Electroanalytical Chemistry

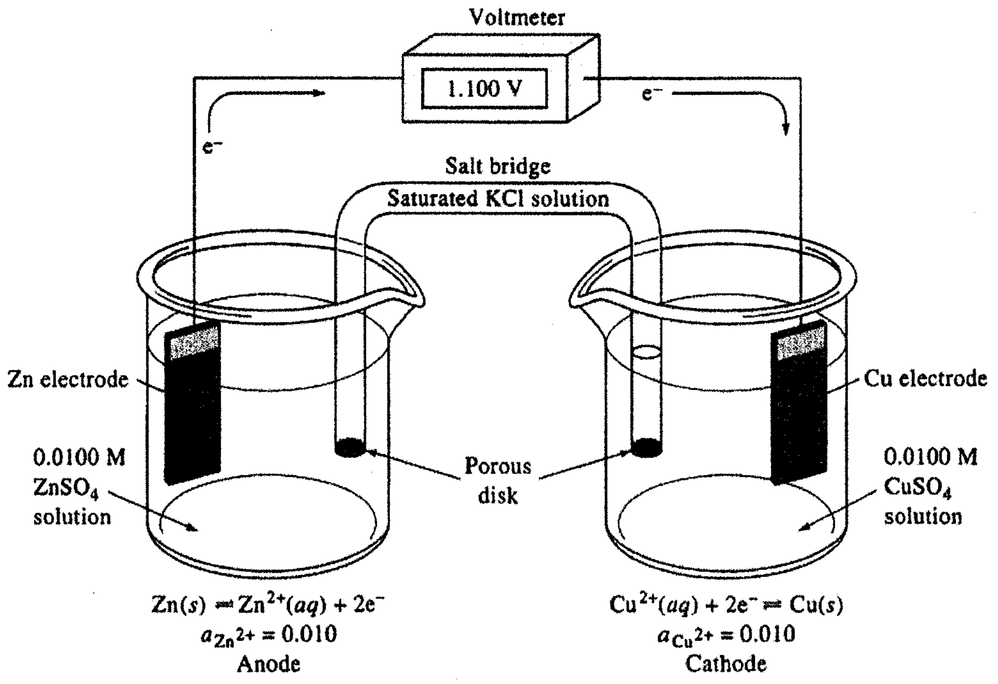
- Introduction to Electrochemistry
- Potentiometry
- Voltammetry

Introduction to Electrochemistry

Many different electroanalytical methods:

- fast
- inexpensive
- in situ
- information about
  - oxidation states
  - stoichiometry
  - rates
  - charge transfer
  - equilibrium constant

Electrochemical Cells



2 electrodes (immersed in suitable solution)

electrolyte (ions carry current)

external wires (electrons carry current)

interfaces or junctions

Electrode rxn→ heterogeneous process

transfer of electrons between electrode surface and molecules in solution *adjacent to the electrode surface*

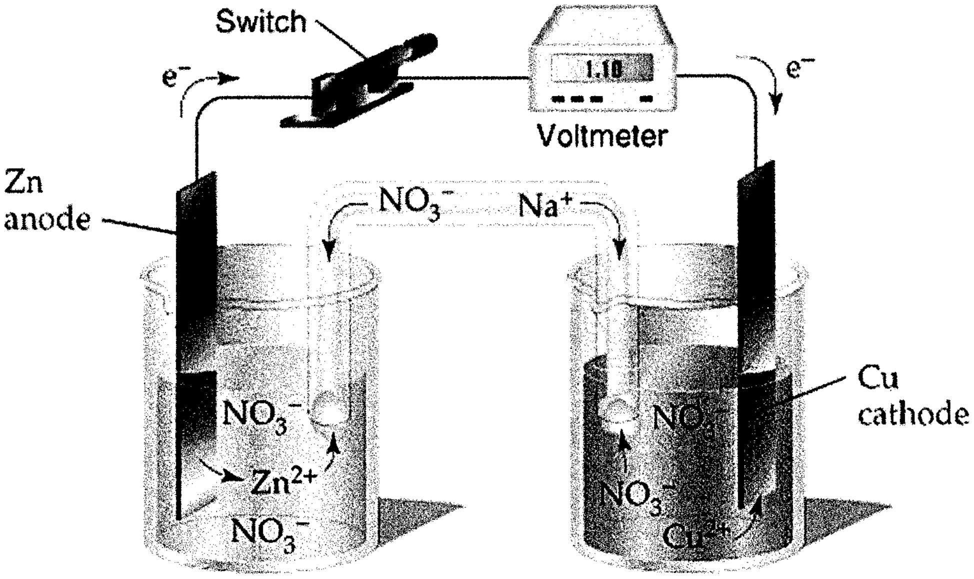
Electrochemical cell consists of two half-cells.

oxidation and reduction half-cell

salt bridge

- allows electrical contact based on ionic conductance
- prevents two solutions from mixing

Galvanic Cell



half rxn: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Movement of cations →

Movement of anions ←

2 electrodes → anode and cathode

Electrolytic Cell

require potential difference greater than galvanic potential difference

Oxidation: $Zn(s) \rightarrow Zn^{2+} + 2e-$

Reduction: $Cu^{2+} + 2e- \rightarrow Cu(s)$

} Galvanic cell

Oxidation: $Cu(s) \rightarrow Cu^{2+} + 2e-$

Reduction: $Zn^{2+} + 2e- \rightarrow Zn(s)$

} Electrolytic cell

Cell Diagram

anode || cathode

| phase boundary

|| salt bridge

Zn (s) | $ZnSO_4$ (0.01 M) || $CuSO_4$ (0.01 M) | Cu (s)

Cell Potential

potential difference between anode and cathode potential

$$E_{cell} = E_{cathode} - E_{anode} \qquad (1)$$

E_{cell}: cell potential

$E_{cathode}$: **reduction potential** of cathode

E_{anode}: **reduction potential** of anode

What is a potential of a half-cell (electrode potential) ?

Can't measure potential on each electrode independently- only differences.

How far is Bangkok ?

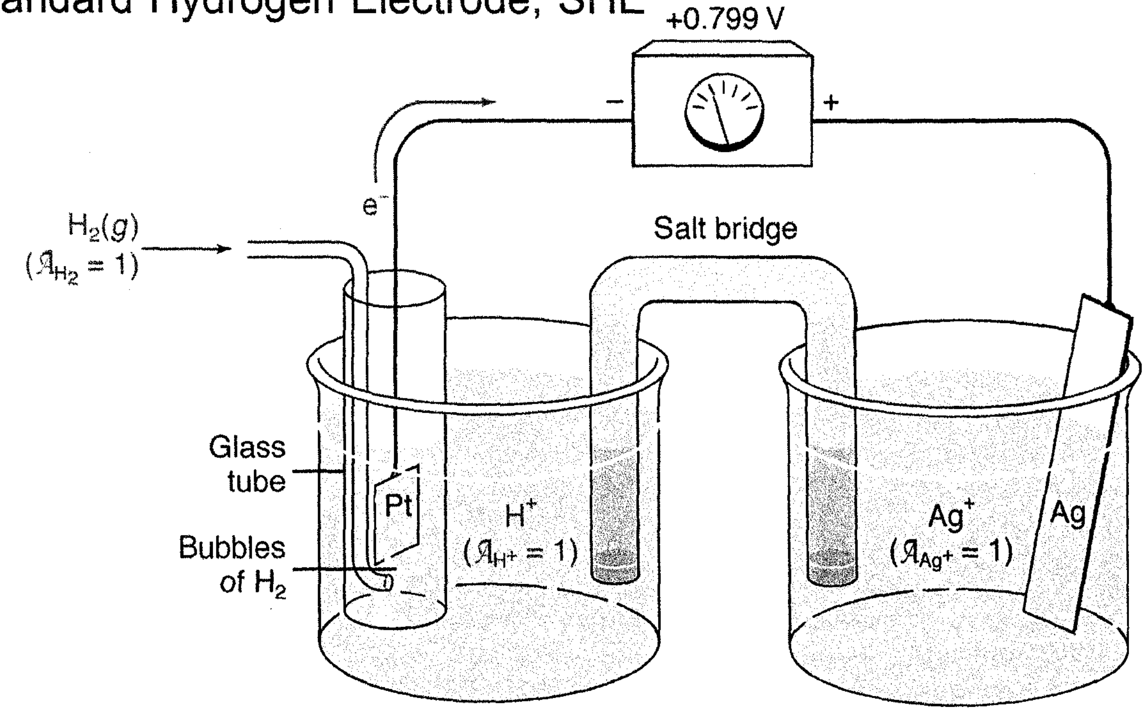
Measure a potential of half-cell of interest against a common reference electrode.

Standard Hydrogen Electrode, SHE

Reference Electrode

- stable
- easily reproducible half-cell potential
- reversible half-cell reaction
- chemical stability of its components
- ease of fabrication and use

Standard Hydrogen Electrode, SHE



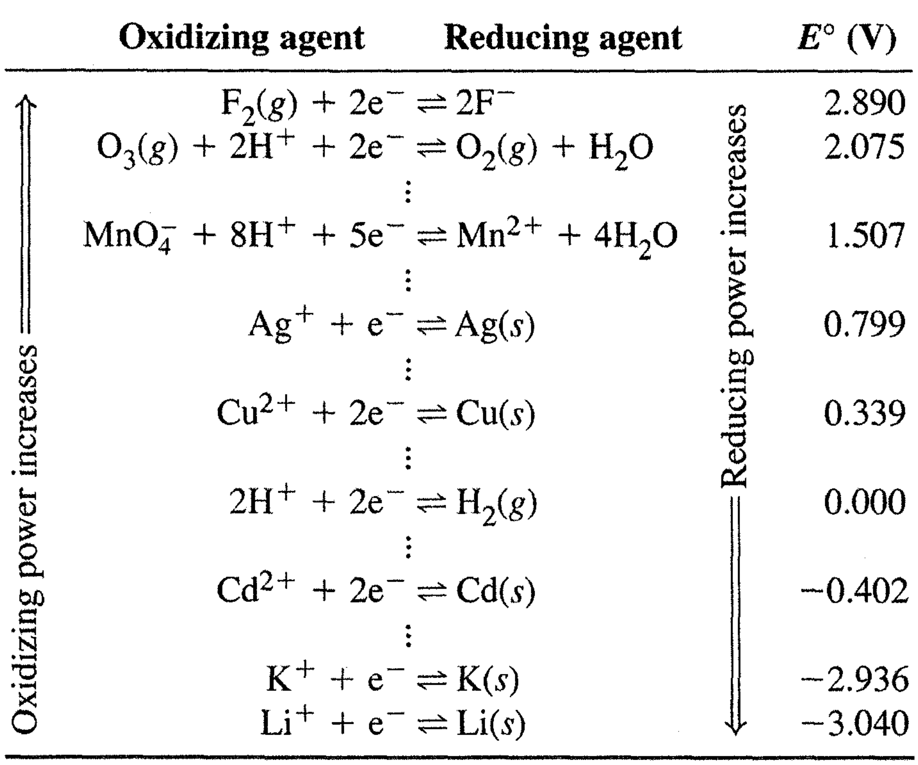
$$\underbrace{Pt(s)\,|\,H_2(g, \mathcal{A}=1)\,|\,H^+(aq, \mathcal{A}=1)}_{\text{Standard hydrogen electrode (S.H.E.)}}\,\|\,Ag^+(aq, \mathcal{A}=1)\,|\,Ag(s)$$

SHE:

- assign 0.000 V
- can be anode or cathode
- Pt does not take part in reaction
- Pt electrode coated with fine particles (Pt black) to provide large surface area
- cumbersome to operate

Alternative reference electrodes:

Ag/AgCl electrode Calomel electrode



Ordered redox potentials

Oxidizing agent		Reducing agent	$E°$ (V)
$F_2(g) + 2e^-$	$\rightleftharpoons$	$2F^-$	2.890
$O_3(g) + 2H^+ + 2e^-$	$\rightleftharpoons$	$O_2(g) + H_2O$	2.075
⋮			
$MnO_4^- + 8H^+ + 5e^-$	$\rightleftharpoons$	$Mn^{2+} + 4H_2O$	1.507
⋮			
$Ag^+ + e^-$	$\rightleftharpoons$	$Ag(s)$	0.799
⋮			
$Cu^{2+} + 2e^-$	$\rightleftharpoons$	$Cu(s)$	0.339
⋮			
$2H^+ + 2e^-$	$\rightleftharpoons$	$H_2(g)$	0.000
⋮			
$Cd^{2+} + 2e^-$	$\rightleftharpoons$	$Cd(s)$	−0.402
⋮			
$K^+ + e^-$	$\rightleftharpoons$	$K(s)$	−2.936
$Li^+ + e^-$	$\rightleftharpoons$	$Li(s)$	−3.040

Free Energy and Cell Potential

How do we know which way reaction will go spontaneously ?

$$\Delta G_{cell} = -nFE_{cell} \qquad (2)$$

At standard state

$$\Delta G°_{cell} = -nFE°_{cell} \qquad (3)$$

ปฏิกิริยา	E_{cell}	ΔG
เกิดเองได้	+	-
เกิดเองไม่ได้	-	+
สมดุล	0	0

aA + ne- <==> cC

bB <==> ne- + dD

Overall rxn: aA + bB <==> cC + dD

$$\Delta G_{cell} = \Delta G^{\circ}_{cell} + RT \ln \frac{a_C^{c}\, a_D^{d}}{a_A^{a}\, a_B^{b}} \qquad (4)$$

Substitution for ΔG_{cell} and $\Delta G^{\circ}{}_{cell}$ from equation (2) and (3) and division by -nF

Nernst Equation

$$E_{cell} = E^{o}_{cell} - \frac{RT}{nF} \ln \frac{a_C^{c}\, a_D^{d}}{a_A^{a}\, a_B^{b}} \qquad (5)$$

thermodynamic derivation

At 25°C

$$E_{cell} = E^{o}_{cell} - \frac{0.0591}{n} \log \frac{a_C^{c}\, a_D^{d}}{a_A^{a}\, a_B^{b}} \qquad (6)$$

Analytical chemists are more interested in measuring concentration than activity.

$$a = \gamma C$$

$$E_{cell} = E^{o}_{cell} - \frac{RT}{nF} \ln \frac{\gamma_C^{c}\, \gamma_D^{d}}{\gamma_A^{a}\, \gamma_B^{b}} - \frac{RT}{nF} \ln \frac{C_C^{c}\, C_D^{d}}{C_A^{a}\, C_B^{b}} \qquad (7)$$

$$E_{cell} = E^{o'}_{cell} - \frac{RT}{nF} \ln \frac{C_C^{c}\, C_D^{d}}{C_A^{a}\, C_B^{b}} \qquad (8)$$

↑

Formal cell potential

If a = 1.00 M, formal cell potential becomes standard cell potential.

