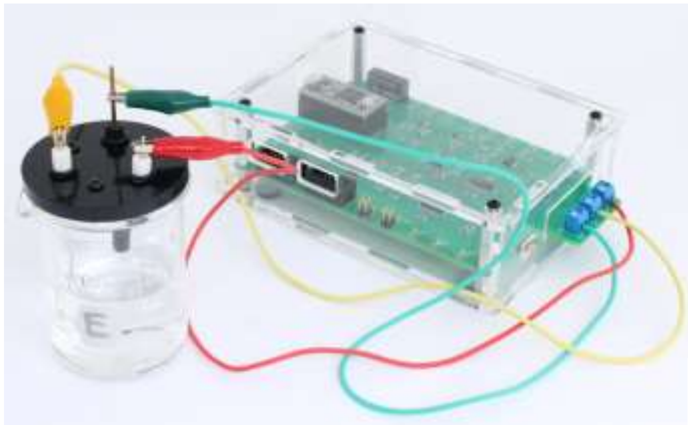
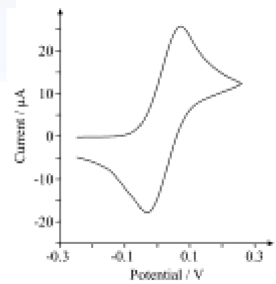
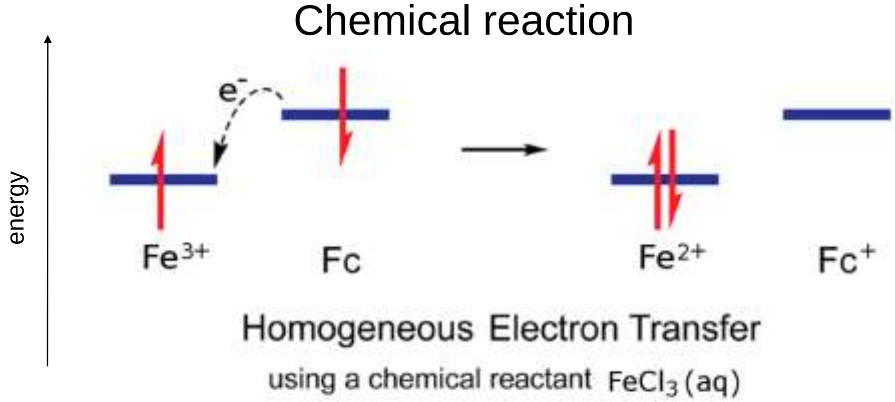
Voltammetry

