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Classical Methods of Analysis

Early years of chemistry

•Separation of analytes by precipitation, extraction, or distillation.

•Qualitative analysis by reaction of analytes with reagents that yielded products that could be recognized by their colors, boiling or melting points, solubilities, optical activities, or refractive indexes.

•Quantitative analysis by gravimetric or by titrimetric techniques.

Instrumental Methods

- Measurement of physical properties of analytes - such as conductivity, electrode potential, light absorption or emission, mass-to-charge ratio, and fluorescence- began to be employed for quantitative analysis of inorganic, organic, and biochemical analytes

- Efficient chromatographic separation techniques are used for the separation of components of complex mixtures.

- Instrumental Methods of analysis (collective name for newer methods for separation and determination of chemical species.)

Applicable Concentration Range
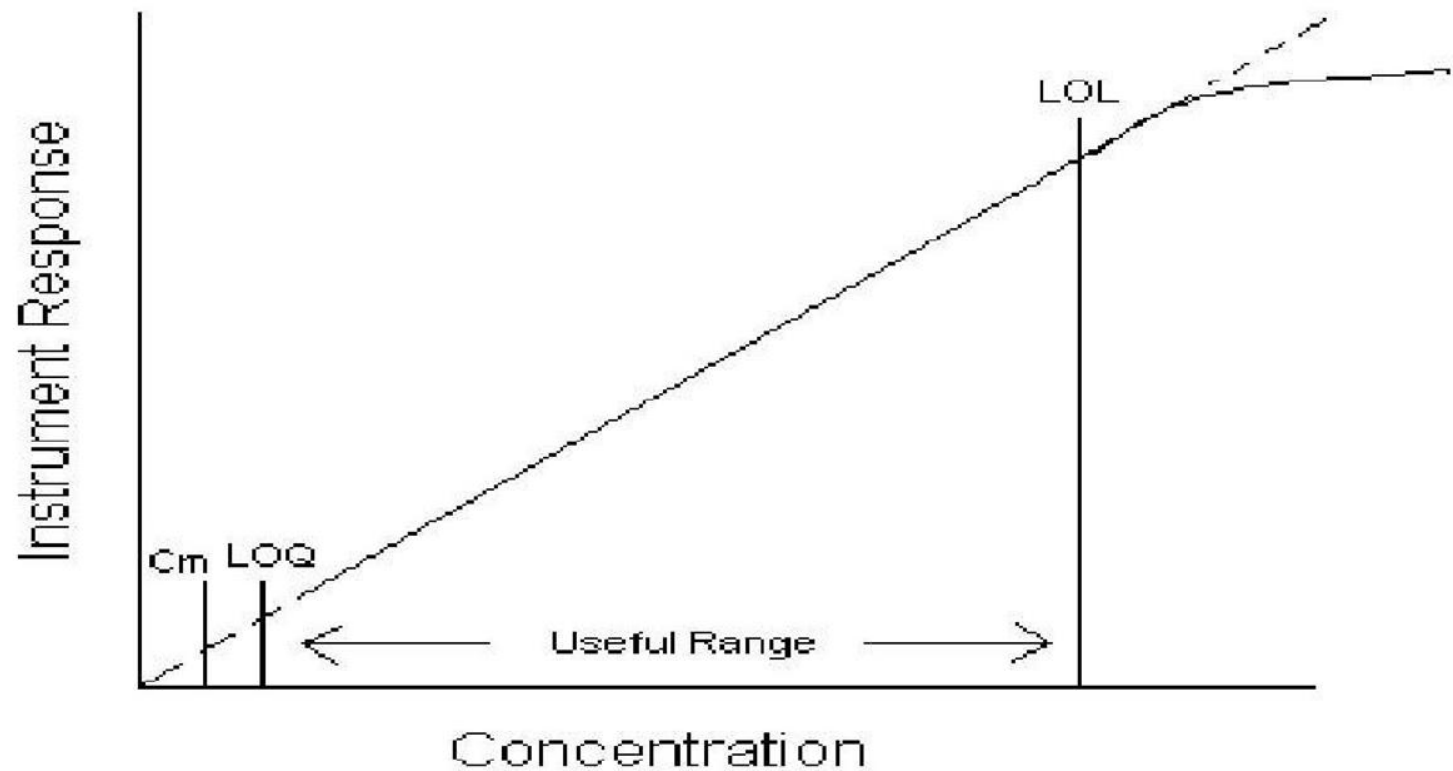
Electroanalytical Chemistry

- A group of quantitative analytical methods that are based upon the electrical properties (electrical response) of a solution of the analyte (chemical system) when it is made part of an electrochemical cell.