Equilibrium Constant, K

Equilibrium, ΔG_{cell} = E_{cell} = substitution in equation (4)

$$0 = \Delta G^{\circ}_{cell} + RT \ln K$$

$$\ln K = \frac{nFE^{\circ}_{cell}}{RT} \qquad (9)$$

พิจารณา (5)

$$E_{cell} = E^{\circ}_{cell} - \frac{RT}{nF} \ln \underbrace{\frac{a_C^{c}\, a_D^{d}}{a_A^{a}\, a_B^{b}}}_{Q=\text{quotient}} \qquad (5)$$

Cell potential →measure of the tendency for the reaction to proceed from a non-equilibrium state to equilibrium state

Calculation of Cell Potential from Half-Cell Potentials

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

$$E_{cathode} = E^{o}_{A,C} - \frac{RT}{nF} \ln \frac{a_C^{c}}{a_A^{a}} \qquad (10)$$

$$E_{anode} = E^{o}_{D,B} - \frac{RT}{nF} \ln \frac{a_B^{b}}{a_D^{d}} \qquad (11)$$

- $E = E^{o}$ when quotient in Nersnt equation is unity
- E^{o} is relative to SHE
- E^{o} is measure of driving force for half-cell reduction

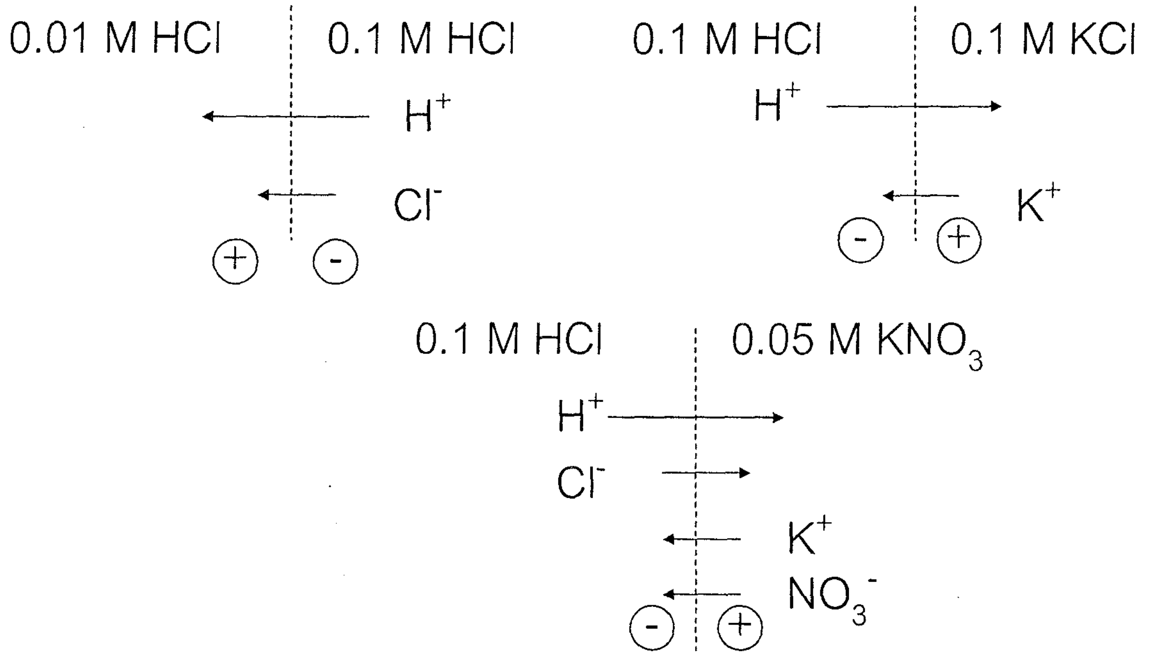
Limitations of Standard Electrode Potentials:

- E^{o} is temperature dependent.
- Substitution of concentration for activity always introduces error. Error is worse at high ionic strength.
- Formation of complexes, association, dissociation alter E^{o}.

Liquid Junction Potential, E_j

develops at the interface between two liquids

different rates of ions moving from one liquid to the other



0.01 M HCl

0.1 M HCl

H^+

Cl^-

⊕ ⊖

0.1 M HCl

0.1 M KCl

H^+

K^+

⊖ ⊕

0.1 M HCl

0.05 M KNO_3

H^+

Cl^-

K^+

NO_3^-

⊖ ⊕

$$E_{cell} = E_{cathode} - E_{anode} + E_j \qquad (12)$$

Ohmic Loss (IR drop)

electrolyte in the cell resisting the movement of ions necessary for electrolysis to occur

$$E_{cell} = E_{cathode} - E_{anode} + E_j - E_{iR} \qquad (13)$$

minimized by adding electrolyte to increase conductivity of the solution in the cell

What happens at electrode surface?

Electrode surface: transfer of electrons between electrode surface and molecules in solution *adjacent to the electrode surface* → ***heterogeneous*** process

useful to consider

quantities per unit area   quantities per total area

important quantities;

- current, i   proportional to electrode surface
- current density, j → current per unit area (A/cm^2)

independent of electrode surface

Current   Coulombs/second = Ampere

Faraday's Law

$$Q = nFN \quad (12)$$

Q: charge, coulomb

n: moles of electrons

N: moles of electrolyzed reactant

$$Q = \int_0^t i\,dt \quad (13)$$

1 C = 1.05 x 10^{-5} mole of e-

Differentiate (12) & (13),

$$i_f = \underbrace{\frac{dQ}{dt}}_{\text{electron transfer rate}} = nF\underbrace{\frac{dN}{dt}}_{\text{rxn rate}} \quad (14)$$

Faradaic current, i_f

rate of electrons moving across the electrode solution interface

i_f α rate of rxn at the interface

↓

measuring i = measuring the rate of chemical rxn

Many steps involving in one electrochemical rxn

- Electron transfer reaction
- Transport of molecules from bulk solution to the electrode surface
- Chemical reaction coupled to electron transfer rxn

Rate of overall rxn is determined by slowest step (rate-determining step)

It's important to know the rate-determining step.

What is the slowest step in analytical electrochemistry of dissolved species?

typically → the transport of molecules to the electrode surface, *but not always the case*

corrosion electrochemistry → rate of heterogeneous electron transfer rxn

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Kinetics of Electrode Reactions

reduction and oxidation at electrode surface
heterogeneous electron transfer rxn

Important characteristics

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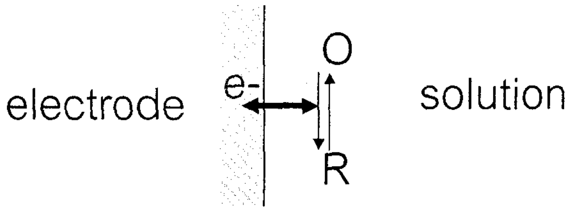
relationship between E and rate of electrode rxn (determines i)

Current and Heterogeneous Rate Constants



O and R must be at the electrode surface (1-2 °A) to participate in redox rxn.

O and R that are distant from the electrode must be transported to electrode surface.

Assumption: homogeneous C_R and C_O throughout the solution and not altered by the reaction at the electrode

$$\mathrm{O} + n\mathrm{e}^- \overset{k_f}{\underset{k_b}{<==>}} \mathrm{R}$$

reduction of O to R depends on heterogeneous forward rate constant, k_f

$$\text{rate of forward rxn} = \nu_f = k_f C_O^s \qquad (15)$$

C^s_O: surface concentration of O

oxidation of R to O depends on heterogeneous backward rate constant, k_b

$$\text{rate of backward rxn} = \nu_b = k_b C_R^s \qquad (16)$$

C^s_R: surface concentration of R

If $\nu_f > \nu_b$

$$\text{rate of formation of R} = \text{rate of loss of O} = \nu_f - \nu_b \qquad (17)$$

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which can be expressed as

$$\frac{dN_R}{dt} = -\frac{dN_O}{dt} = k_f C_O^s - k_b C_R^s \qquad (18)$$

dN/dt: rate of conversion per unit area , mol $cm^{-2}s^{-1}$

C^s: solution concentration at electrode surface, mol cm^{-3}

k: heterogeneous rate constant, cm s^{-1}

Net conversion rate of O to R determines the measured current at the electrode.

$$i = nFA\frac{dN_R}{dt} = -nFA\frac{dN_O}{dt} \qquad (19)$$

A: electrode surface area, cm^2

combining (18) and (19)

$$i = nFA(k_f C_O^s - k_b C_R^s) \qquad (20)$$

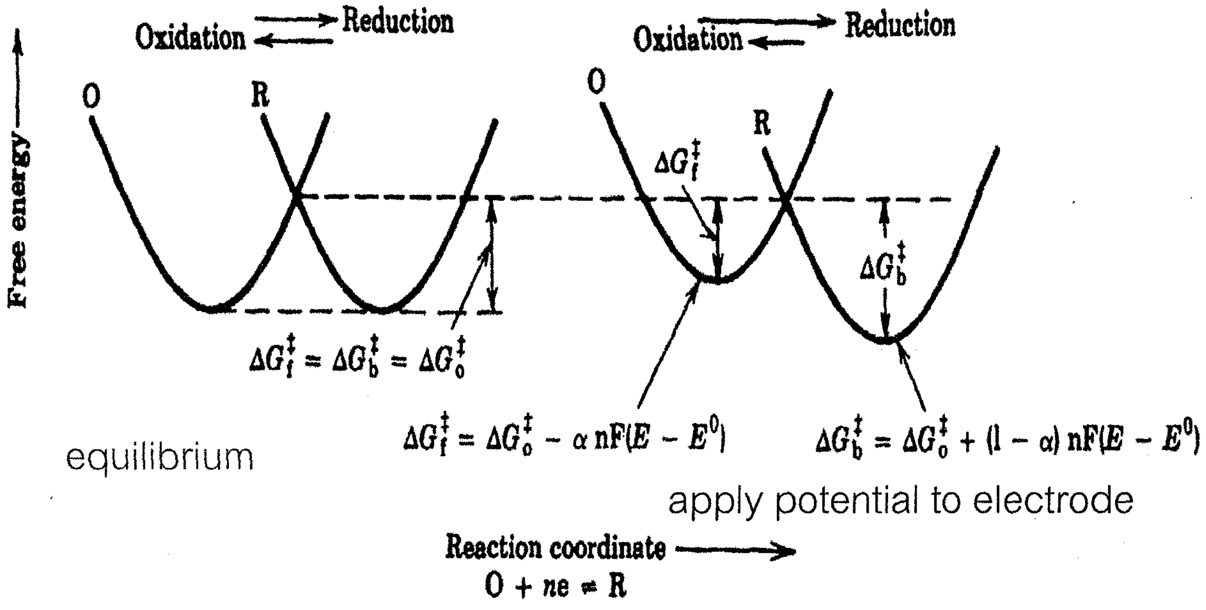
$$i = nFA(k_f C_O^s - k_b C_R^s) \qquad (20)$$

$k_f C_O^s = k_b C_R^s$ $\quad$ $i = 0$

$k_f C_O^s > k_b C_R^s$ $\quad$ $i =$ $\quad$ i_c: $\quad$ current

$k_f C_O^s < k_b C_R^s$ $\quad$ $i =$ $\quad$ i_a: $\quad$ current

Potential Dependence of Heterogeneous Rate Constants



equilibrium

apply potential to electrode

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at equilibrium

$$\Delta G_f^\ddagger = \Delta G_b^\ddagger = \Delta G_o^\ddagger \quad (23)$$

$G^\ddagger$: activation free-energy barrier

free energy required for convert mole of reactant to
the activated state in the reaction

same probability for electron transfer in forward and backward

$i_c + i_a = 0,\ i_c = -i_a = i_0$ No net current is observed.