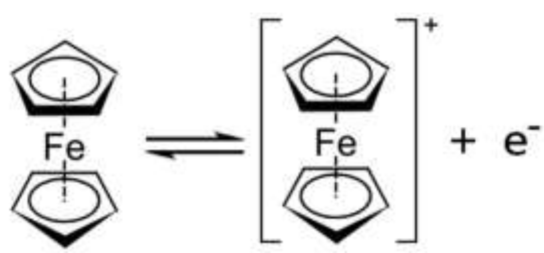




1

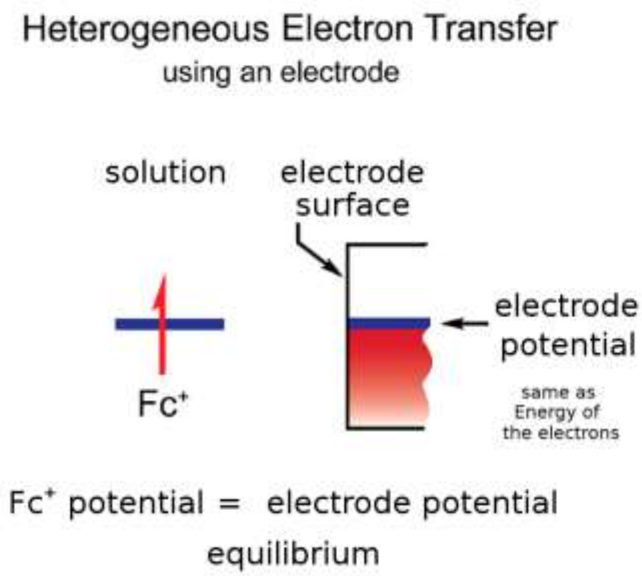
Chemical reaction



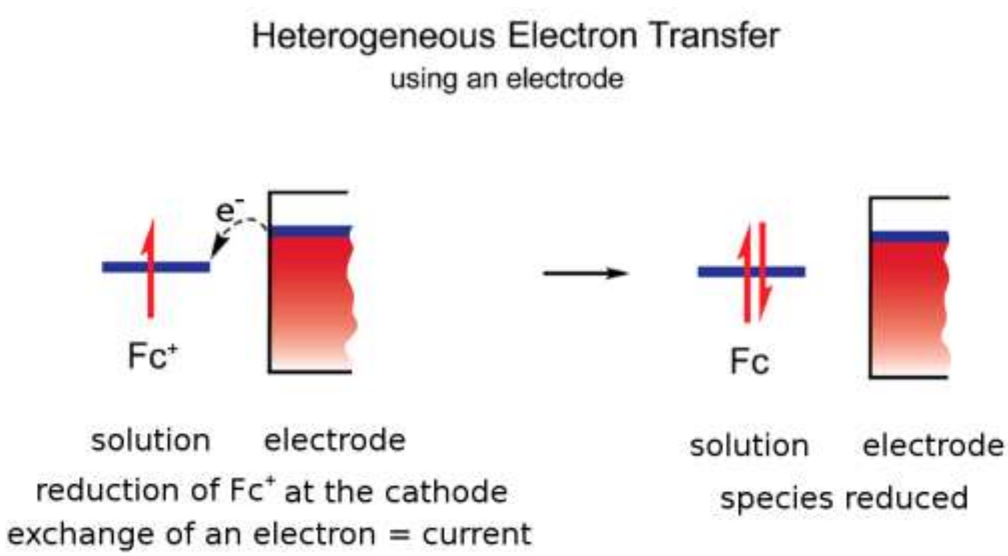


2

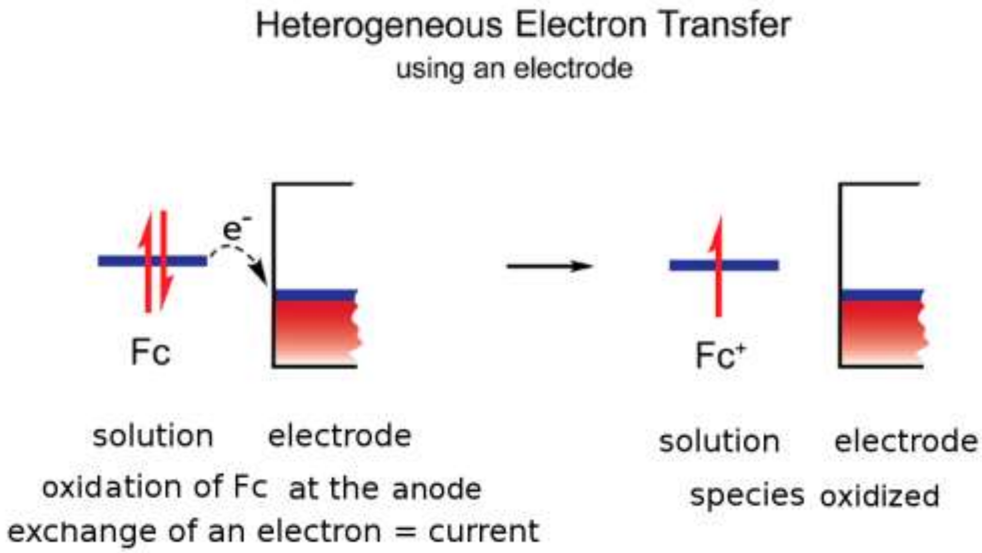
Voltammetry



Voltammetry

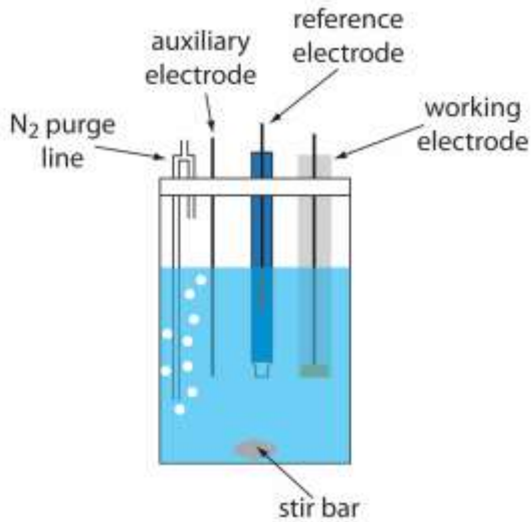


Voltammetry



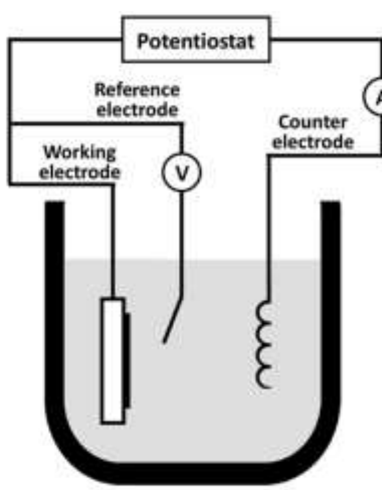
Voltammetry

Voltammetry



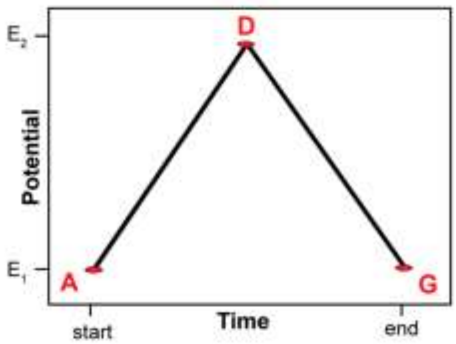
Voltammetry

Circuit