- Chemical System: Electrolyte; measuring electrical circute; Elcrodes

USES OF ELECTROANALYTICAL CHEMISTRY

- Electroanalytical techniques are capable of producing very low detection limits.
- Electroanalytical techniques can provide a lot of characterization information about

  electrochemically addressable systems.
  - Stoichiometry and rate of charge transfer.
  - Rate of mass transfer.
  - Extent of adsorption or chemisorption.
 - Rates and equilibrium constants for chemical reactions.

ADVANTAGES COMPARED TO OTHER METHODS

- Inexpensive

- Used for ionic species not total concentration

- Responds to ionic activity rather than concentration

- Ion selective electrodes and developing of the measuring devices in voltammetry made wider spread of the methods

REVIEW OF FUNDAMENTAL TERMINOLOGY

- Electrochemistry - study of redox processes at interfaces
  - Heterogeneous
- So two reactions occurring:
  - oxidation
  - reduction

- **For the reaction,**
  $$O + ne^- \rightleftarrows R$$
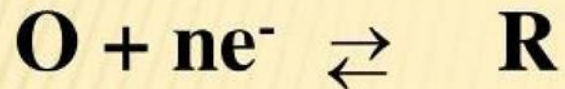
- **Oxidation**: $R \rightleftarrows O + ne^-$
  – loss of electrons by R

- **Reduction**: $O + ne^- \rightleftarrows R$
  – gain of electrons by O

OXIDANTS AND REDUCTANTS

× **Oxidant = oxidizing agent**

  + reactant which oxidizes another reactant and which is itself reduced

× **Reductant = reducing agent**

  + reactant which reduces another reactant and which is itself oxidized

ELECTROCHEMICAL CELLS

CONSISTS OF TWO CONDUCTORS (CALLED ELECTRODES) EACH IMMERSED IN A SUITABLE ELECTROLYTE SOLUTION.

FOR ELECTRICITY TO FLOW:
THE ELECTRODES MUST BE CONNECTED EXTERNALLY BY MEANS OF A (METAL) CONDUCTOR.

THE TWO ELECTROLYTE SOLUTIONS ARE IN CONTACT TO PERMIT MOVEMENT OF IONS FROM ONE TO THE OTHER.
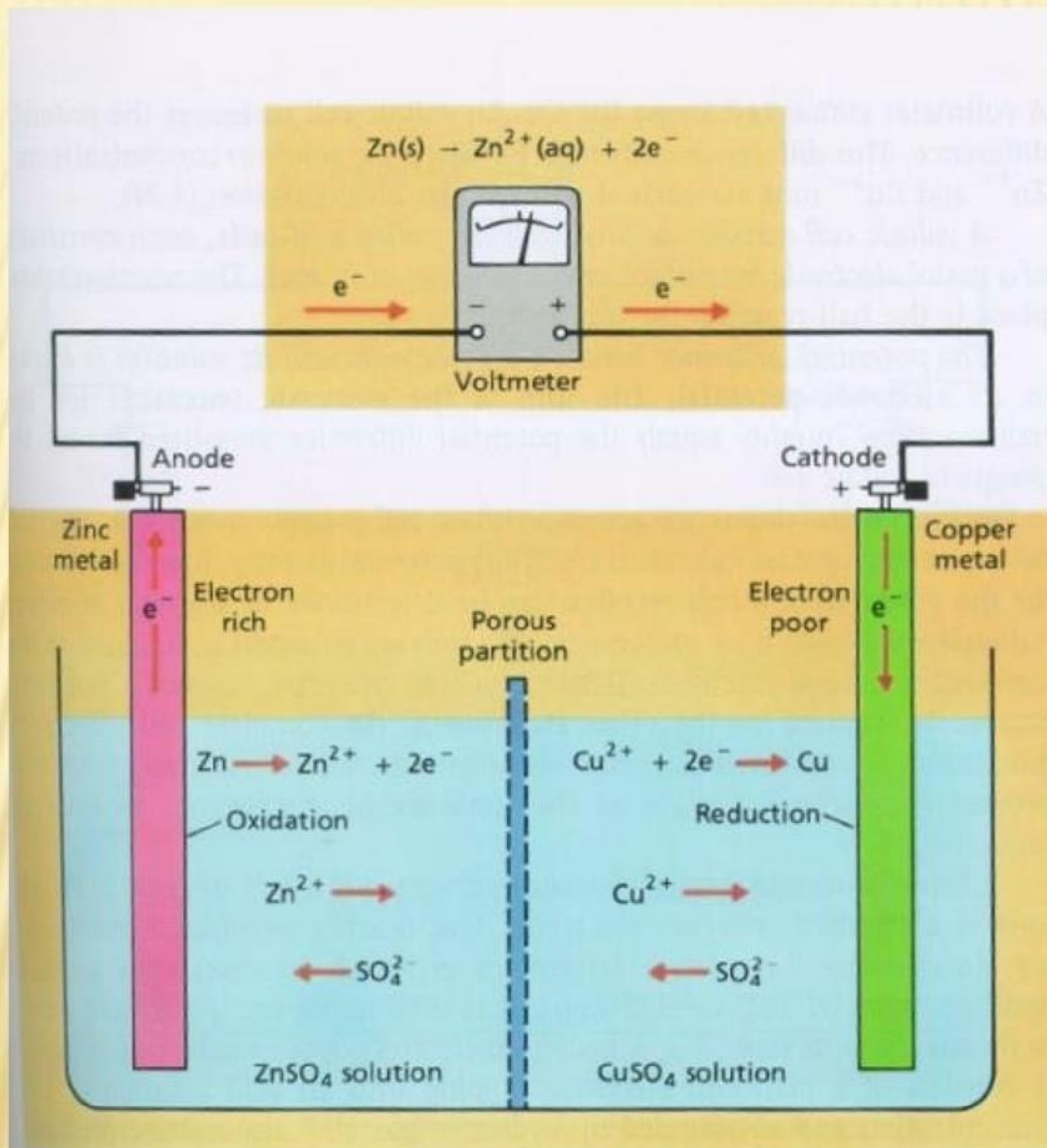
Electrochemical Cells