i_0: exchange current

Rate of forward and backward rxn are determined by magnitude of energy barrier in proportion to exp($-\Delta G^{\ddagger}/RT$)

$$k \,\alpha\, \exp(-\Delta G^{\ddagger}/RT)$$

$$i_0 \,\alpha\, k$$

$$\Delta G^{\ddagger} \downarrow \quad i_0$$

Application of a potential to the electrode changes k.

negative potential k_f k_b positive potential k_f k_b

If move potential to a negative value of E^0

$\Delta G_f^{\ddagger}$ $\Delta G_b^{\ddagger}$

If a potential change is $E - E^0$

forward rection

$$\Delta G_f^{\ddagger} = \Delta G_o^{\ddagger} + \alpha nF(E - E^0) \quad (24)$$

backward reaction

$$\Delta G_b^{\ddagger} = \Delta G_o^{\ddagger} - (1 - \alpha)nF(E - E^0) \quad (25)$$

α: transfer coefficient — fraction of energy to increase energy barrier for *forward rxn*

typical:0.5-0.7

$1 - \alpha$ — fraction of energy to increase energy barrier for *backward rxn*

Effect of potential change on rate constant can be expressed as

$$k_f = k^0 \exp[-\alpha nF(E - E^0)/RT] \quad (26)$$

$$k_b = k^0 \exp[(1 - \alpha)nF(E - E^0)/RT] \quad (27)$$

k^0:standard rate constant

Current and Potential Relationship

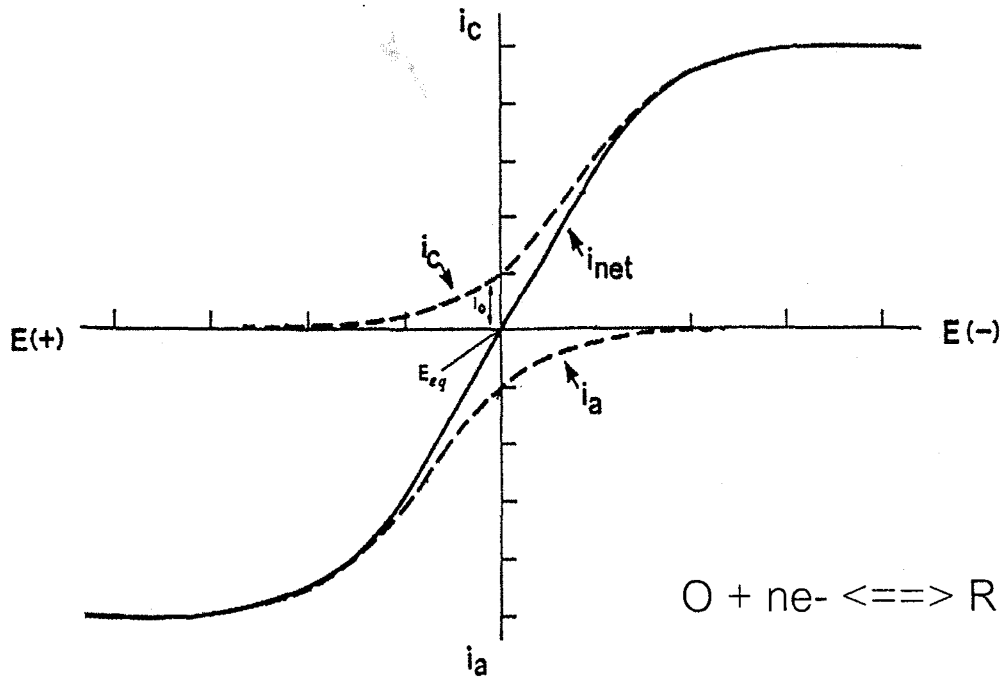
net current, $i = i_c + i_a$

$$\left.\begin{aligned} i_c &= nFAC_O^s k_f \quad (28) \\ i_a &= -nFAC_R^s k_b \quad (29) \end{aligned}\right\}$$

substitution of k_f and k_b from (26) and (27)

$$i_c = nFAC_O^s k^0 \exp[-\alpha nF(E - E^0)/RT] \quad (30)$$

$$i_a = -nFAC_R^s k^0 \exp[(1-\alpha)nF(E - E^0)/RT] \quad (31)$$



O + ne- <==> R

Rate of electron transfer is dominant, $C_O^s = C_R^s$, $\alpha = 0.5$

k^0 and i_0 a measure of ability of redox system to pass charges at the interface

fast rxn: k^0 1-50 cm s^{-1}

slow rxn: k^0 10^{-9} cm s^{-1}

Fast kinetic→ simple redox rxn

Slow kinetics→ multiple step rxn

At equilibrium, $i_c = -i_a$

$$nFAC_O^s k^0 \exp[-\alpha nF(E-E^0)/RT] =$$

$$nFAC_R^s k^0 \exp[(1-\alpha)nF(E-E^0)/RT]$$

$$\frac{C_R^s}{C_O^s} = -\exp[nF(E-E^0)/RT] \quad (32)$$

$$E = E^0 - \frac{RT}{nF}\ln\frac{C_R^s}{C_O^s} \quad (33)$$

kinetic-based derivation of Nernst Equation

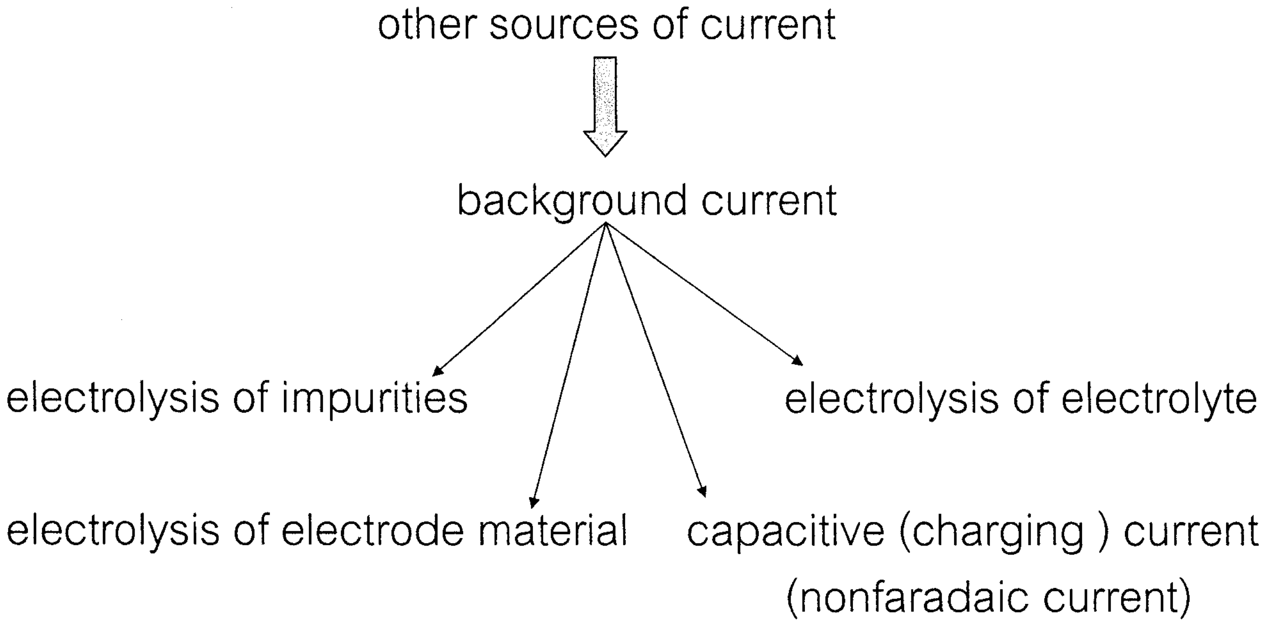
Factors affecting current;

- Electrode surface
- Reactant concentration
- Temperature
- Viscosity of the solution

Have to make sure these factors are constant, so

$i \ \alpha$ reactant concentration

important for quantitative analysis



other sources of current

background current

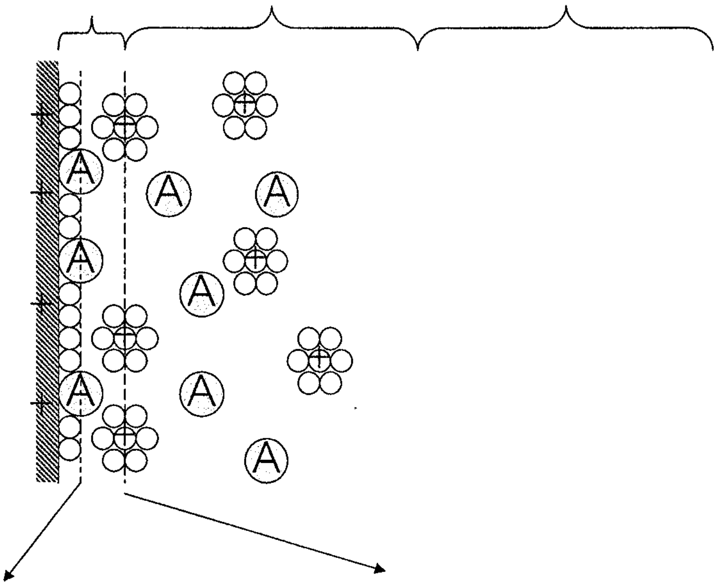
electrolysis of impurities

electrolysis of electrolyte

electrolysis of electrode material

capacitive (charging) current
(nonfaradaic current)

Electric Double Layer



diffuse layer
0.3 – 10 nm

compact layer

bulk solution

Inner Helmholtz Plane, IHP

Outer Helmholtz Plane, OHP

Capacitive current is a property of the interface between the electrode and the solution.

The interface behaves like an electrical capacitor (store charge).

$$Q = CV \quad (34)$$

Q: the charge stored

C: capacitance in farads

V: the potential difference across the interface

Capacitive current, i_c

$$i_C = \frac{dQ}{dt} = C\frac{dV}{dt} \qquad (35)$$

Total current→ faradaic current for analyte, electrolyte, and electrode material and capacitive current

Attention must be given to eliminate or minimizing background current.

Mass Transport (Mass Transfer)

Chemical species must be transported to the electrode surface to participate in electron transfer rxn.

Mechanism

1. Convection
2. Diffusion
3. migration

1. Convection

   - Hydrodynamic movement

     physical movement of the solution

     physical movement of electrode

2. Diffusion

   movement of chemical species due to their kinetic motion

- movement of molecules or ions from high concentration region to low concentration region (entropy of the system increases)
- random process

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3. Migration

movement of charged particles under influence of electric field

+ve charged electrode attracts –ve charge particles

-ve charged electrode attracts +ve charge particles

Migration is eliminated in some electroanalytical techniques.

addition of supporting electrolyte, such as KCl to increase dielectric constant of the medium→ decrease field strength near electrode surface

Flux (J)

A common measure of the rate of mass transport at a fixed point

net number of moles of solute species crossing a unit area of an imaginary plane per unit time

⇓

rate of transport of molecules from one side of the imaginary plane to the other

$\text{mol cm}^{-2}\ \text{s}^{-1}$

The flux to the electrode is described by Nenrst-Planck equation

$$J(x,t) = -D\frac{\partial C(x,t)}{\partial x} - \frac{zFDC}{RT}\frac{\partial \phi(x,t)}{\partial x} + C(x,t)V(x,t) \qquad (36)$$

D: diffusion coefficient $(\text{cm}^2\text{s}^{-1})$ 10^{-5}-10^{-6} cm^2s^{-1}

$\partial C(x,t)/\partial x$: concentration gradient

$\partial \phi(x,t)/\partial x$: potential gradient

z: charge of electroactive species

V (x, t): hydrodynamic velocity in x direction

Current is directly proportional to flux:

$$i = -nFAJ \qquad (37)$$

complex situation with the three modes of mass transport occurring simultaneously

difficult to relate current to

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suppress migration and convection

relationship of flux and slope of concentration-distance profile

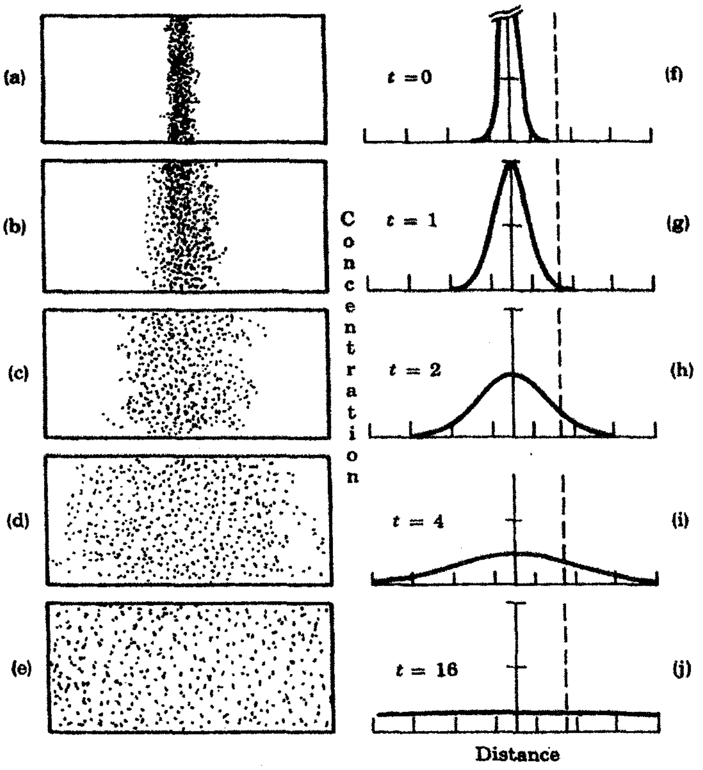
according to Fick's first law

$$J(x,t) = -D\frac{\partial C(x,t)}{\partial x} \qquad (38)$$

$J(x,t)$: flux, mol $cm^{-2} s^{-1}$

$\frac{\partial C(x,t)}{\partial x}$: concentration gradient at positon x and time t

concentration profile



Expressed as Gaussian function

$$C(x,t) = \frac{C_0}{\sqrt{4\pi Dt}} \exp\left(\frac{-x^2}{4Dt}\right) \qquad (39)$$

