential of cell is

$$E^\circ = E_{\text{cathode}} - E_{\text{anode}}$$

From Standard Tables

$$= 0.340 - (-0.7626) = +1.103 \text{ V}$$

$$dG^\circ = -(zFE^\circ)_{P,T,n_i} \quad \text{E.8}$$

$$2 \times 96490 \times 1.103 = 213 \times \text{KJ}$$

$$[(\text{mole of electrons}) \times (\text{coulombs/mole}) \times \text{Joules/Coulomb}] = \text{Joules}$$

SHE not very useful most potentials are commonly measured relative to either silver/silver chloride or calomel electrodes

$\text{Ag}|\text{AgCl}|\text{KCl}(\text{saturated in water})$

- The electrode is a silver wire that is coated with a thin layer of silver chloride either by electroplating or by dipping the wire in molten silver chloride.
- Electrode is placed in a saturated potassium chloride solution it develops a potential of 0.199 V vs the SHE.
- The potential developed is determined by the chloride concentration of the solution and remains constant as long as the chloride concentration remains constant.

$\text{Hg}|\text{HgCl}_2|\text{KCl}(\text{saturated in water})$

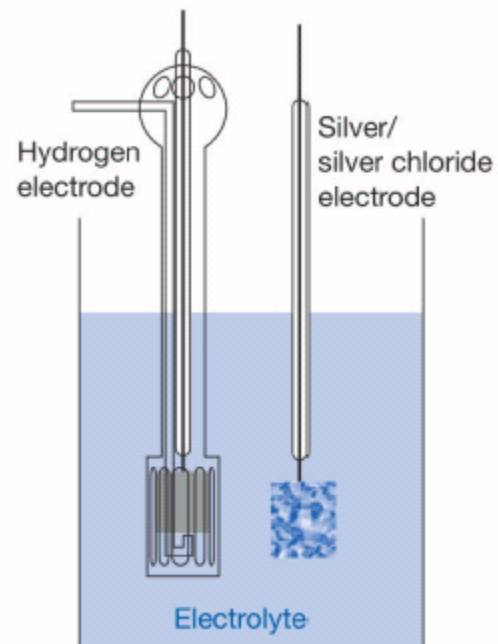
- a mercury-mercurous chloride cell
- a mercury-mercurous chloride cell, develops 0.244 V vs. SHE
- Calomel electrodes should not be used above 50 °C because the mercurous chloride breaks down, This will yield unstable readings and may be toxic.

Calculating EMF of a cell when activities do not equal 1

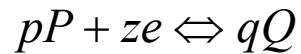


Problem

Calculate E_{cell} for cell, where temperature is at 25 °C and mean activity coefficients of HCl is 0.758



Nernst Equation when a system is at equilibrium



$$E = E^{\circ} + \frac{RT}{zF} \ln \frac{a_p^p}{a_Q^q}$$

← Reactants

← Products

$$E = E^{\circ} - \frac{RT}{zF} \ln \frac{a_Q^q}{a_p^p}$$

← Products

← Reactants

E° : standard potential of cell, V

T : temperature, Kelvin

R : gas constant, ($8.314 \text{ JK}^{-1} \text{ mol}^{-1}$)

F : Faraday constant (96490 Cmol^{-1})

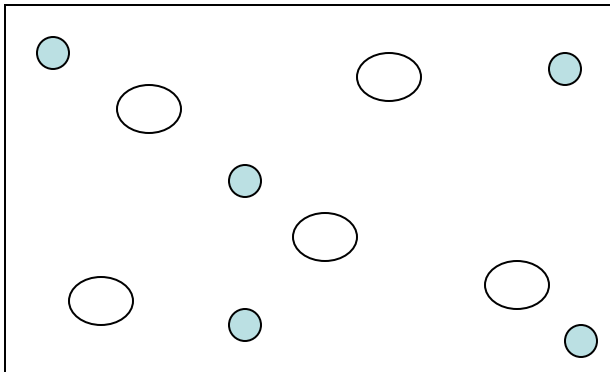
z : number of electrons

Chemical Potential of Electrolyte Solutions

➤ Dilute ionic Solutions

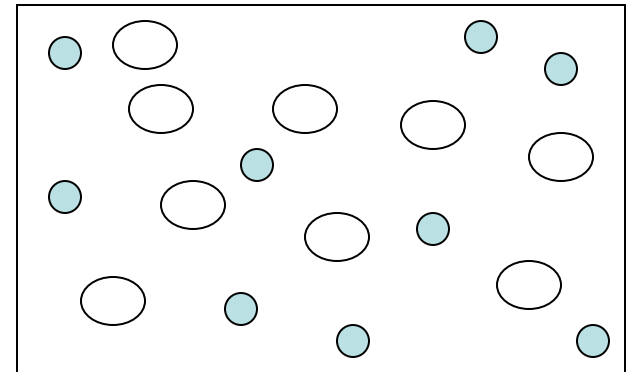
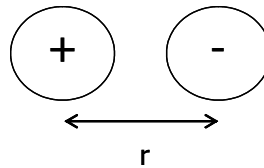
Ions behave ideally no ion-ion interactions or solvation effects with solvent.

$$\mu_{NaCl} = \mu_{NaCl}^o + RT \ln[Na][Cl]$$



➤ Ions in concentrated solution ($> 10^{-3}$ M)

Ions interact by Coulombic forces. The solution is no longer ideal. The chemical potential of ions is affected by these interactions. (The entropy is lowered). This is accounted for by describing the ions in terms of their activity, a instead of their concentration.