- **Cathode** is electrode at which reduction occurs.

- **Anode** is electrode at which oxidation occurs.

- Indicator and Reference electrodes

- **Junction potential** is small potential at the interface between two electrolytic solutions that differ in composition.
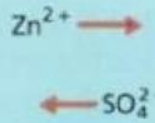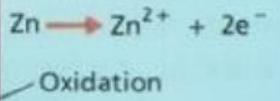
GALVANIC AND ELECTROLYTIC CELLS

- **Galvanic cells** produce electrical energy.
- **Electrolytic cells** consume energy.
  - If the cell is a chemically reversible cell, then it can be made electrolytic by connecting the negative terminal of a DC power supply to the zinc electrode and the positive terminal to the copper electrode.

Galvanic Cells
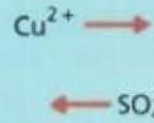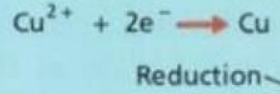
ELECTROLYTIC CELLS
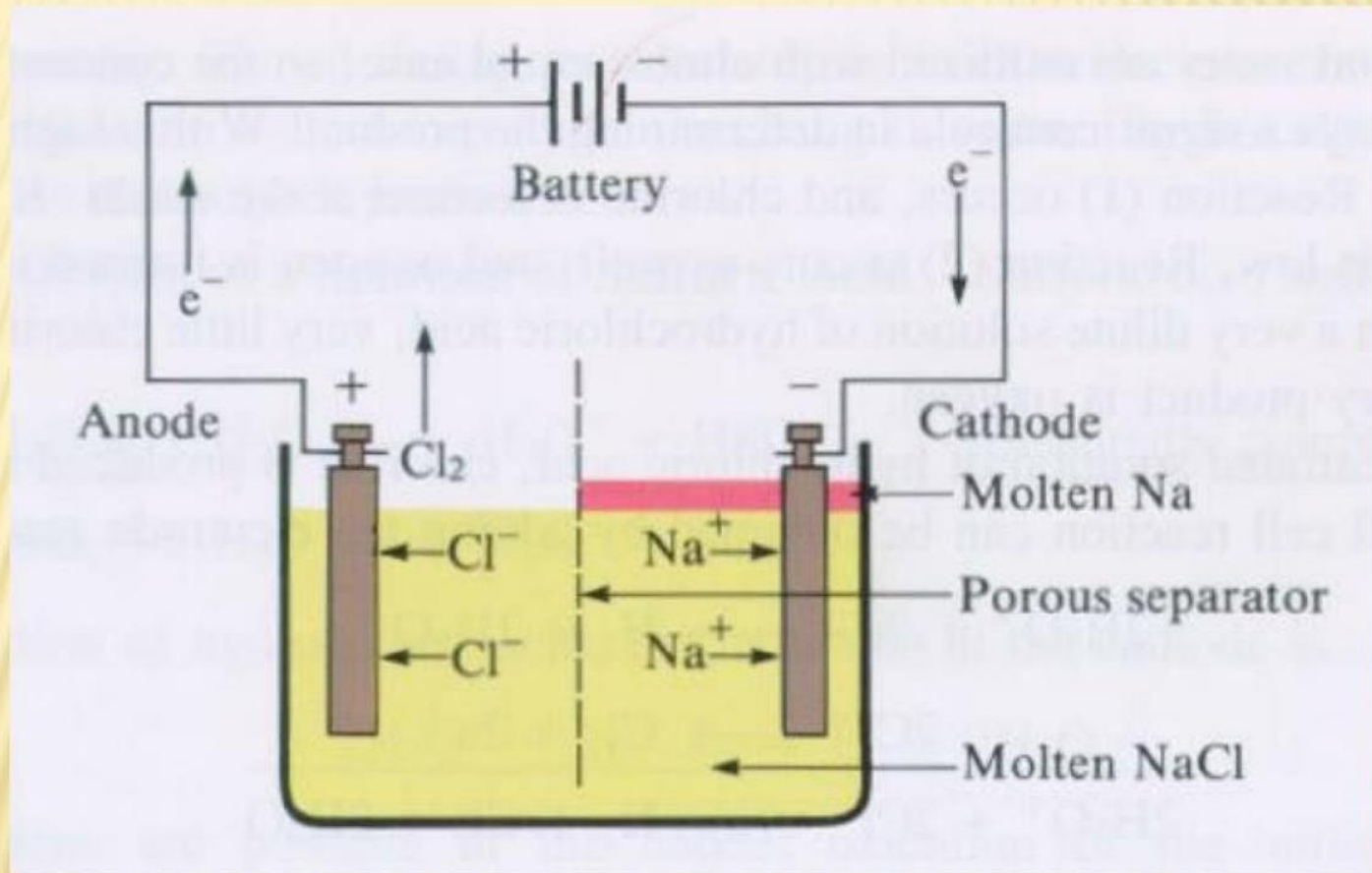
Schematic Representation of Electrochemical Cells