$C_{x,t}$: concentration of solute molecules at x and t , mol cm^{-3}

C_0 : initial concentration of solute molecules, mol cm^{-3}

x : distance from center of band of solute molecules, cm

t : time, s

D: diffusion coefficient, cm^2 s^{-1}

random movement of molecules with speed defined by D

Distribution width, σ

$$\sigma = \sqrt{2Dt} \qquad (40)$$

Equation (37) is useful for estimating the diffusion distance of molecules

1σ : 68.3% of population diffuse less than σ

2 σ: 95.5% of population diffuse less than 2σ

Consider slope of concentration-distance profile (see profile figure)

steeper slope → greater flux

zero slope → no net flux (f) & (j)

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combine (37) & (38)

$$i = nFAD\frac{\partial C(x,t)}{\partial x} \qquad (41)$$

current is proportional to

Diffusional flux is time dependent which is described by Fick's second law

$$\frac{\partial C(x,t)}{\partial t} = D\frac{\partial^2 C(x,t)}{\partial x^2} \qquad (42)$$

equation (42)

rate of concentration change with time between two parallel planes at point x and x + dx

Fick's second law is valid for two parallel planes that are perpendicular to the direction of diffusion.

In case of diffusion toward a spherical electrode

$$\frac{\partial C(x,t)}{\partial t} = D\left[\frac{\partial^2 C(x,t)}{\partial r^2} + \frac{2}{r}\frac{\partial C(x,t)}{\partial r}\right] \quad (43)$$

r: distance from center of the electrode

Potential Step Experiment Under Diffusion Control

O + ne- <==> R

boundary conditions:

$$C_O(x,0) = C_O(b)$$

$$\lim_{x\to\infty} C_O(x,t) = C_O(b)$$

$$C_O(0,t) = 0\,,\, t > 0$$

Solution to Fick's law

$$C_O(x,t) = C_O(b)\left\{1 - \mathrm{erfc}\left[\frac{x}{(4D_O t)^{1/2}}\right]\right\} \quad (44)$$

$$\Big\downarrow$$

$$\frac{\partial C(x,t)}{\partial t} = \frac{C_O(b)}{(\pi D_O t)^{1/2}} \quad (45)$$

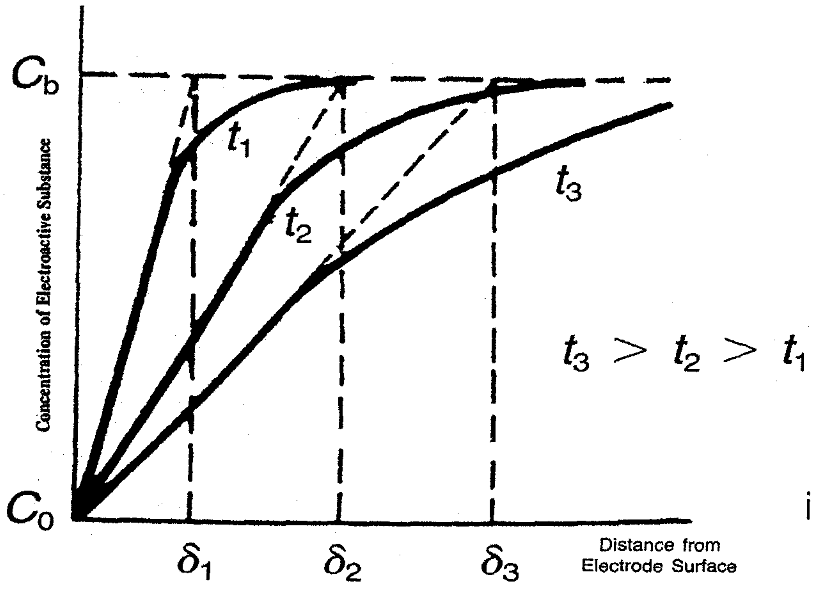
$C_O(b)$: bulk concentration of species o substitute (45) into (41)

$$i(t) = \frac{nFAD_O C_O(b)}{(\pi D_O t)^{1/2}} \qquad (46)$$

Cottrell equation

Current decreases proportional to $1/(t)^{1/2}$

$(\pi D_o t)^{1/2}$ diffusion layer thickness



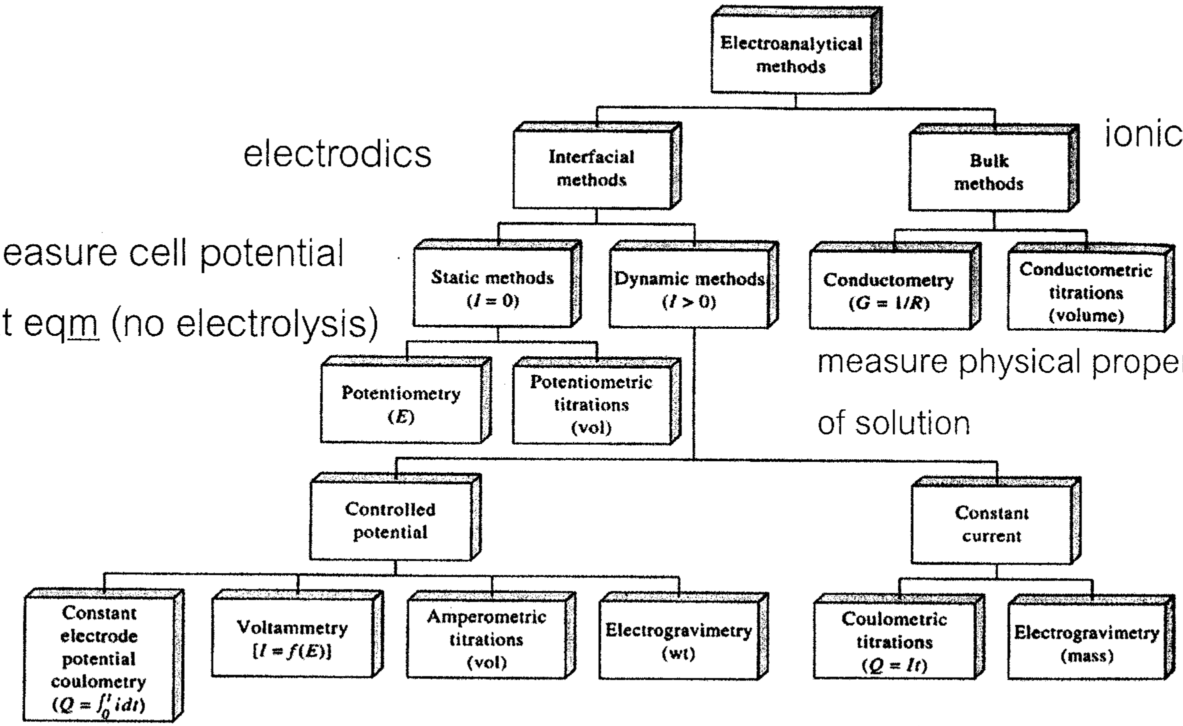
$$i(t) = \frac{nFAD_O C_O(b)}{(\pi D_O t)^{1/2}} \qquad (46)$$

δ:thickness of diffuse layer

C_O: surface concentration

C_b: bulk concentration

longer time, i decreases



electrodics

ionics

measure cell potential

at eq<u>m</u> (no electrolysis)

measure physical properties

of solution

measure charge required to

complete electrolysis

Potentiometry

Measurement of difference of potential between two electrodes.

indicator electrode

reference electrode

galvanic cell under condition of zero current

$$E_{cell} = E_{cathode} - E_{anode} \qquad (1)$$

$$E_{cell} = E^{o'}_{cell} - \frac{RT}{nF} \ln \frac{C_C^c \, C_D^d}{C_A^a \, C_B^b} \qquad (2)$$

aA + ne <==> bB

at 25 °C

$$E = E^{0'} - \frac{0.0591}{n} \log \frac{C_B^b}{C_A^a} \qquad (3)$$

In a one-electron half reaction, a change in concentration by 10 folds results in a voltage change of 59 mV.

Measuring instrumentation must be very sensitive.

Temperature is also an important factor that affects the potential response.

Indicator electrodes

Redox Electrode

respond to redox potential of a solution consisting of redox couple

Pt, Au, Pd

Potential response of the electrode may not correspond to the predicted value if the electron-transfer process is not reversible.

Electrode of the First Kind

Consist of a metal immersed in a solution containing its metal.

$$M^{n+} + ne <==> M(s)$$

$$E_{ind} = E^0 - \frac{RT}{nF} \ln \frac{1}{a_{M^{n+}}} \quad (4)$$

Examples; Ag/Ag^+, Cu/Cu^{2+}

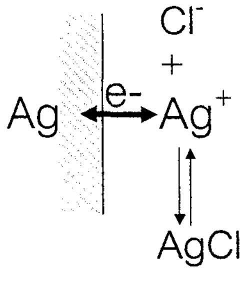
Electrodes of this type should be used in suitable conditions.

Acidic and air-saturated solution can be a problem.

Electrode of the Second Kind

Consist of a metal in contact with a solution saturated with a slightly soluble salt of the metal. The salt can also be coated on the metal.

Example: Ag/AgCl



$$AgCl + e <==> Ag + Cl^-$$

$$E_{ind} = E^0_{Ag^+,Ag} - \frac{RT}{F} \ln \frac{1}{a_{Ag^+}} \quad (5)$$

$$K_{sp} = (a_{Ag+})(a_{Cl-}) \quad (6)$$

$$E_{ind} = E^0_{Ag^+,Ag} - \frac{RT}{F} \ln \frac{a_{Cl^-}}{K_{sp}} \quad (7)$$

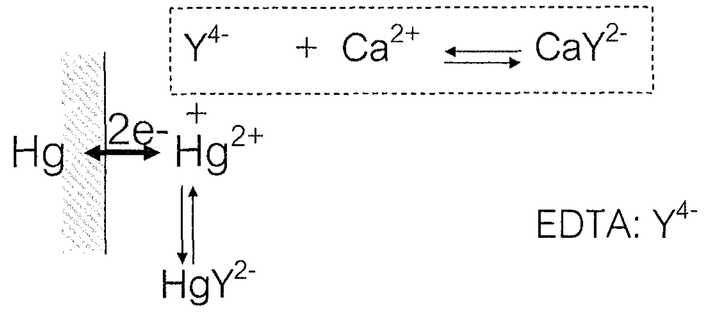
$$E_{ind} = E^0_{Ag,AgCl} - \frac{RT}{F} \ln a_{Cl^-} \quad (8)$$

(7) = (8)

Electrode of the Third Kind

Consist of metal in contact with a slightly soluble salt of the metal. The anion of the salt also involves in a reaction with another metal ion (analyte) that can form a more soluble salt.