Activities of ions



$$\mu_{\text{Na}^+} = \mu_{\text{Na}^+}^o + RT \ln a_{\text{Na}^+}$$

$$\mu_{\text{Cl}^-} = \mu_{\text{Cl}^-}^o + RT \ln a_{\text{Cl}^-}$$

$$\mu_{\text{Na}} + \mu_{\text{Cl}} = \mu_{\text{NaCl}}$$

$$\mu_{\text{Na}}^o + \mu_{\text{Cl}}^o = \mu_{\text{NaCl}}^o$$

Therefore

$$\mu_{\text{NaCl}} = \mu_{\text{NaCl}}^o + RT \ln a_{\text{Na}^+} a_{\text{Cl}^-} \quad \text{E.9}$$

However cannot measure activity of cation and anions independently. Define the total activity for a 1:1 electrolyte, eg. NaCl in terms of the geometric mean of the individual ionic activities

$$a = a_+ a_- = a_{\pm}^2$$

Therefore

$$\mu_{\text{NaCl}} = \mu_{\text{NaCl}}^o + 2RT \ln a_{\pm} \quad \text{E.10a}$$

For infinitely dilute solutions

$$\mu_{\text{NaCl}} = \mu_{\text{NaCl}}^o + 2RT \ln c_{\text{NaCl}} \quad \text{E.10b}$$

Mean activity coefficient of 1:1 electrolytes



$$a_{\text{Na}^+} \equiv \gamma_{\text{Na}^+} C_{\text{Na}^+}$$

$$a_{\text{Cl}^-} \equiv \gamma_{\text{Cl}^-} C_{\text{Cl}^-} \quad \text{E.11}$$

$$\mu_{\text{NaCl}} = \mu_{\text{NaCl}}^o + RT \ln \gamma_{\text{Na}^+} C_{\text{Na}^+} \gamma_{\text{Cl}^-} C_{\text{Cl}^-}$$

Where γ_+ or γ_- are the un-measurable activity coefficient for the ions

Determine the geometric mean activity coefficient

$$\gamma_{\pm} = (\gamma_+ \gamma_-)^{1/2}$$

$$\gamma_{\pm}^2 = (\gamma_+ \gamma_-)$$

$$2 \ln(\gamma_{\pm}) = \ln(\gamma_+ \gamma_-)$$

If we also use

$$C_{\text{NaCl}} = C_{\text{Na}^+} = C_{\text{Cl}^-}$$

Then

$$\mu_{\text{NaCl}} = \mu_{\text{NaCl}}^o + 2RT \ln \gamma_{\pm} C_{\text{NaCl}} \quad \text{E.12}$$

Back to Example calculating E_{cell} with Nernst Equation

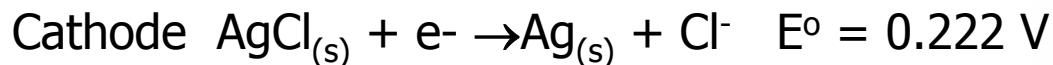
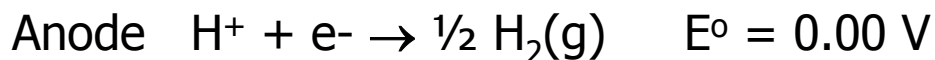


Problem

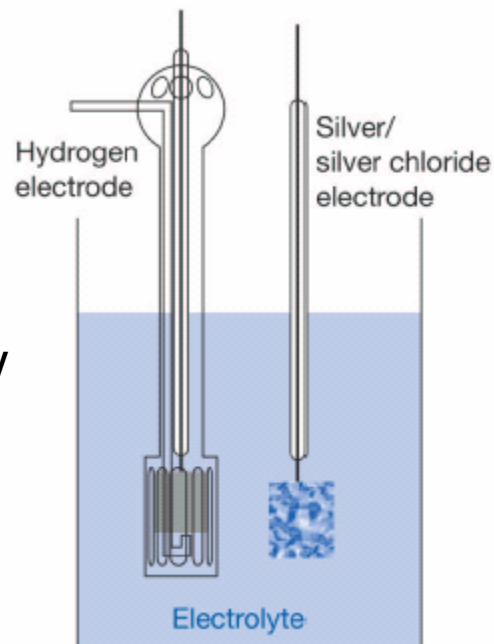
Calculate E_{cell} for cell, where temperature is at 25 °C and mean activity coefficients of HCl is 0.758



Write half cell reactions as reductions

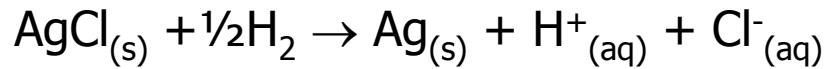


$$E^\circ = E_{\text{cathode}} - E_{\text{anode}} = 0.222 \text{ V}$$



Example, continued

➤ Write overall reaction



➤ Write Nernst Equation for reaction

$$E = E^o + \frac{RT}{zF} \ln \frac{a_{\text{H}_2}^{1/2} a_{\text{AgCl}(s)}}{a_{\text{H}^+} a_{\text{Cl}^-} a_{\text{Ag}(s)}}$$

$$E^o - \frac{RT}{F} \ln a_{\text{HCl}}$$

$$E^o - \frac{2RT}{F} \ln \gamma_{\pm} [\text{HCl}]$$

T : temperature, Kelvin

R : gas constant, ($8.314 \text{ JK}^{-1} \text{ mol}^{-1}$)

F : Faraday constant ($96490 \text{ Coulombs mol}^{-1}$)

z : number of electrons

γ_{\pm} mean activity coefficient

$$= 0.222 - \frac{2 \cdot 8.314 \cdot 298}{1 \cdot 96490} [\ln(0.758 \cdot 0.5)]$$