Rather that attempt to draw out an entire cell, a type of shorthand can be used.

For our copper - zinc cell, it would be:

$$Zn\ /\ Zn^{2+}\ (1M)\ //\ Cu^{2+}\ (1M)\ /\ Cu$$

The anode is always on the left

/ = boundaries

// = salt bridge

Other conditions like concentration are listed just after each species.

Other examples

Pt, H_2 (1atm) / H^+ (1M)
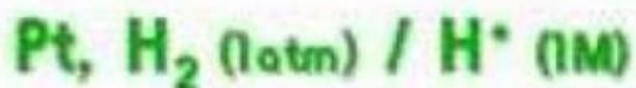
This is the SHE. Pt is used to maintain electrical contact so is listed. The pressure of H_2 is given in atmospheres.

Pt, H_2 (1atm) / HCl (0.01M) // Ag^+ (sat) / Ag

A saturated silver solution ($1.8 \times 10^{-8}M$) based on the K_{SP} of AgCl and the [Cl−].

Use shorthand-notation to represent this cell.

V

Salt bridge

Cd

NO_3^- K^+

Ag

Porous glass plates

NO_3^-

$Cd(NO_3)_2(aq)$

K^+

$AgNO_3(aq)$

Cd^{2+}

e^-

NO_3^-

Anode
$Cd(s) \rightarrow Cd^{2+}(aq) + 2e^-$

Cathode
$2Ag^+(aq) + 2e^- \rightarrow 2Ag(s)$
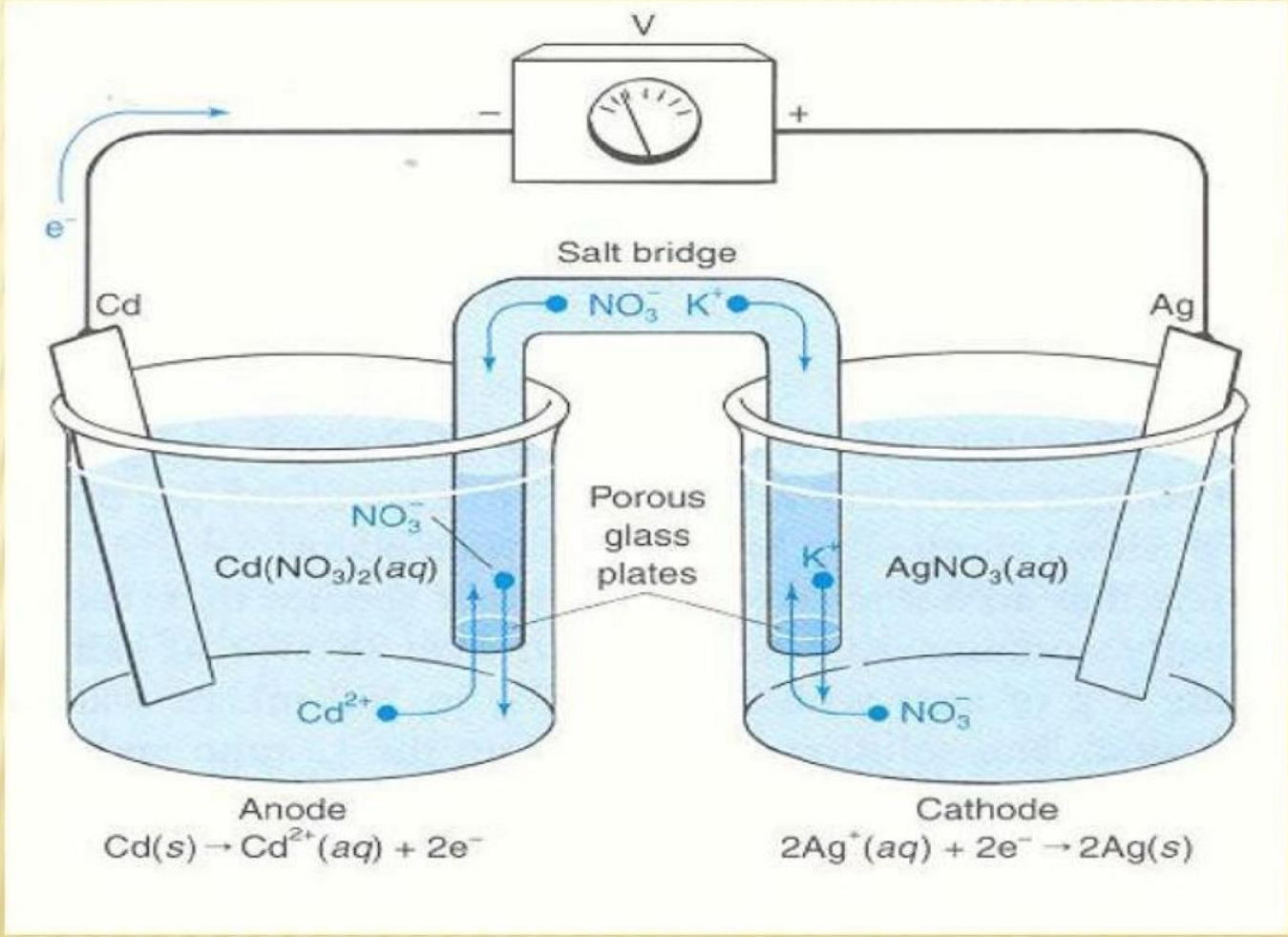
Use shorthand-notation to represent this cell.
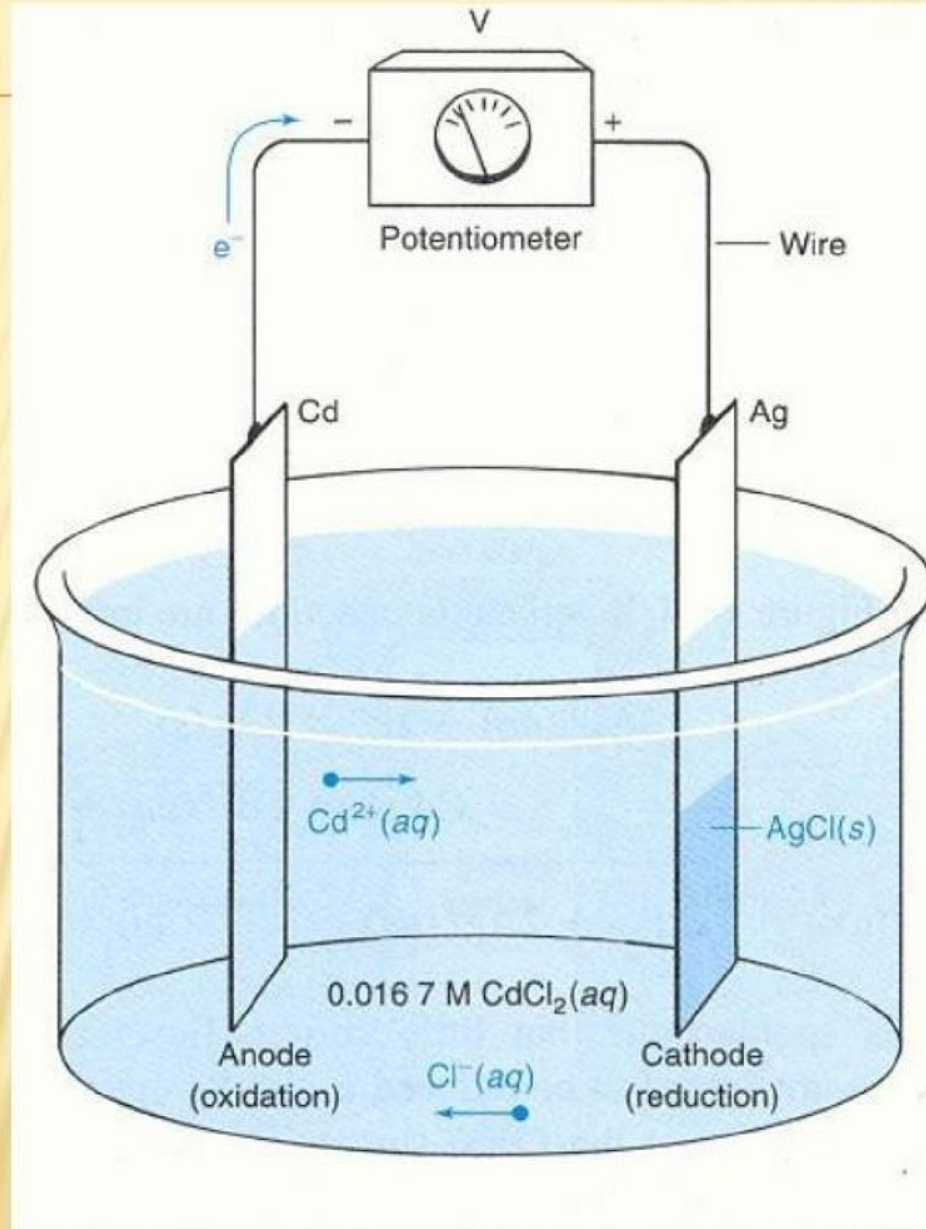
Types of Electroanalytical Procedures