Example: Hg/Hg^{2+}-EDTA



$Y^{4-} + Ca^{2+} \rightleftharpoons CaY^{2-}$

+

Hg $\xleftrightarrow{2e-}$ Hg^{2+}

HgY^{2-}

EDTA: Y^{4-}

$$E_{ind} = E^0_{Hg^{2+},Hg} - \frac{RT}{2F}\ln\frac{1}{a_{Hg^{2+}}} \qquad (9)$$

Mercury-EDTA reaction

$$Y^{4-} + Hg^{2+} <==> HgY^{2-}$$

$$K_{HgY^{2-}} = \frac{a_{HgY^{2-}}}{(a_{Y^{4-}})(a_{Hg^{2+}})} \qquad (10)$$

$$\underbrace{E_{ind} = E^0_{Hg^{2+},Hg} - \frac{RT}{2F}\ln K_{HgY^{2-}}} - \frac{RT}{2F}\ln\frac{1}{a_{HgY^{2-}}} - \frac{RT}{2F}\ln a_{Y^{4-}} \qquad (11)$$

$$\downarrow$$

$$E_{ind} = E^0_{HgY^{2-},Hg} - \frac{RT}{2F}\ln\frac{1}{a_{HgY^{2-}}} - \frac{RT}{2F}\ln a_{Y^{4-}} \qquad (12)$$

Calcium-EDTA reaction

$$Y^{4-} + Ca^{2+} <==> CaY^{2-}$$

$$K_{CaY^{2-}} = \frac{a_{CaY^{2-}}}{(a_{Y^{4-}})(a_{Ca^{2+}})} \qquad (13)$$

substitute a_{Y4-} from (13) into (12)

$$E_{ind} = E^{0}_{HgY^{2-},Hg} - \frac{RT}{2F} \ln \frac{a_{CaY^{2-}}}{a_{HgY^{2-}} K_{CaY^{2-}}} + \frac{RT}{2F} \ln a_{Ca^{2+}} \qquad (14)$$

when $\frac{a_{CaY^{2-}}}{(a_{HgY^{2-}})}$ ~constant $\qquad E_{ind} \cong K + \frac{RT}{2F} \ln a_{Ca^{2+}} \qquad (15)$

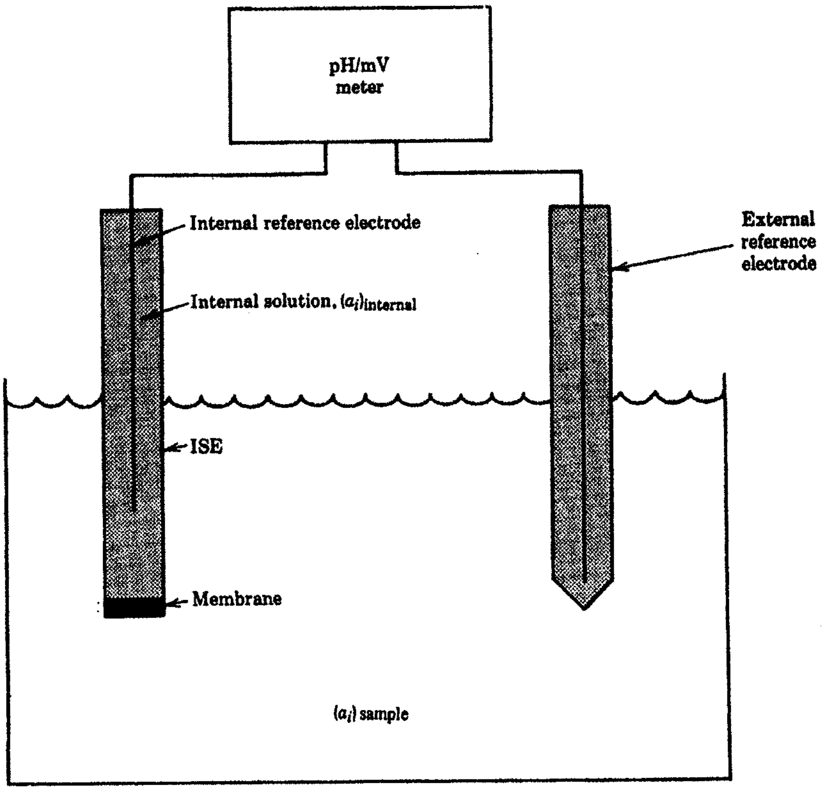
Ion-Selective Electrode (ISE)

Membrane based-device consists of permselective ion-conducting materials.

nonporous

water insoluble

mechanically stable



$$E_{cell} = E_{ref,ext} - E_{ref,int} + E_{memb} + E_j \qquad (16)$$

Potential develops across membrane;

$$E_{memb} = \frac{RT}{zF} \ln \frac{(a_i)_{sample}}{(a_i)_{internal}} \qquad (17)$$

z: ionic charge

substitute (17) into (16),

$$E_{cell} = E_{ref,ext} - E_{ref,int} + \frac{RT}{zF} \ln \frac{1}{(a_i)_{internal}} + \frac{RT}{zF} \ln(a_i)_{sample} + E_j \qquad (18)$$

$$E_{cell} = K + \frac{RT}{zF} \ln(a_i)_{sample} \qquad (19)$$

Membrane responds to ions other than analyte

Nikolskii-Eisenman equation;

$$E_{cell} = K + \frac{RT}{zF} \ln(a_i + k_{ij} a_j^{z_i/z_j}) \qquad (20)$$

k_{ij}: selectivity coefficient

a_i: activity of analyte

a_j: activity of interferent ion

k_{ij} is a characteristic of the electrode.

$k_{ij} = 1$ electrode responds to ion i and j equally

$k_{ij} > 1$ electrode responds more to ion j than i

ISE senses the activity not concentration of ions in solution.

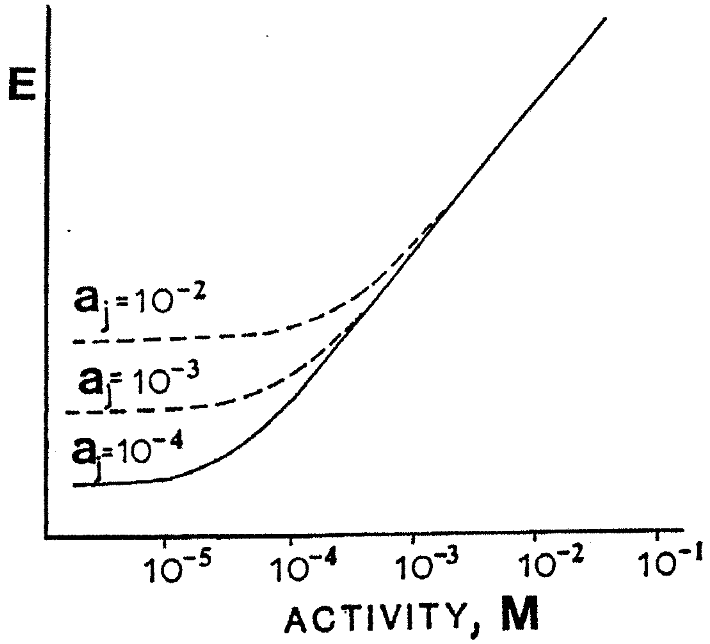
Practical approach to convert potentiometric from activity to concentration is to construct a calibration curve.

$$E_{cell} = K + \frac{RT}{zF} \ln(\gamma_i C_i) \qquad (21)$$

$$E_{cell} = K' + \frac{RT}{zF} \ln C_i \qquad (22)$$

Since ionic strength of the sample solution is usually not known, so electrolyte is added to both the sample and the standard solution, so K' is about constant either at high or low analyte concentration.

Ionic strength affects γ.



Nonlinearity at low analyte concentration due to the presence of other ions.

Most commonly used calibration technique is standard addition.

ISE

- glass
- liquid (solid matrix)
- solid

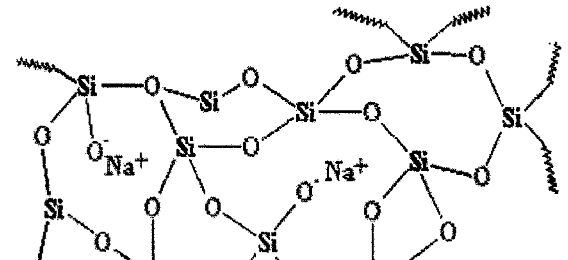
Glass Electrode

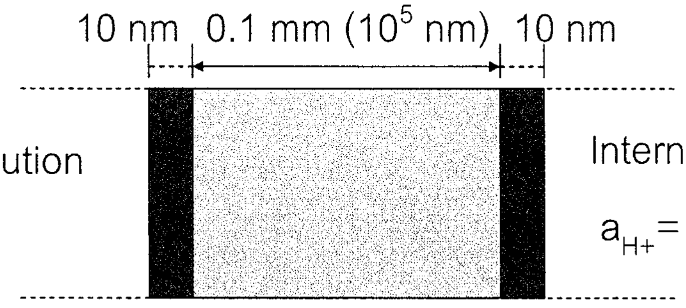
respond to univalent cations

selectivity achieved by varying the composition of the membrane

---

pH electrode





10 nm 0.1 mm (10^5 nm) 10 nm

Sample solution

Internal solution

a_{H+} = 0.1 M

hydrated gel layer

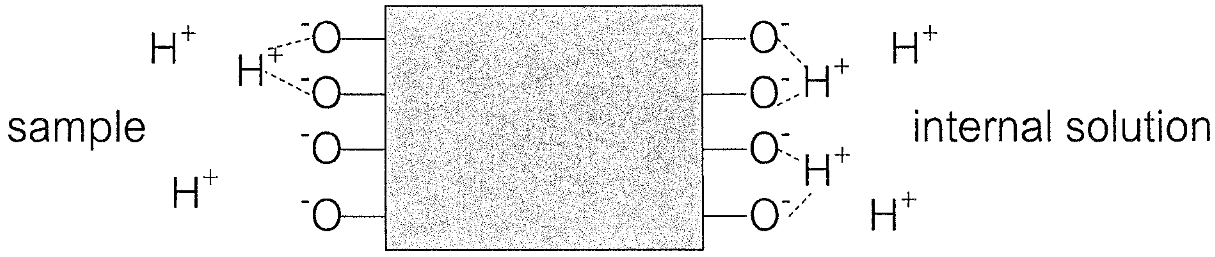
dry glass layer

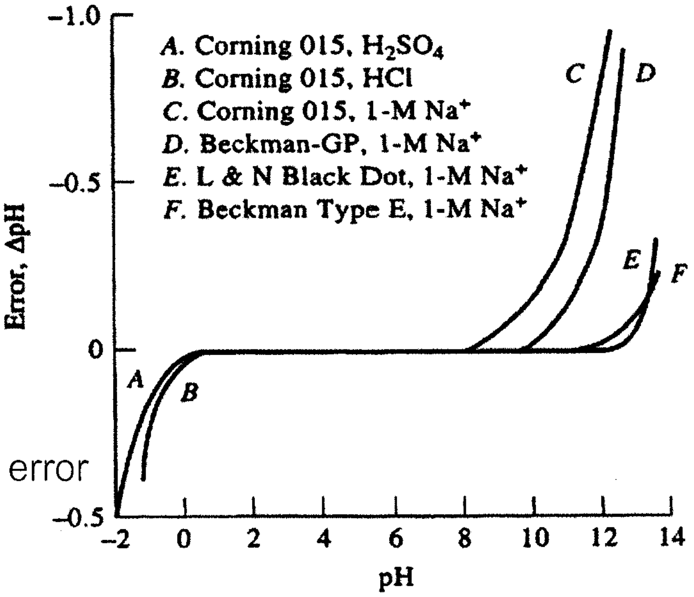
hydrated gel layer

ion-exchange reaction

$$H^+ + NaGl <==> Na^+ + HGl$$

solution glass solution glass





Alkaline error

solution with low H^+

high Na^+

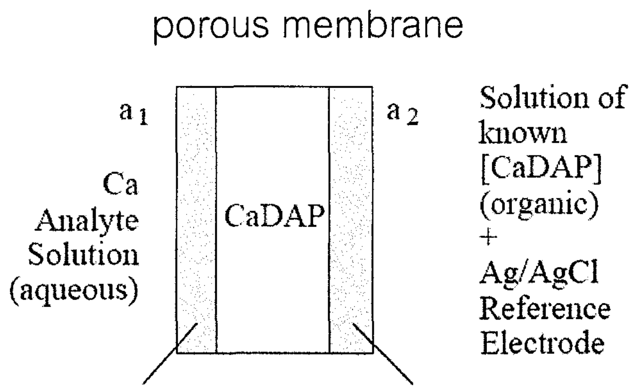
Acid error

$$E_{cell} = K + \frac{RT}{F}\ln(a_{H^+} + k_{H^+,Na^+}a_{Na^+})$$

Liquid Membrane Electrode

Based on immiscible liquid impregnated in a polymeric membrane.

example



$$Ca^{2+} + \underbrace{2(RO)_2PO_2^-}_{\text{dialkyl phosphate}} \leftrightarrow [(RO)_2PO_2]_2Ca$$

Controlled-Potential Techniques

Measurement of current response to an applied potential

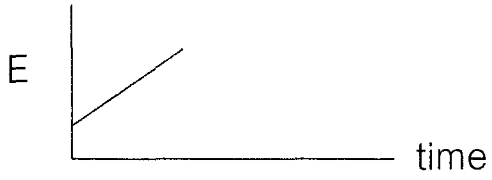
Voltammetry

Polarography

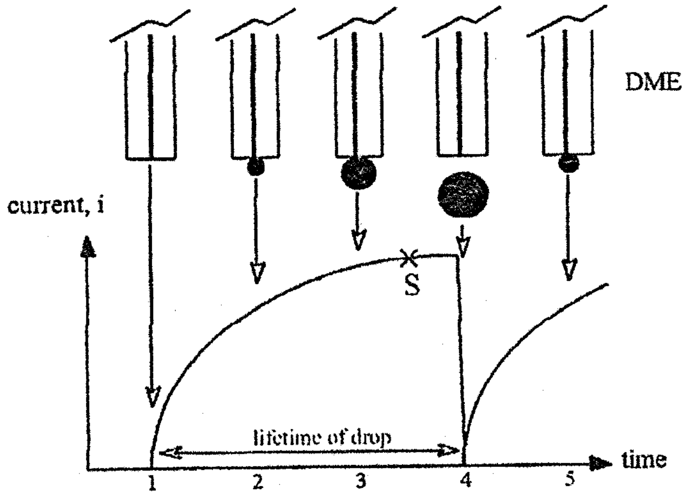
Subclass of voltammetry

Dropping mercury electrode (DME) is used as working electrode

Potential excitation signal→ linear sweep



Dropping Mercury Electrode, DME



very reproducible dropping action

continuously renewed surface → no permanently modified electrode by electrode reaction