$$= 0.222 + 0.0361$$

$$= 0.258 \text{ V}$$

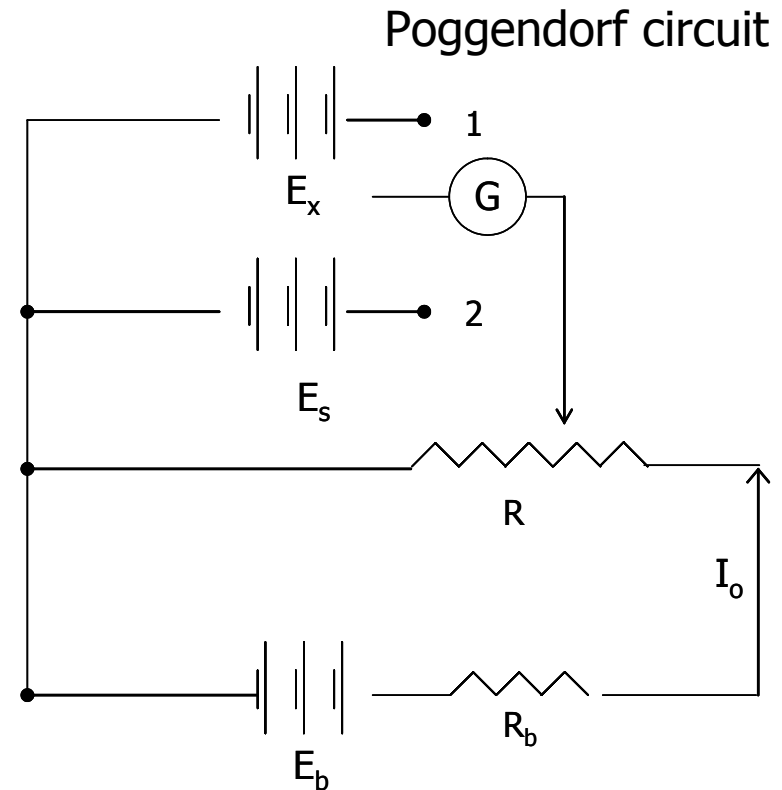
Measuring the EMF of a cell or the open-circuit or zero-current cell potential

➤ EMF is defined as the cell potential when there is no current through the cell.
The emf is sometimes coined the zero-current or open-circuit cell potential.

➤ Measuring EMF
Potentiometer slide wire is adjusted until there is no current through the galvanometer, G when the switch is in position 2. In this position $R = R_s$. The process is repeated for switch position 1 where $R = R_x$.

$$E_x = I_o R_x \text{ and } E_s = I_o R_s$$

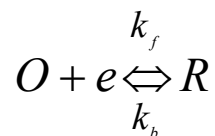
$$E_x = (R_x/R_s)E_s$$



E : power supply
 E_s : standard cell of known potential
 E_x : unknown cell potential

Exchange Current Density is a function of the rate constant of the reaction (at equilibrium)

For any redox reaction



k_f rate constant of the forward reaction

k_b rate constant of the backward reaction

$$j_o = j_{cathode} = \frac{zFm_o k_f}{A} \text{ (at equilibrium)}$$

$$j_o = j_{anode} = \frac{zFm_R k_b}{A} \text{ (at equilibrium)}$$

At equilibrium when voltage, E equals the equilibrium voltage E_{eq} the rate of forward reaction rate equals backward reaction rate then

$$zFm_o k_f + zFm_R k_b = 0$$

and the net current is zero

$$i_{cathode} + i_{anode} = 0$$

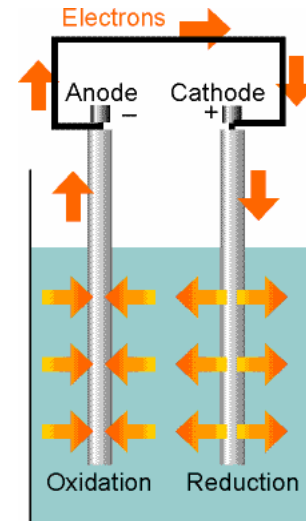
The current at each electrode when the system is at equilibrium is called the exchange current density, j_o



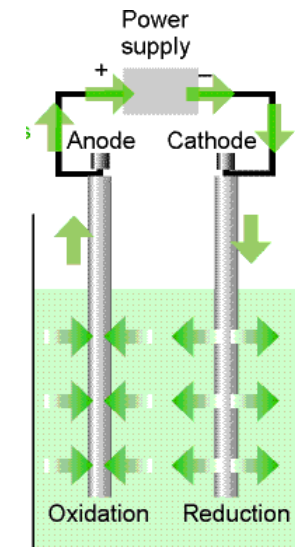
A system with a high exchange current density or large rate constant, k has fast kinetics and will attain equilibrium after a short time. A system with small k will be sluggish.

Types of Cells

➤ Galvanic cell: reactions occur spontaneously at the electrodes when they are connected externally by a conductor. A battery is a commonly used electrochemical cell. When a battery is connected to a device it discharges it's stored chemical energy providing energy to drive the device.



➤ Electrolytic Cell: reactions do not occur spontaneously but are driven by external source of current. Reactions that occur are affected by external voltage supply which is greater than the open-circuit potential of the cell.