- Based on relationship between analyte concentration and electrical quantities such as current, potential, resistance (or conductance), capacitance, or charge.

- Electrical measurement serves to establish end-point of titration of analyte.

- Electrical current converts analyte to form that can be measured gravimetrically or volumetrically.

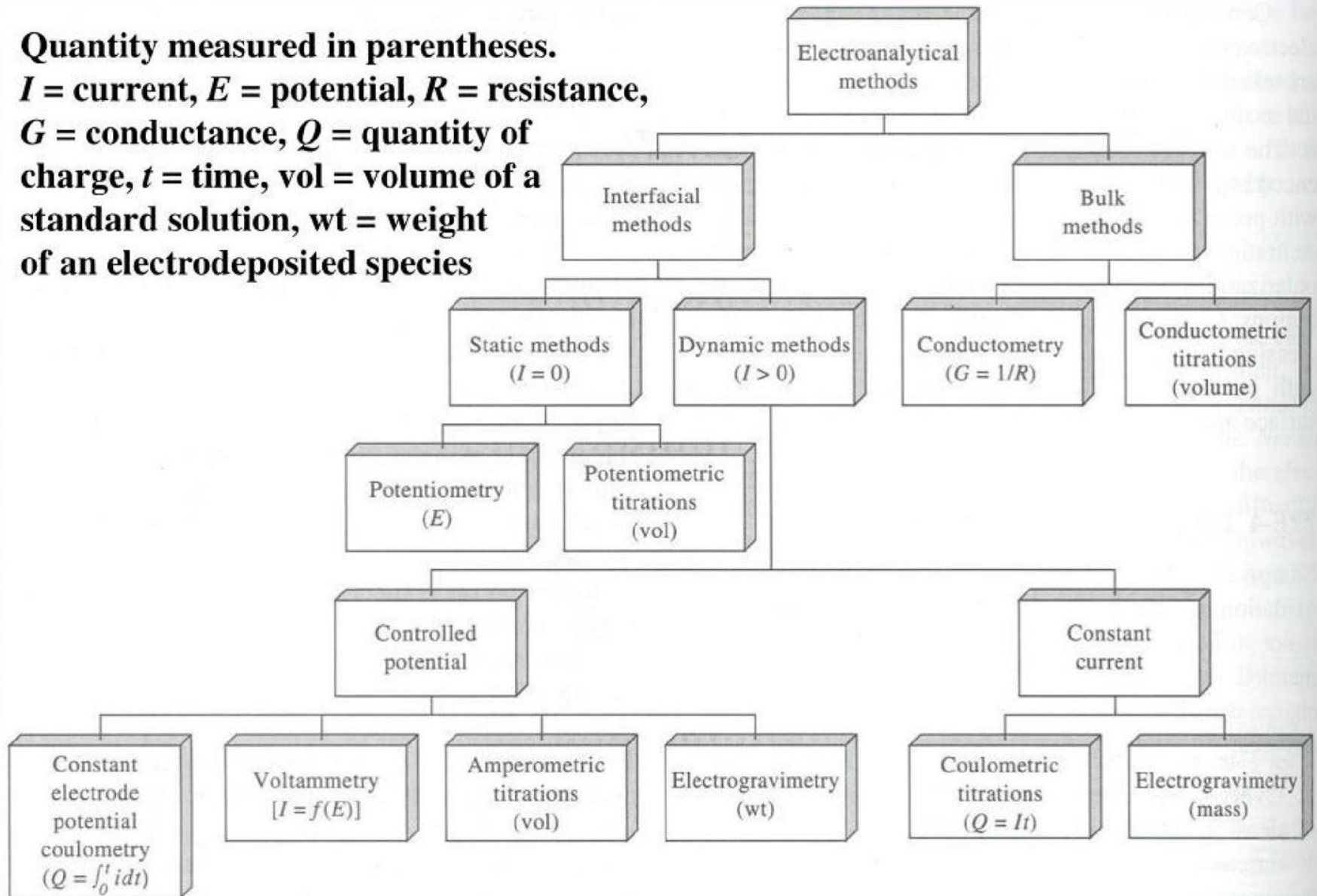| METHOD	MEASUREMENT	PRINCIPLE APPLICATIONS	QUALIT-ATIVE INFORM-ATION	DESIRED MINIMUM SAMPLE SIZE	DETECTION LIMIT	COMMENTS
Voltammetry (Polarography) (amperometric titrations) (chronoamperometry)	Current as a function of voltage at a polarized electrode	Quantitative analysis of electrochemically reducible organic or inorganic material	Reversibility of reaction	100 μg	10^{-1}-10^{-3} ppm 10 μg	A large number of voltage programs may be used. Pulse Polarography and Differential Pulse Polarography improve detection limits.
Potentiometry (potentiometric titration) (chronopotentiometry)	Potential at 0 current	Quantitative analysis of ions in solutions, pH.	Defined by electrode (*e.g.*, F^-, Cl^-, Ca^{2+})	100 μg	10^{-2} -10^2 ppm	Measures activity rather than concentration.
Conductimetry (conductometric titrations)	Resistance or conductance at inert electrodes	Quantification of an ionized species, titrations	Little qualitative identification information	100 μg		Commonly used as a detector for ion chromatography.
Coulometry	Current and time as number of Faradays	Exhaustive electrolysis	Little qualitative identification information	100 μg	10^{-9} -1 g	High precision possible.
Anodic Stripping Voltammetry (Electrodeposition)	Weight	Quantitative trace analysis of electrochemically reducible metals that form amalgams with mercury	Oxidation potential permits identification of metal.	100 μg	10^{-3} -10^3 g 10 ng	Electrodeposition step provides improved detection limits over normal voltammetry.