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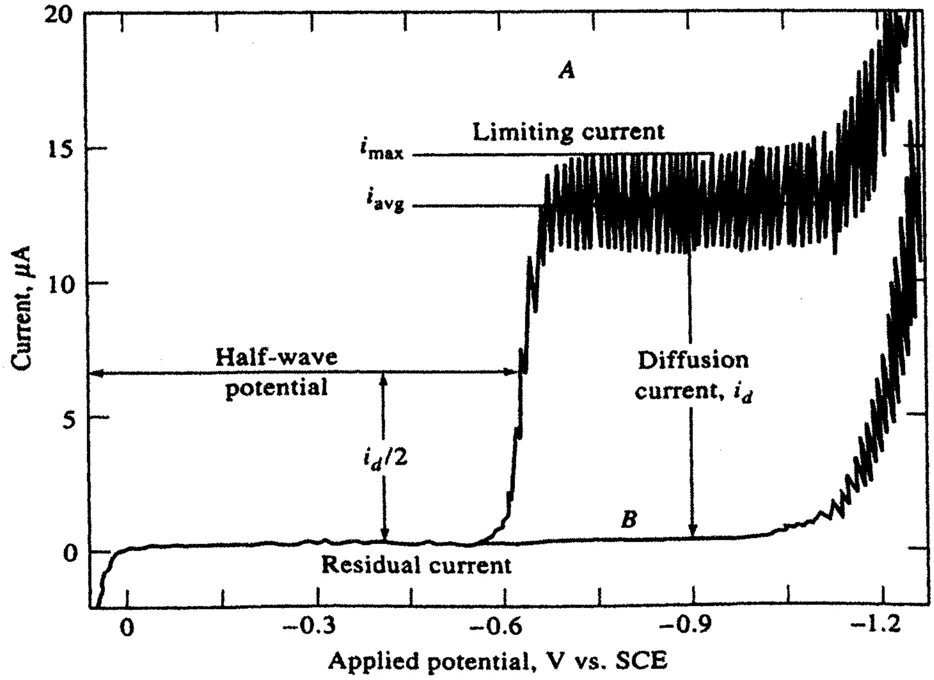


A: 1 M HCl

current oscillation

B: 4 x 10^{-4} M Cd^{2+} in 1 M HCl

From Cottrell equation

$$i(t) = \frac{nFAD_0C_0(b)}{(\pi D_0 t)^{1/2}} \qquad (46)$$

to derive current-diffusion equation for DME, appropriate area of the electrode is needed

$$V = \frac{4}{3}\pi r^3 = \frac{mt}{d} \qquad (47)$$

r: radius of the mercury drop

m: mass flow rate of the mercury

t: life time of the drop

d: density if the mercury

$$A = 4\pi\left(\frac{3mt}{4\pi d}\right)^{2/3} = 0.85(mt)^{2/3} \qquad (48)$$

substitute (48) into (46) and account for the growth of the mercury drop

$$i_d = 708nD^{1/2}m^{2/3}t^{1/6}C \qquad (49)$$ **Ilkovic equation**

i: μA, D: cm^2s^{-1}, m: mg s^{-1}, t: s, C: mmol L^{-1}

This is the current at the end of the drop life.

$$i_{aver} = 607nD^{1/2}m^{2/3}t^{1/6}C \qquad (50)$$

To obtain i_d from a polarogram, one must subtract residual current from maximum current, i_{max}

Residual current is measured from a blank solution.

Current-Potential Relations

From Nernst equation

$$E = E^{0'} - \frac{RT}{nF} \ln \frac{C_R^s}{C_O^s}$$

To relate E and i, need concentration and i relationship

consider, O+ ne <==> R

and $$i_d = 708nD^{1/2}m^{2/3}t^{1/6}C \qquad (49)$$

Initially only O is present in the solution. When a potential is applied and reductive current flows, O diffuses towards the electrode.

$$i = 708\left(C_O(b) - C_O^s\right)nD^{1/2}m^{2/3}t^{1/6}$$

$$= i_d - 708C_O^s nD^{1/2}m^{2/3}t^{1/6}$$

$$C_O^s = \frac{i_d - i}{708nD_O^{1/2}m^{2/3}t^{1/6}} \qquad (50)$$

After O is reduced, R diffuses either into the bulk solution or into the mercury to form an amalgam.

$$i = 708\left(C_R^s - C_R(b)\right)nD^{1/2}m^{2/3}t^{1/6}$$

$C_R(b) = 0$

$$C_R^s = \frac{i}{708nD_R^{1/2}m^{2/3}t^{1/6}} \qquad (51)$$

Substitute (50) and (51) into Nernst equation

$$\underbrace{E = E^{0'} + \frac{RT}{nF}\ln\left(\frac{D_R}{D_O}\right)^{1/2}} + \frac{RT}{nF}\ln\frac{i_d - i}{i} \qquad (52)$$

half-wave potential, $E_{1/2}$ when $i = i_d/2$

when $D_R \approx D_O, E = E^{0'}$

Half-wave potential is a characteristic of a particular species in a given medium.

It can be used to identify chemical species responsible for polarographic wave.

For reduction of metal complex

ML_p + ne- + Hg <==> M(Hg) + pL

MLp: metal complex (neglect the charge)

L: ligand

P: stoichiometric number

$E_{1/2}$ is shifted to more negative potential → more energy is required for complex decomposition.

$$(E_{1/2})_c - (E_{1/2})_{free} = \frac{RT}{nF}\ln K_d - \frac{RT}{nF}p\ln[L] + \frac{RT}{nF}\ln\left[\frac{D_{free}}{D_c}\right]^{1/2} \qquad (53)$$

complex uncomplex

dissociation constant (formation constant)

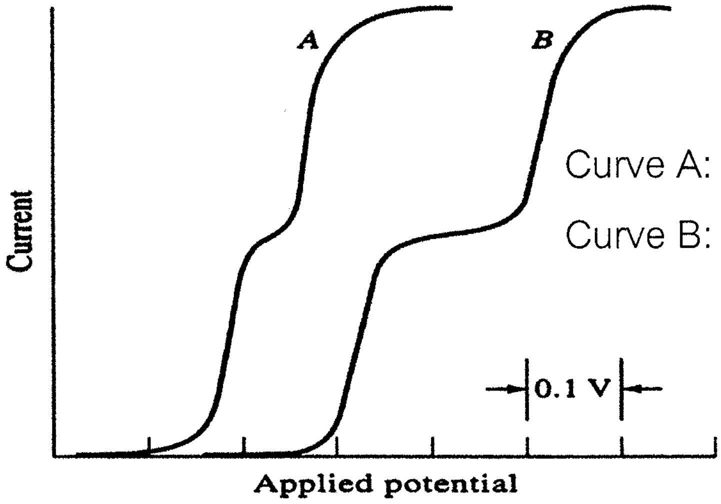
A lot of organic compounds reduced at DME do not behave reversibly.

For irreversible reduction process

$$E = E^{0'} + \frac{RT}{\alpha nF}\ln\left[1.35k_f^0\left(\frac{i_d - i}{i}\right)\left(\frac{t}{D}\right)^{1/2}\right] \qquad (54)$$

k_f^0 : rate constant of forward reaction at $E = 0$ V

Mixtures of Reactants



Curve A: difference in voltage is 0.1 V

Curve B: difference in voltage is 0.2 V

A reasonable difference of the half-wave potential should be > 0.2 V.

Single analyte undergone reduction in two or more steps also gives successive waves.   example 1, 4-bezodiazepine, tetracycline

Background (residual) current

- redox reaction of impurities

evolution of H_2 and mercury oxidation

↓

limit the working potential range

- charging current

insignificant in the analyte concentration range of 10^{-4}-10^{-2} M

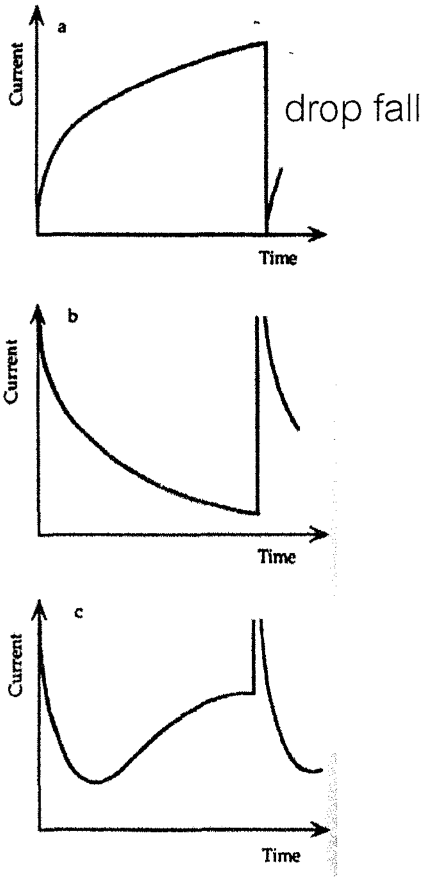
Equation for charging current

$$i_C = 0.00567 C_i (E_Z - E) m^{2/3} t^{-1/3} \qquad (55)$$

i_c: charging current

C_i: capacitance of double layer, 10-20 $\mu F/cm^2$

E_z: potential of zero charge



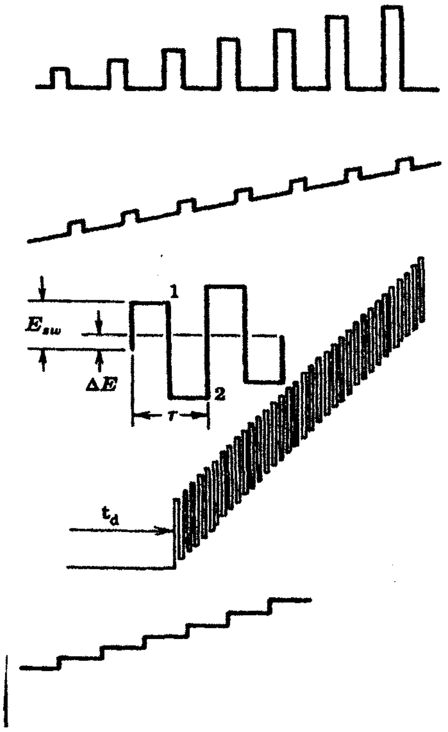
Faradaic current

Charging current

Current at DME

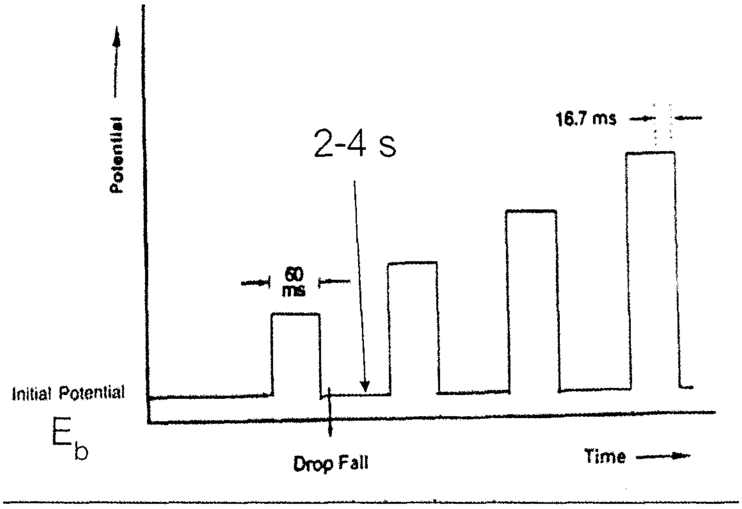
Current-Sampled Voltammetry

Pulse Voltammetry



E pulses with increasing amplitude	**Pulse voltammetry**
E pulses superimposed on linear E scan	**Differential pulse voltammetry**
Symmetrical pulse train added to a staircase	**Square wave voltammetry**
Staircase	**Staircase voltammetry**
	Hydrodynamic voltammetry (steady-state)

Normal Pulse Polarography

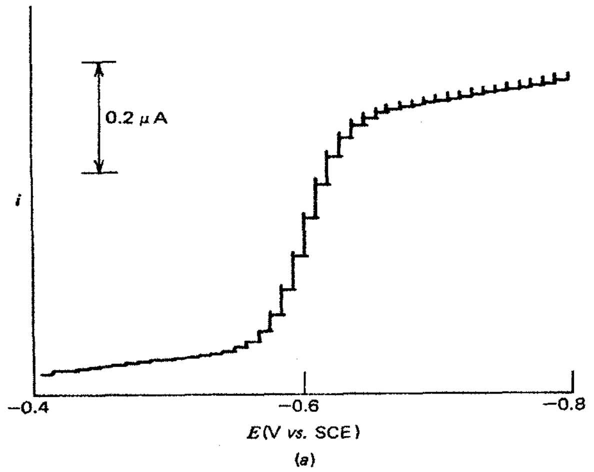


drop time ~2 s

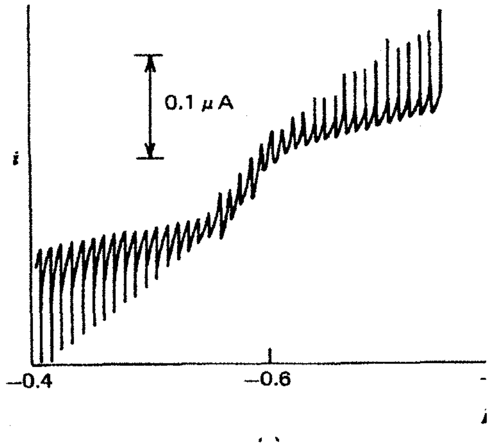
Electrode potential is held at E_b, negligible electrolysis occurs.