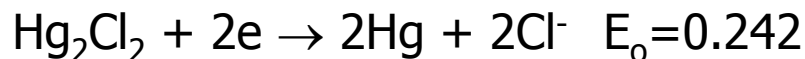


Lets consider an electrolytic cell



calomel reference electrode

anode

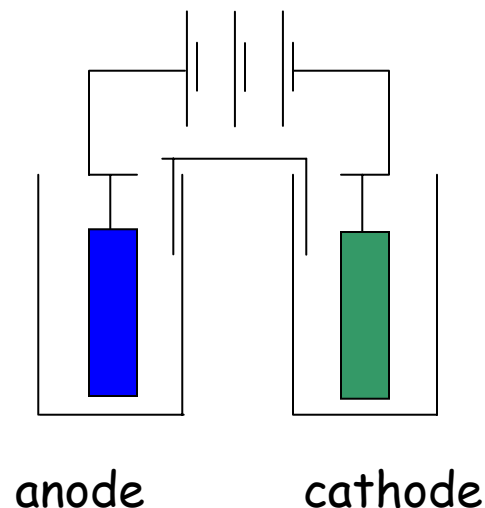


cathode



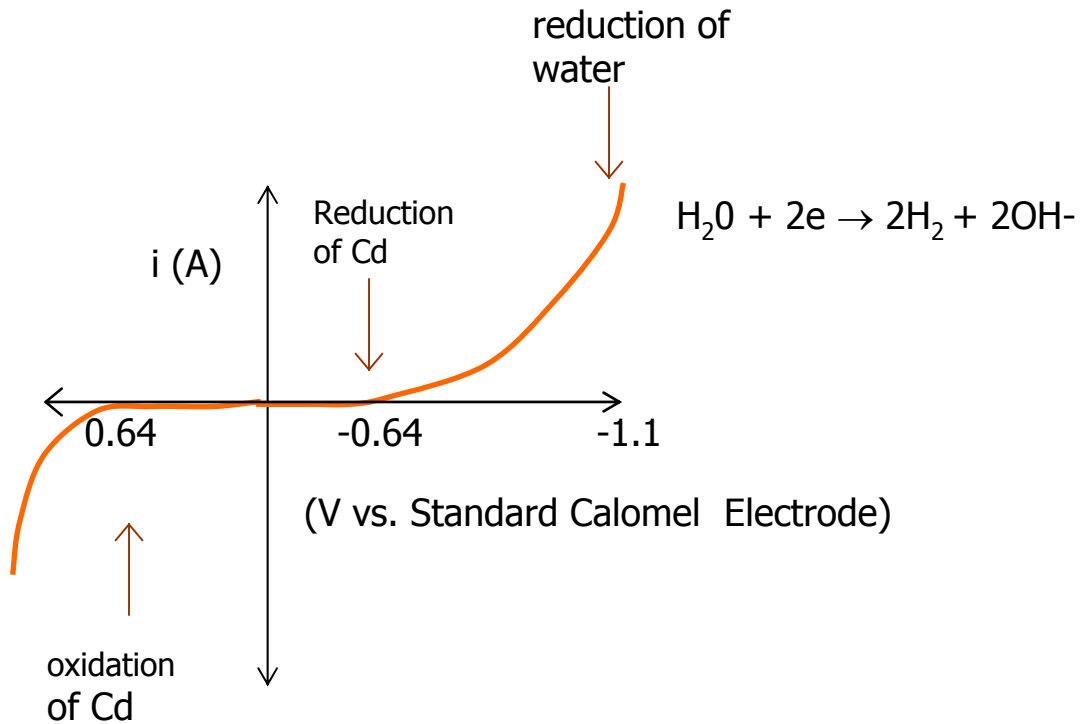
Open circuit potential: $E_{\text{cathode}} - E_{\text{anode}} = -0.64 \text{ V}$

The net current, i is zero at the open circuit potential of EMF

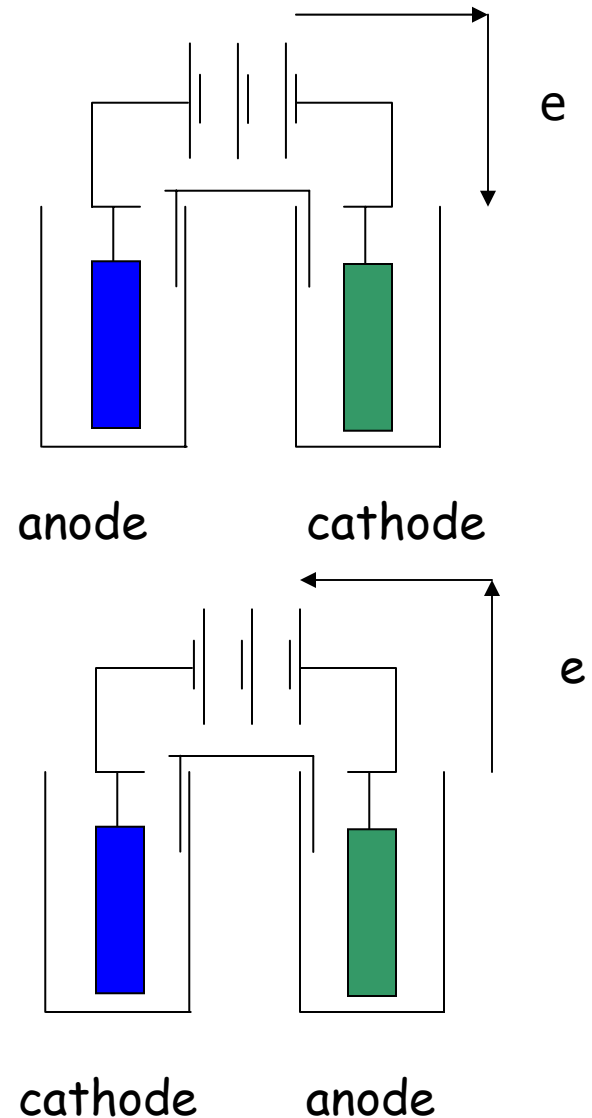


When Cd electrode is made more negative or more positive relative to reference calomel electrode current will flow