Summary of Common Electroanalytical Methods

Quantity measured in parentheses.
I = current, E = potential, R = resistance, G = conductance, Q = quantity of charge, t = time, vol = volume of a standard solution, wt = weight of an electrodeposited species

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                        Electroanalytical
                            methods
                    ┌───────────┴───────────┐
              Interfacial                  Bulk
               methods                    methods
         ┌────────┴────────┐        ┌───────┴────────┐
    Static methods   Dynamic methods  Conductometry   Conductometric
      (I = 0)          (I > 0)         (G = 1/R)        titrations
                                                         (volume)
   ┌──────┴──────┐
Potentiometry  Potentiometric
    (E)          titrations
                  (vol)
```

Controlled potential:

- Constant electrode potential coulometry $(Q = \int_0^t i\,dt)$
- Voltammetry $[I = f(E)]$
- Amperometric titrations (vol)
- Electrogravimetry (wt)

Constant current:

- Coulometric titrations $(Q = It)$
- Electrogravimetry (mass)

Fundamental Terminology

Faradaic Procsess

- Charge is transferred across the electrode solution interface. Redox process takes place

Non-Faradaic Process

- A transitory changes in current or potential as a result of changes in the structure of the electrode-solution interface e.g adsorption
- The electrode may be in a potential region that does not facilitate occurrence of a charge transfer reaction. The process is thermodynamically or kinetically unfavorable
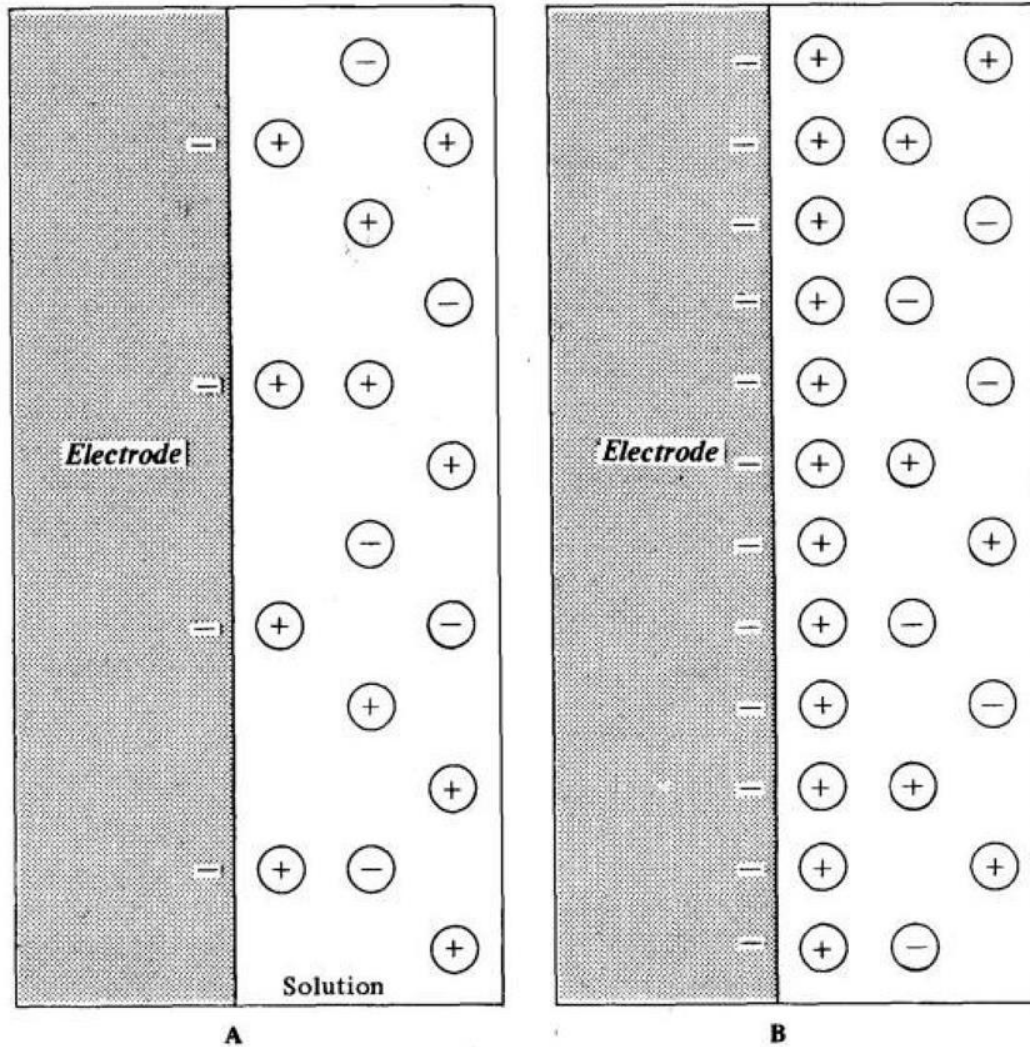
Charging Current

FIGURE 1.1. *Arrangement of charge at the electrode-solution interface. In case B, the electrode is at a more negative potential than in A; hence the greater amount of negative charge at the electrode surface in B.*

IDEALLY POLARIZED ELECTRODE

- Electrodes at which no charge transfer takes place. Only nonfaradaic process takes place regardless of the applied potential

- E.g. Hg electrode in contact of NaCl solution at pot. 0 to −2 V.

- Capacitance of the electrode, $C = q / V$

  q = charge in Coulombs

  V = voltage across the capacitor

- Current, i , ∝electrode capacity and resistance of solution

- With constant electrode area, i, dies within a fraction of second

- With DME, i, dies more slowly.

FARADAIC PROCESS