Potential changes abruptly to E for ~60 ms, current is sampled near the end of the pulse.

Polarogram of normal pulse technique



10^{-5} M Cd^{2+} in 0.01 M HCl



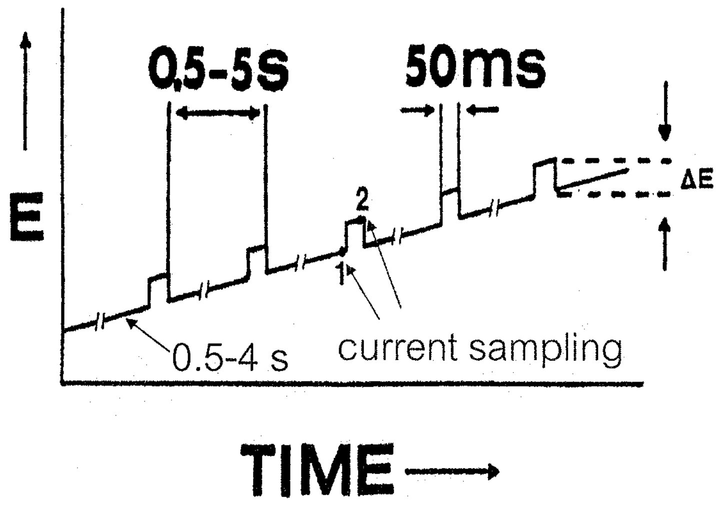
conventional polarography

$$i = \frac{nFAD_O^{1/2}C_O(b)}{\pi^{1/2}(\tau-\tau')^{1/2}} \quad (56)$$

τ: time that current is sampled

τ': time at the beginning of the pulse

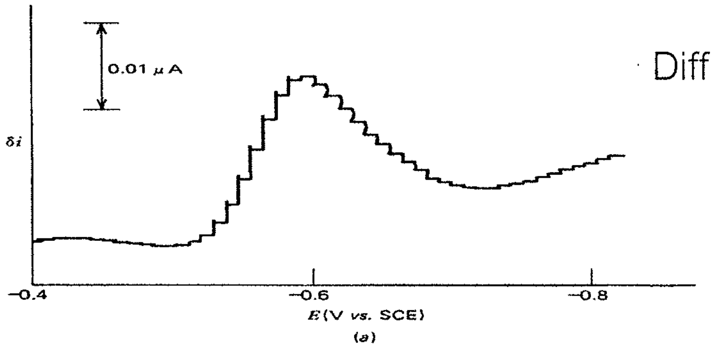
Differential-Pulse Polarography



ΔE: 10-100 mV

Fixed-magnitude (ΔE) pulses are applied to DME just before the end of the drop.

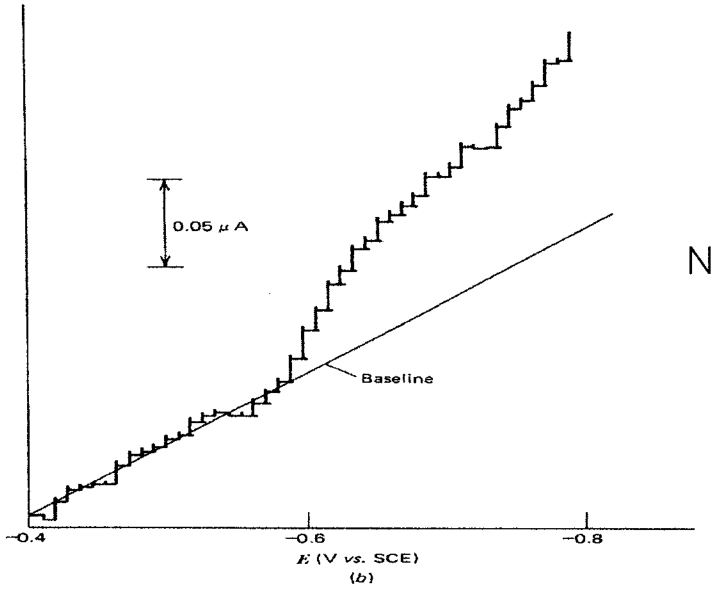
Current is sampled twice, first at time τ', immediately before the pulse and second at time τ just before the drop is dislodged.



Differential-pulse polarography plot

current difference, $i(\tau) - i(\tau')$

vs base potential→ peak



Normal pulse polarography

10^{-6} M Cd^{2+} in 0.01 M HCl

Height of the peak is directly proportional to analyte concentration

$$i_p = \frac{nFAD_O^{1/2}C_O(b)}{\pi^{1/2}(\tau-\tau')^{1/2}}\left[\frac{1-\sigma}{1+\sigma}\right] \qquad (57)$$

$$\sigma = \exp\left[\frac{nF}{RT}\frac{\Delta E}{2}\right] \qquad (58)$$

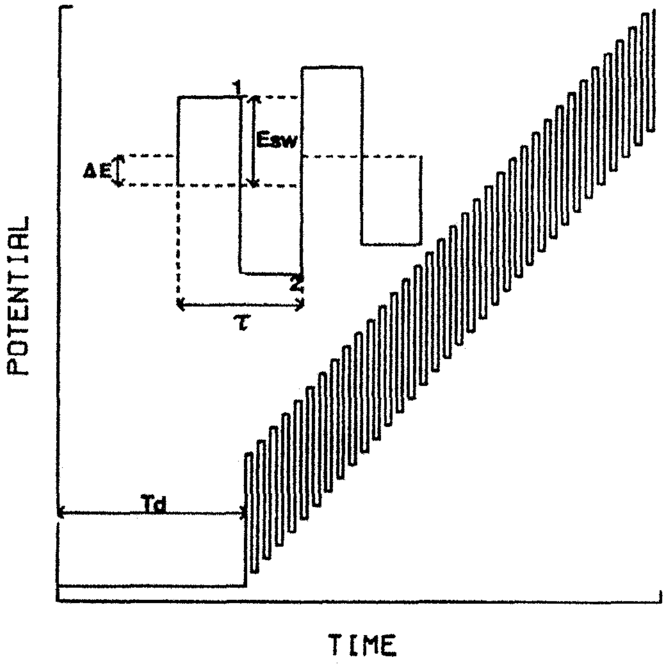
Peak potential (E_p) can be used to identify analyte species.

$$E_p = \underbrace{E^{0'} + \frac{RT}{nF}\ln\left(\frac{D_R}{D_O}\right)^{1/2}}_{E_{1/2}} - \frac{\Delta E}{2} \qquad (59)$$

ΔE is small, so i_p lies close to $E_{1/2}$.

Square-Wave Polarography

symmetrical square wave superimposed on a base stair case potential

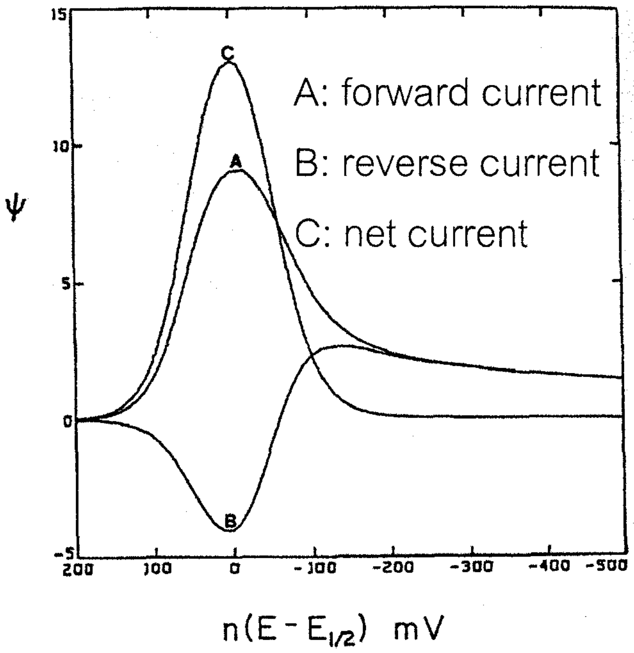


Sample current twice

first at the end of forward pulse

second at the end of reverse pulse

Reverse pulses cause the reverse reaction of the product.



different of the two measured current vs the base stair case potential

Peak shape is symmetrical about $E_{1/2}$.

scan rate = $f\Delta E_{sw}$

f: square wave frequency

scan rate can be up to 5 V/s, complete voltammogram in a single Hg drop within a few seconds DL near 1 x 10^{-8} M

DPP, 2-3 min

Stripping Analysis

- electrolytic deposition of metal ions in the solution into the electrode
- dissolution of the deposit → stripping process
  which is a measurement step

Anodic Stripping Voltammetry

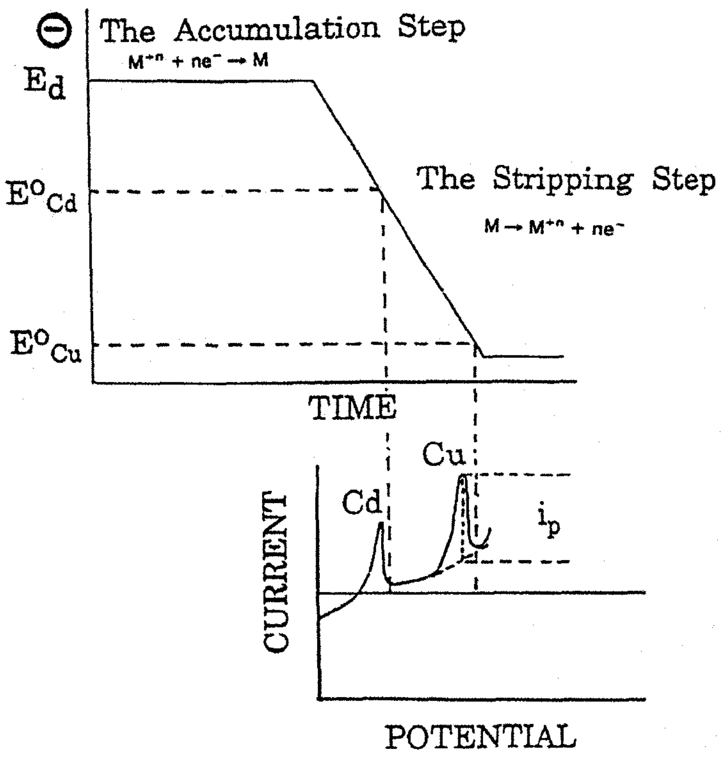
Metal ions are preconcentrated into Hg electrode by cathodic deposition at a controlled potential and time.

E: 0.3-0.5 V more negative than $E^{0'}$

time: less than 0.5 min at 10^{-7} M, ~20 min at 10^{-10} M

$$M^{n+} + ne + Hg \rightarrow M(Hg)$$

Solution is stirred during preconcentration step.



After preconcentration step convection is stopped and the potential is scanned anodically.

The amalgamated metal are oxidized→ stripped out of the electrode.

Potentiometric Stripping Analysis

Potential control after accumulation step is disconnected.

The concentrated metals are reoxidized by oxidizing agent in the solution.

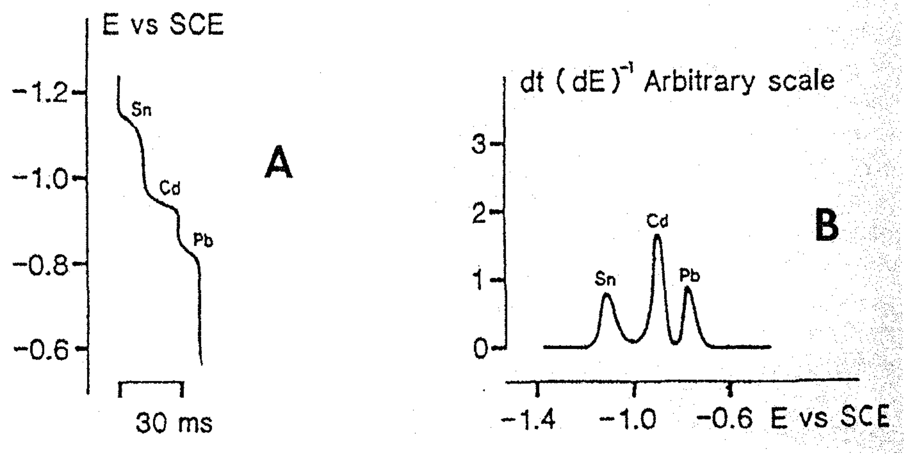
$$M(Hg) + \text{oxidant} \rightarrow M^{n+} + Hg$$

Potential of the working electrode is recorded during stripping step.