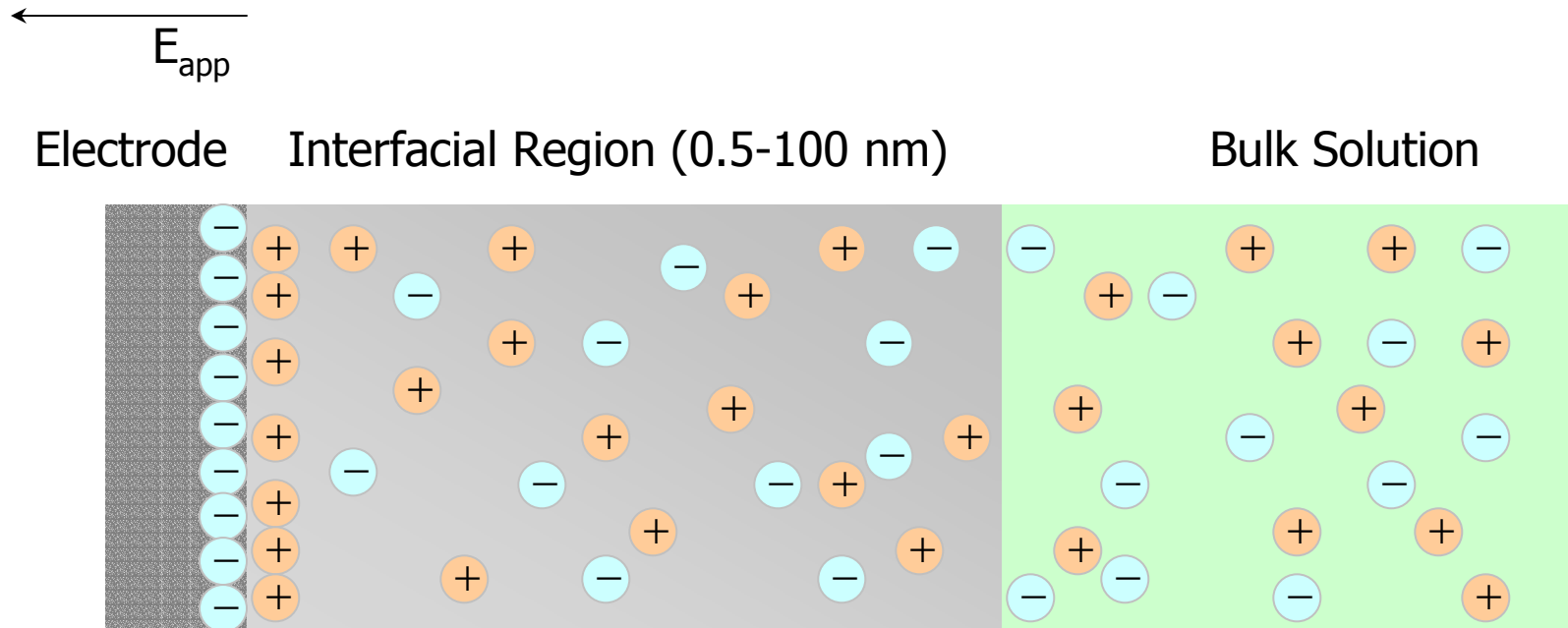
Cathodic current: reduction current electron flow from electrode to species in solution. Defined as positive, but there is no strict convention.



Anodic current: is an oxidation current electron flow from species in solution to an electrode. Defined as negative current.

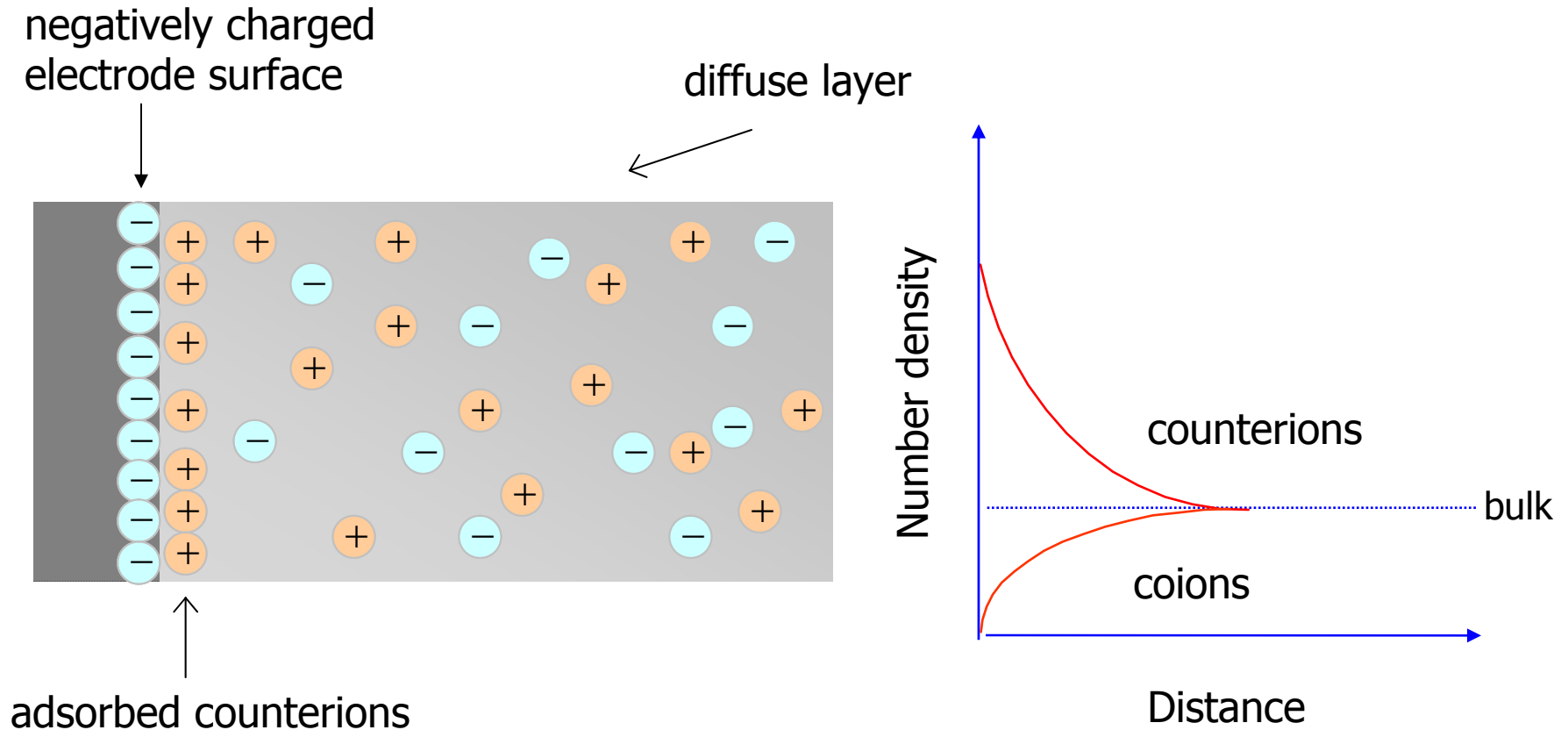


.. application of a potential, E_{app} can cause the surface of the electrode to become charged forming a double layer. This alters the I vs E curve