- When a substance is added to the electrolyte and it is oxidized or reduced at a particular potential the current flows and the electrode is depolarized, (Non-polarizable electrode). The substance is called "Depolarizer"

REVERSIBLE PROCESS

- When the Faradaic process is rapid, oxidized and reduced species will be in equilibrium and the Nernst equation is applicable. The process is then reversible. The elctrode is call reversible elctrode?
- Reversibility and irreversibility depends upon
  * Rate of electrode process
  * Rapidity of the electrochemical measurement

OVERPOTENTIAL OR OVERVOLTAGE

- When the electorde potential changes from its equilibrium value, the extra potential required to cause equilibrium reestablished is called overpotential
- If the electrode process is very fast overpotential is zero (Fast charge transfer, mass transport, and possibly adsorption or chemical reactions should be achieved). The electrode is then nonpolarizable electrode.
- When the system shows overpotential it is polarized
    * Activation polarization: Charge transfer is slow
    * Concentration polarization: movement of depolarizer or product is slow

AN INTERFACIAL PROCESS

- For: O + ne$^-$ = R

- 5 separate events must occur:

  - O must be successfully transported from bulk solution (mass transport)

  - O must be adsorbed *transiently* onto electrode surface (non-faradaic)

  - Charge transfer must occur between electrode and O (faradaic)

  - R must desorb from electrode surface (non-faradaic)

  - R must be transported away from electrode surface back into bulk solution (mass transport)

Modes of Electrochemical Mass Transport

- ## Three Modes:
  - ### Diffusion
  - ### Migration
  - ### Convection
    - #### Natural
    - #### Mechanical

Migration

- **Movement of a charged species due to a potential gradient**

- **Opposites attract**

- **Mechanism by which charge passes through electrolyte**

- **Base or Supporting electrolyte (KCl or HNO_3) is used to minimize (make it negligible) migration of electroactive species** *(makes it move under diffusion only)*

Convection

- Movement of mass due to a natural or mechanical force

- At long times (> 10 s), diffusing ions set up a natural eddy of matter

Diffusion

- Movement of mass due to a concentration gradient

- Occurs whenever there is chemical change at a surface, e.g., $O \rightarrow R$

- Diffusion is controlled by Cottrel equation

- $i_t = (nFAD^{1/2}C)/\pi^{1/2}t^{1/2}$

- $i_t =$ curent at time t; n= # electrons involved

  A = area of the elctroe; C=concentration of

  electroacrive species

THANK YOU