$t_M \propto C_M t_d / C_{ox}$

$\downarrow$

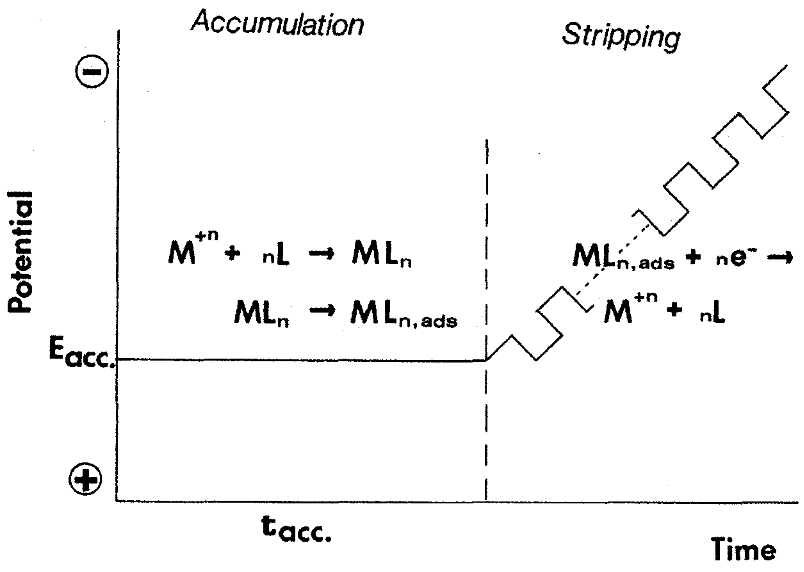
transition time



Solution: 100 ppb tin, cadmium, and lead accumulation time: 80 s E: -1.40 V

Adsorptive Stripping Voltammetry

- complex formation
- adsorptive accumulation
- reduction of a surface active complex



improvement of metal selectivity

Cathodic Stripping Voltammetry

- anodic deposition of analyte
- potential is scanned cathodically (more negative potential)

Stripping Analysis

- remarkable sensitivity
- over 30 trace elements can be analyzed
- DL ~ 10^{-11} M

Voltammetric Instrumentation

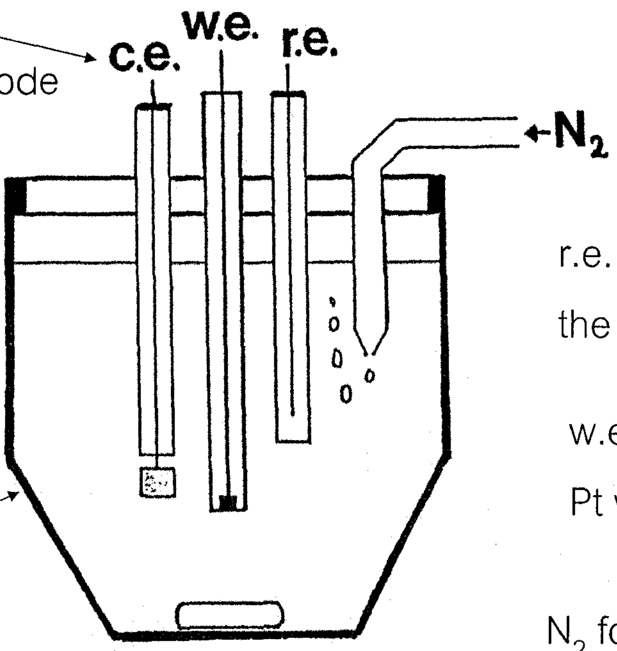
Basic requirements

- a cell with three-electrode system
- voltametric analyzer→ potentiostatics circuitry and
  voltage ramp generator
- recorder or computer

location for operation: a room free from major electrical interferences,
vibrations, and fluctuation of temperature

Electrochemical Cells

counter or
auxiliary electrode



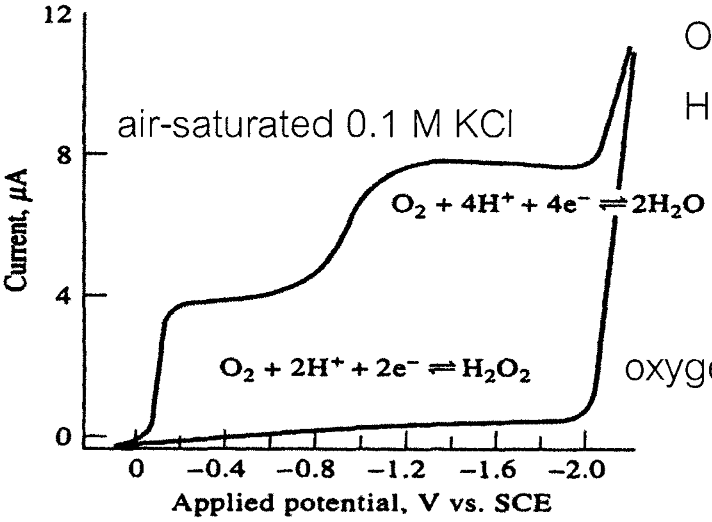
r.e. may be separated from the sample

w.e. conducting material
Pt wire, graphite rod

5-50 mL
glass, Teflon, quartz

N_2 for purging (4-8 min) to remove O_2

Reduction of Oxygen



oxygen-free 0.1 M KCl

$O_2 + 2H^+ + 2e- <==> H_2O_2$

$H_2O_2 + 2H^+ + 2e- <==> 2H_2O$

other methods for removal of $O_2 \rightarrow$ chemical scrubber,
chemical reduction by addition of sodium sulfite or ascorbic acid

Solvents and Supporting Electrolytes

Solvent

- not react with analyte and products
- not undergo electrolysis

water: double or triple distilled water

organics: drying or purification is needed

acetonitrile, dimethylsulfoxide (DMSO), methanol

Supporting electrolytes

- decrease solution resistance
- eliminate migration effect
- maintain a constant ionic strength

inorganic salt, mineral acid,

Buffer

concentration range: 0.1-1.0 M

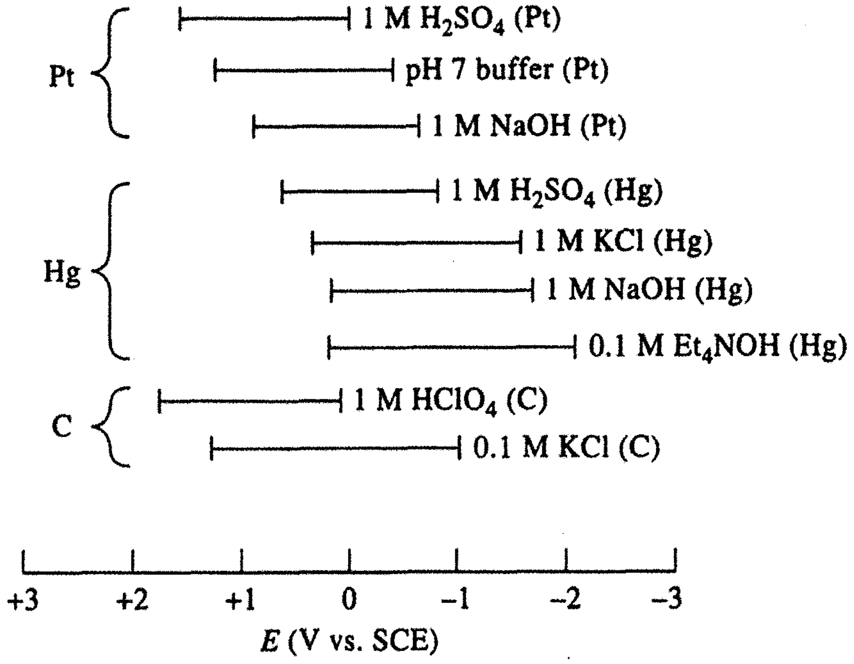
For trace analysis, purity of chemicals needs to be concerned.

Working Electrode

consideration for selection

- redox behavior of the target analyte over the potential range for the measurement
- potential window
- electrical conductivity
- surface reproducibility
- availability
- cost
- toxicity

Potential window of some electrodes in aqueous solution



Typically for aqueous solution the reduction and oxidation of water will limit the use of the working electrode.

Oxidation: $H_2O \rightarrow \frac{1}{2} O_2 + 2H^+ + 2e-$ positive potential

Reduction: $H_2O + e- \rightarrow \frac{1}{2} H^+ + OH^-$ negative potential

$2H^+ + 2e- \rightarrow H_2$

Mercury Electrode

Advantages

- high hydrogen over voltage
- renewable surface
- high reproducibility

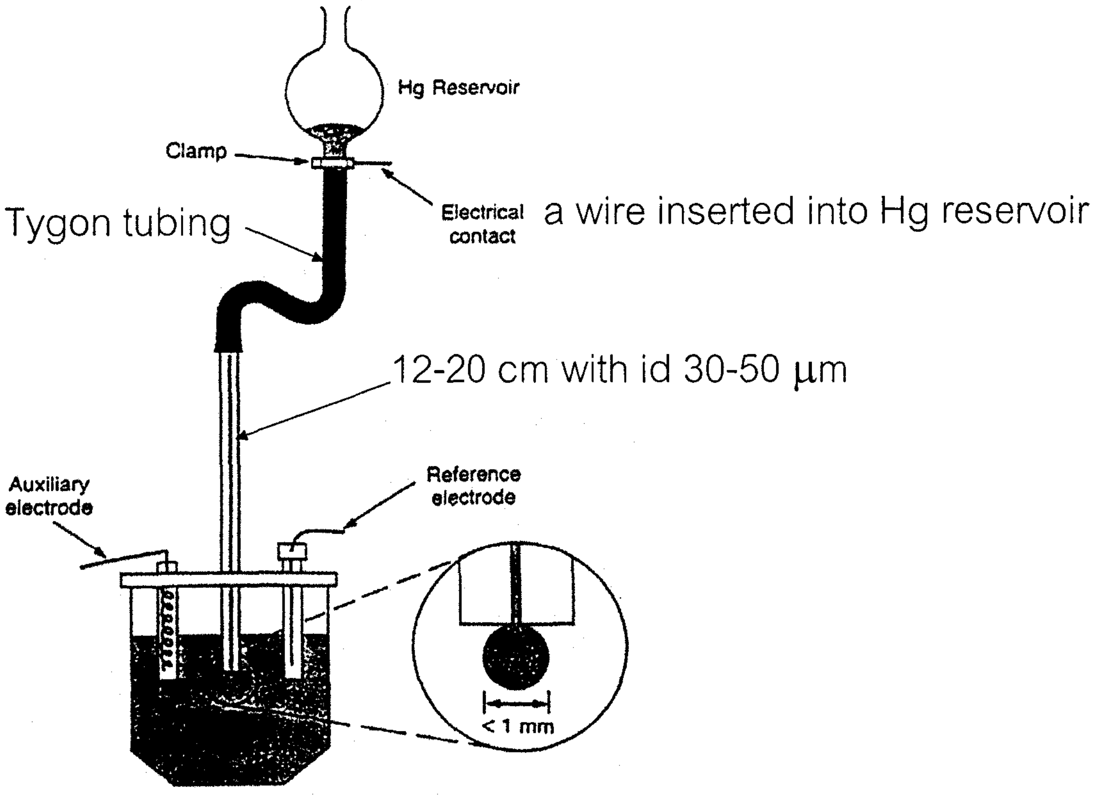
Disadvantages

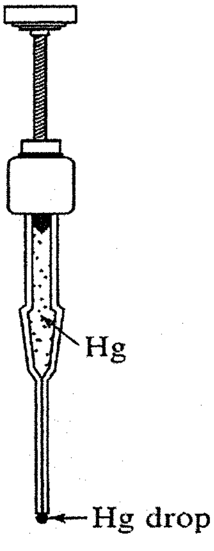
- limited anodic range due to mercury oxidation
- toxicity

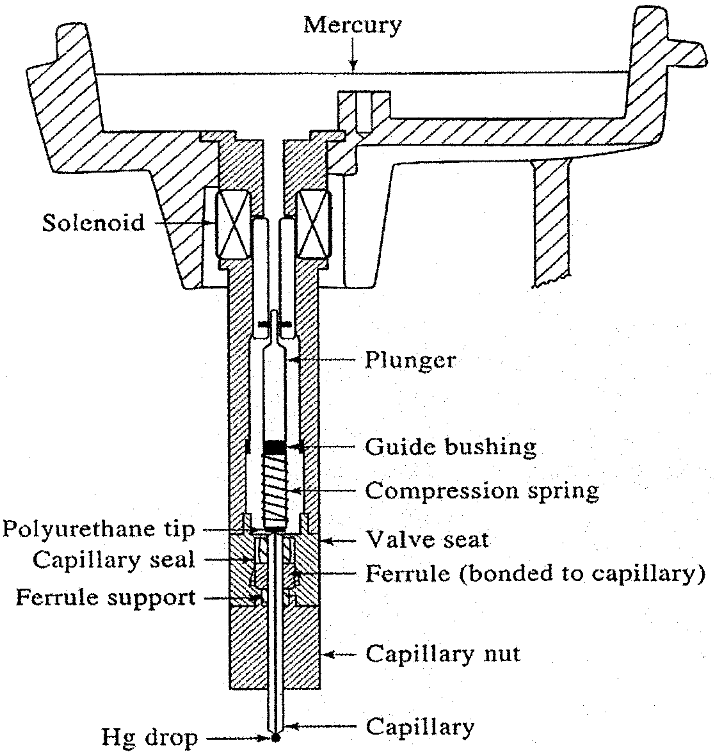
Three most frequently used mercury electrodes are;

1. Dropping mercury electrode (DME)
2. Hanging mercury electrode (HDME)
3. Mercury film electrode (MFE)

Dropping Mercury Electrode







Mercury Film Electrode

for stripping and flow analysis

Layer of mercury (10-100 μm) covering on a conducting and inert support

Hg droplet

Quantitative Analysis

- calibration curve
- standard addition
- internal standard