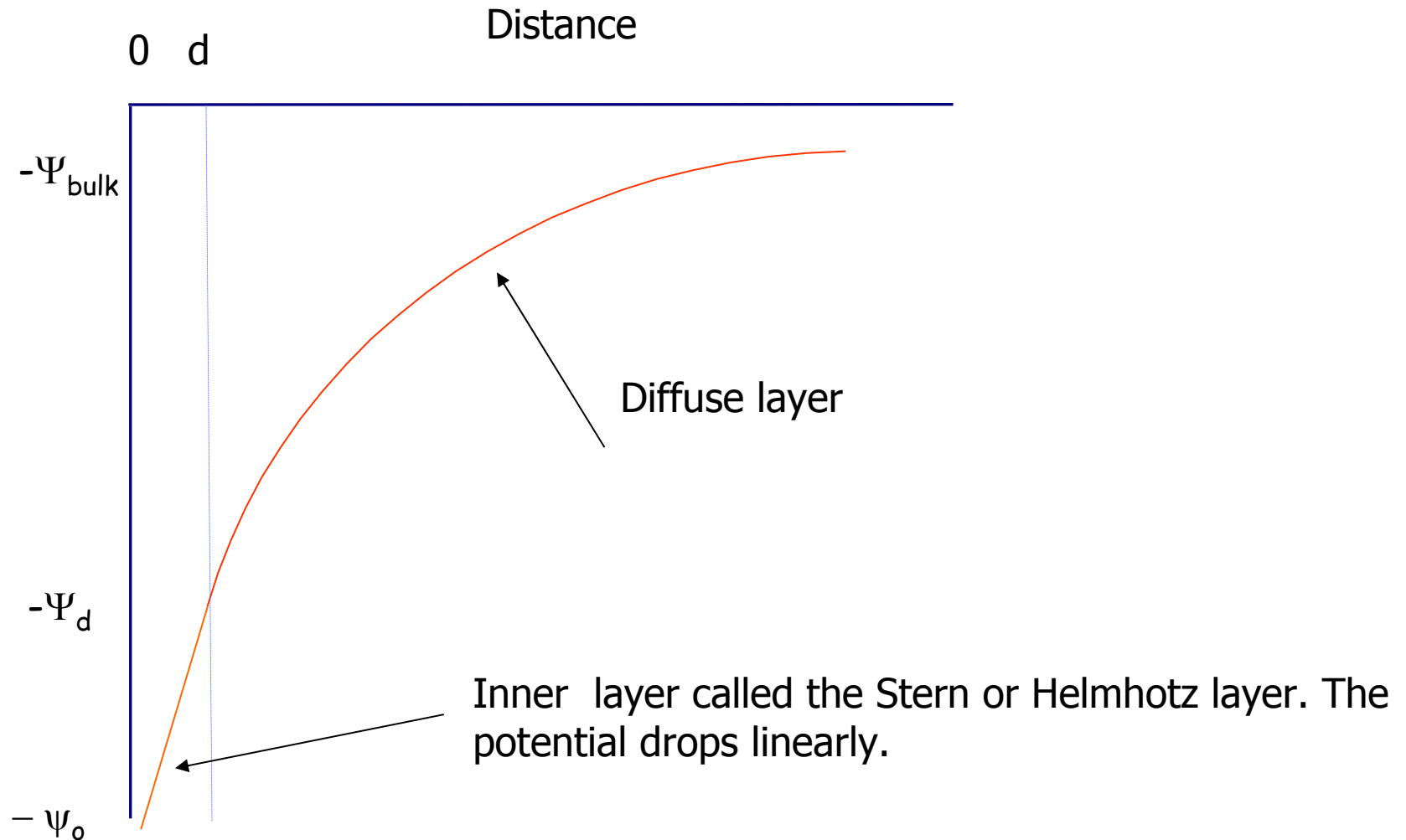
- Electrode becomes charged by specific adsorption of molecules onto surface, charging of surface atoms e.g. OH^- , O^{2-}

Double layer: adsorption of counterions and desorption of coions at the interface relative to concentration in the bulk



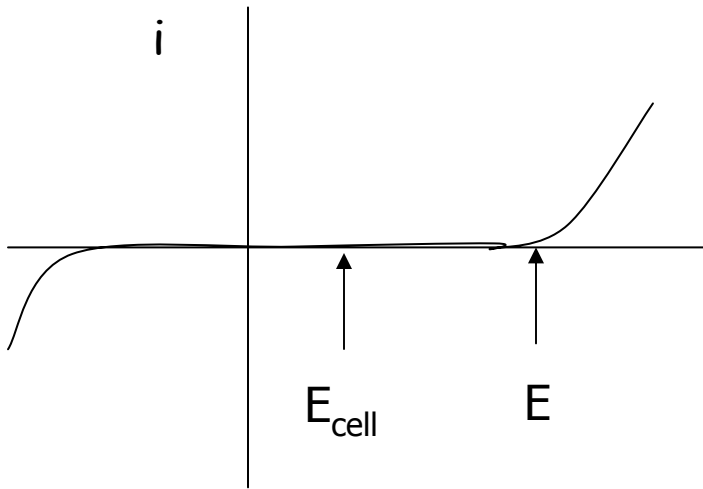
Ions accumulate around a charged surface as a consequence of the equilibrium between the electric attraction of the surface charge and the thermal motion which tends to distribute them over the entire solution

Surface Potential as a Function of Distance from a Negatively Charged Electrode Surface