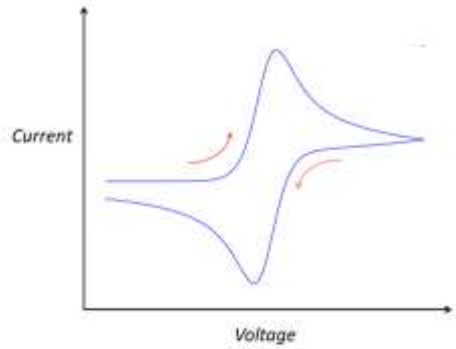


Voltammetry

Voltammetric scan



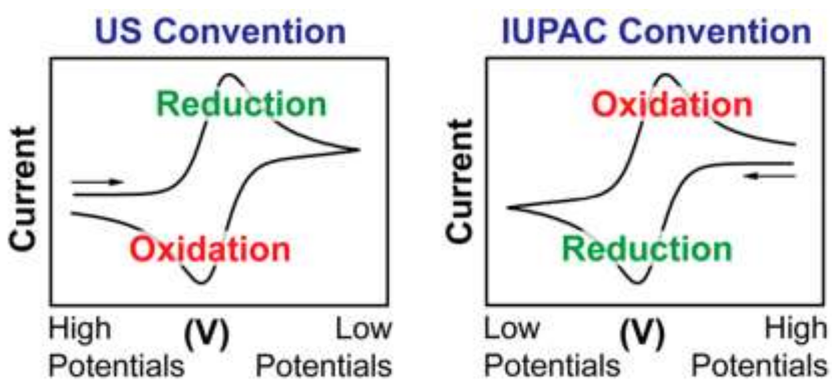
signal



response

9

Voltammetry



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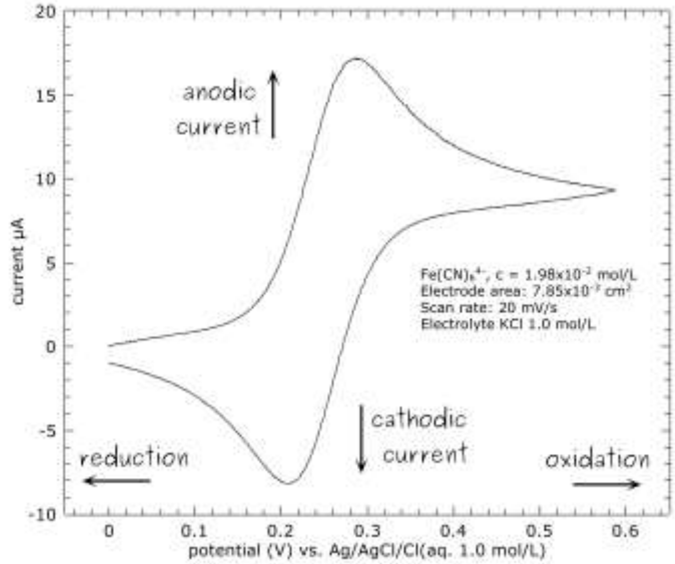
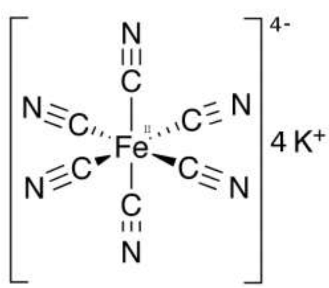
Voltammetry

Experiment 10



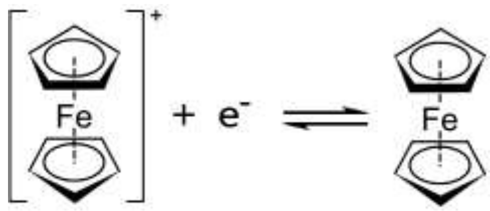
Voltammetry



Potassium ferrocyanide $K_4Fe(CN)_6{\cdot}3H_2O$ (Fe^{2+})