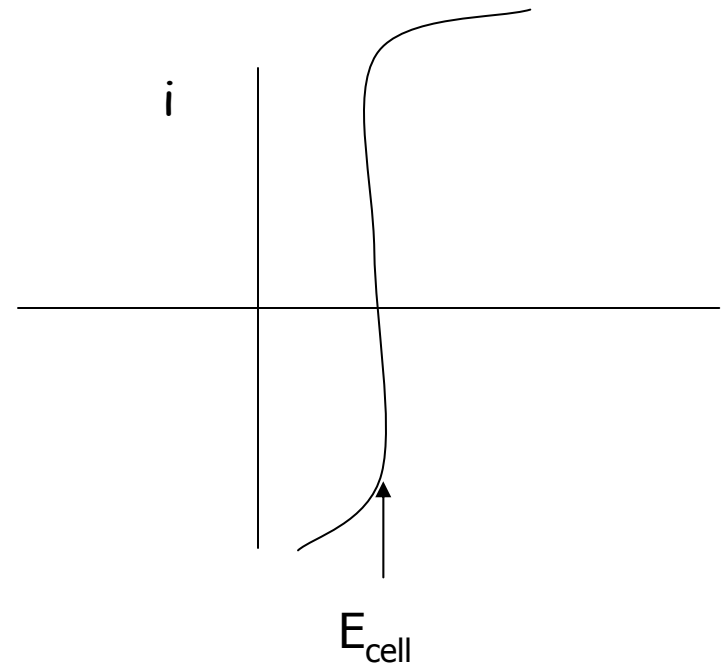
Polarization vs Nonpolarization

Polarizable electrode: large change in potential upon passage of small faradic current because of double layer. (e.g. mercury electrode in contact with de-aerated potassium chloride solution)



overpotential, $\eta = E - E_{\text{cell}}$

Non-Polarizable electrode: no change in potential upon passage of small faradic current. (e.g. required of reference electrode eg. Standard Calomel electrode)

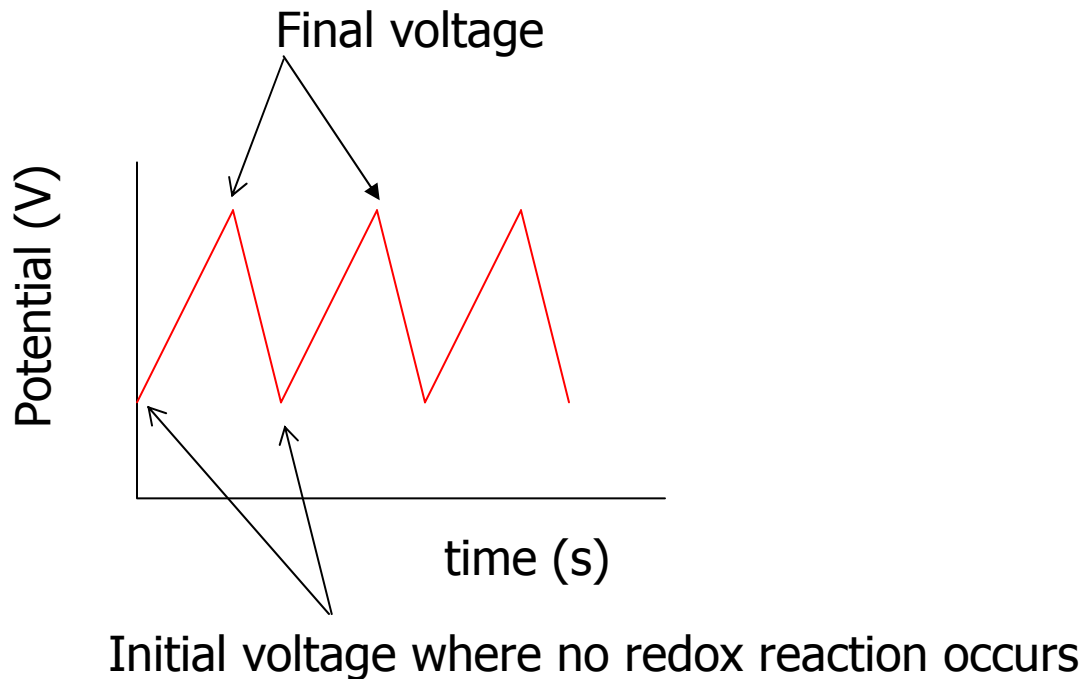


Consequences of double layer effects

- Concentration of species in the bulk of the solution does not represent the concentration of species at the electrode surface where the redox reaction is occurring
- An electrode with a positive charge ($\Psi_d > 0$) will attract anions (valence, $z = \text{negative}$) while cations ($z = \text{positive}$) will be repelled. An electrode with a negative charge ($\Psi_d < 0$) will attract cations (valence = positive) while anions will be repelled. An electrode at the point of zero charge (no net charge), the concentration at the surface is the same as in the bulk.
- The effective potential at each electrode is $E - \Psi_d$ where $\Psi_d = 0$ is the potential when the charge on the electrode is zero. Because Ψ_d varies with E it influences the rate of redox reactions. Require more potential -an overpotential- to measure the expected faradic current densities.
- An overpotential is sometimes useful. For example, the reduction of water often interferes with measurements, a high overpotential for the reduction of water is observed on many electrodes. This allows a electrochemical process to occur without interference from reduction of water.

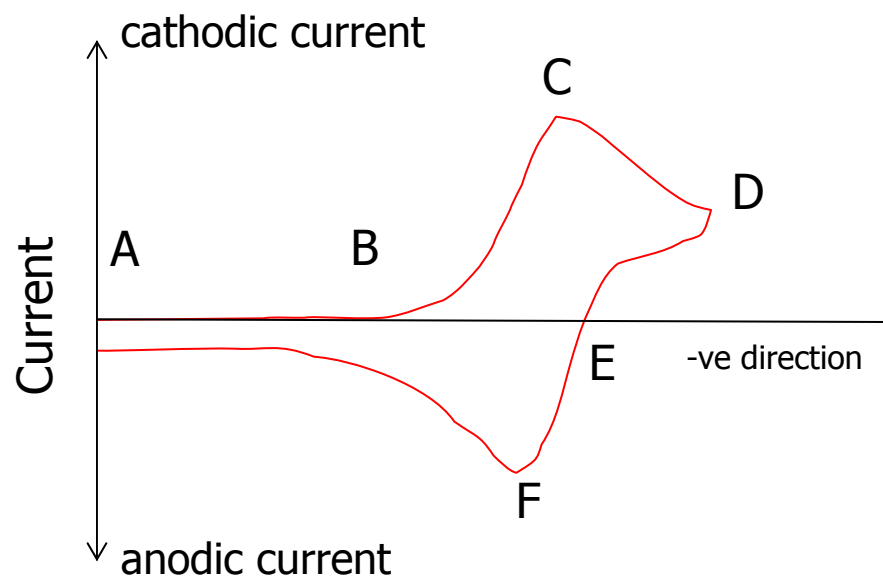
Cyclic Voltammetry

- Used to detect electroactive species. By electroactive a analyte that is readily reduced or oxidized. For example used to detect release of neurotransmitters dopamine, serotonin in the brain.
- Stimulus: Triangle waveform repeated many times at a specific rate cycles/second



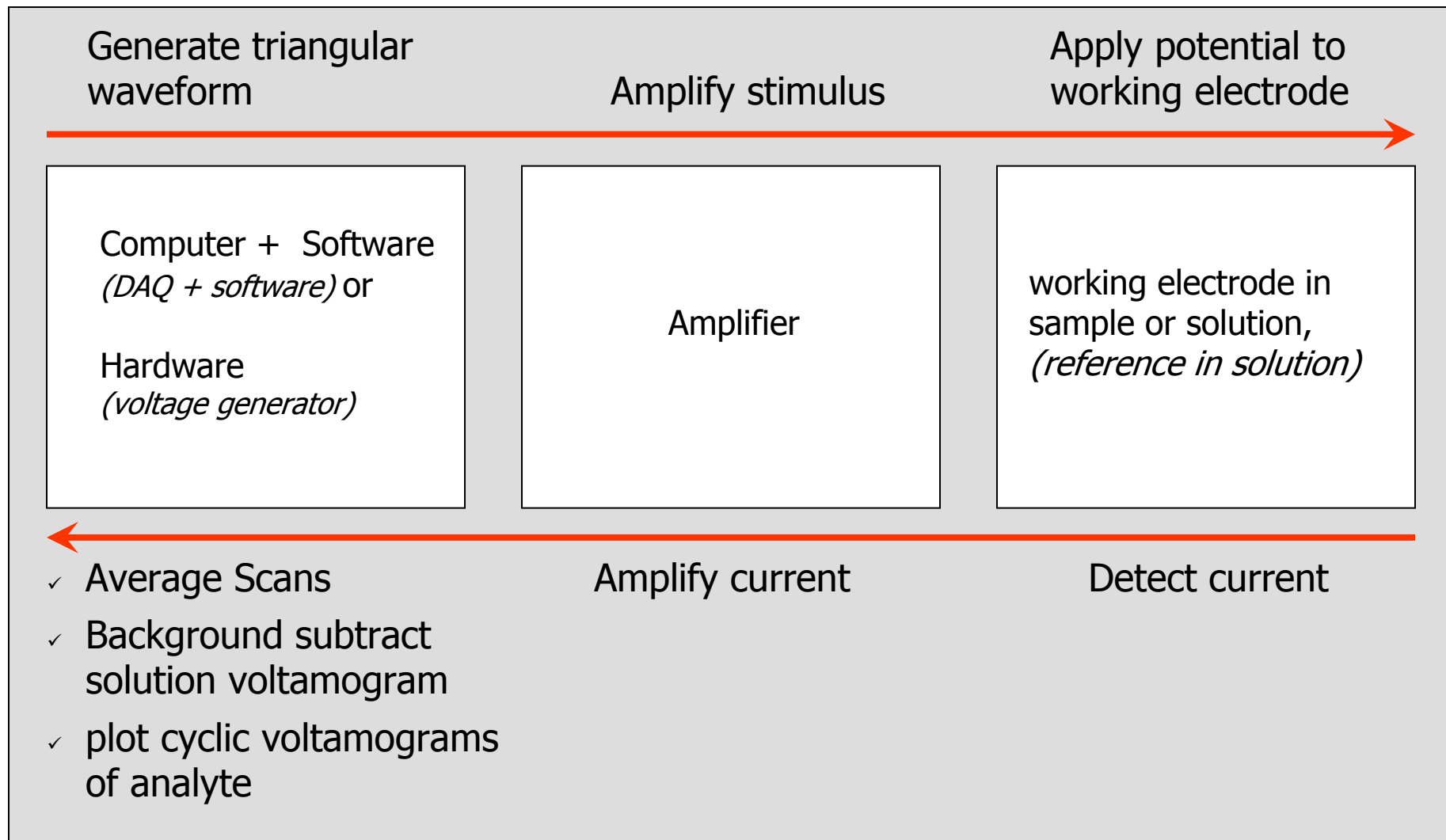
Response the current measured is the average of many stimulus cycles

- Starting at an initial voltage (A), the potential is scanned in one direction in this case in the negative direction.
- At B, a cathodic current is detected as the analyte starts to be reduced.
- The current continues to increase as more analyte is reduced and then peaks at (C). The current then decays for the rest of the forward scan.
- At (D) the polarity of the voltage is reversed and the cathodic current decays till it reaches (E) where the analyte starts to be oxidized. The anodic current then peaks at F as more analyte is re-oxidized. It then decays as the voltage is made more positive and the scan is complete



E vs reference electrode

Currents measured are usually small nAmps require sophisticated electronic instrumentation and working electrodes with small surface areas



Summary of lecture

- Be able to calculate the cell potential of a cell from two half cells at standard state and not at standard state
- Explain what a negative or positive cell potential implies
- Understand the notation to describe electrochemical cells
- Explain the formation of a double layer in a electrolytic cell and explain how it affects the cell potential
- Know what is meant by cathodic and anodic current and the exchange current density, j_0 of a redox reaction
- Be able to interpret a cyclic voltamogram