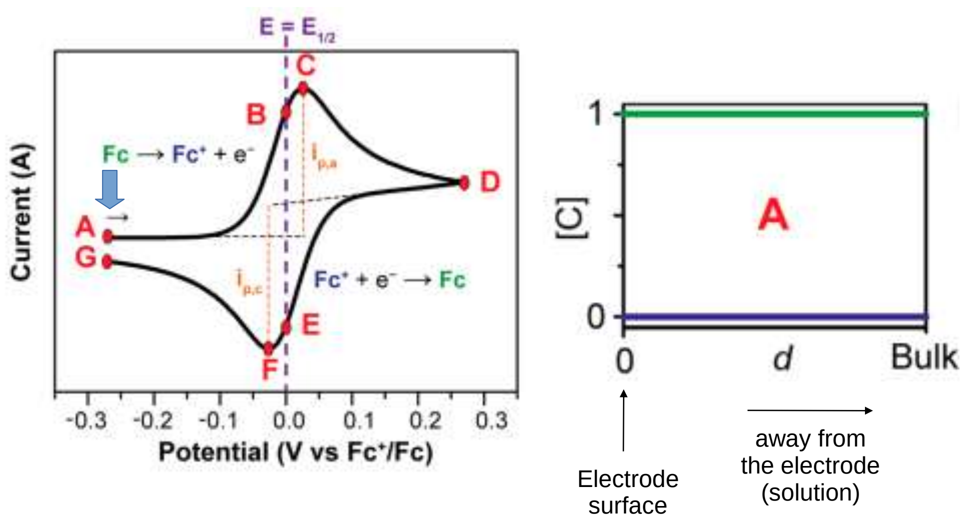
Reversible system often used as a type III reference electrode in water

Voltammetry

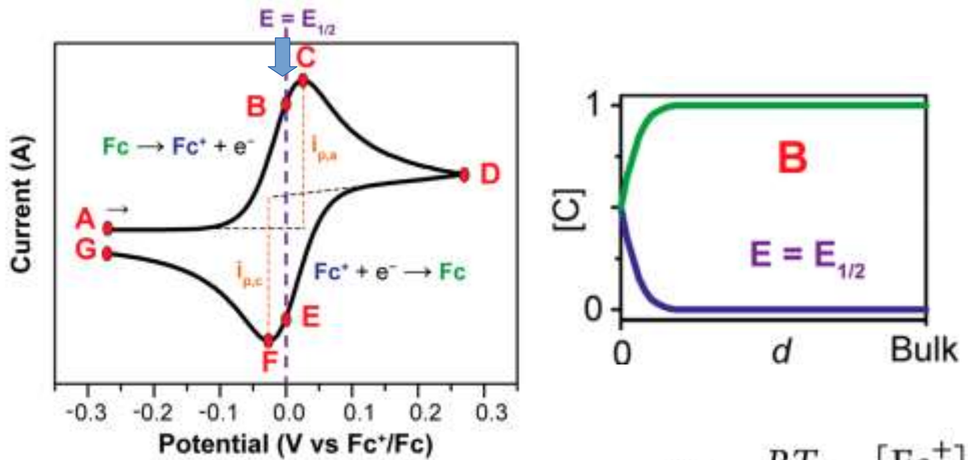


Other iron based redox-system: Ferrocene
Reversible system often used as a type III reference electrode in organic solvent

Voltammetry

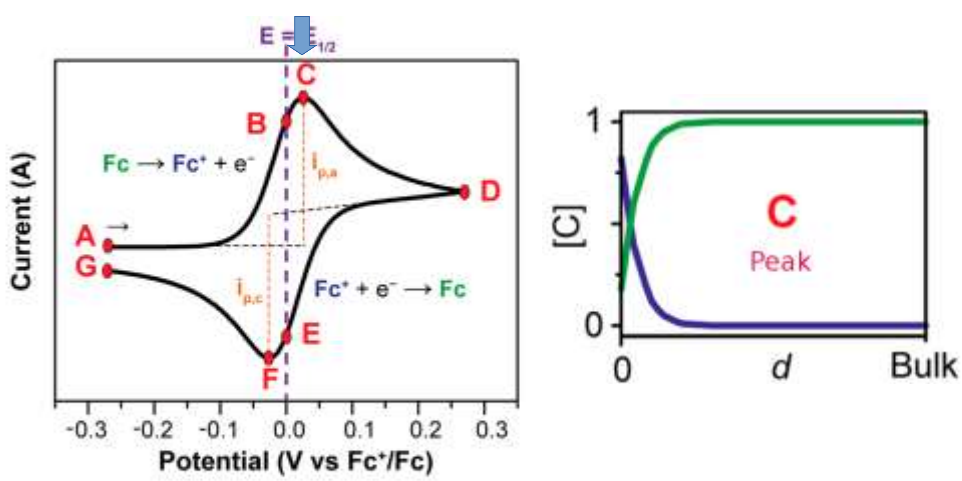


Voltammetry

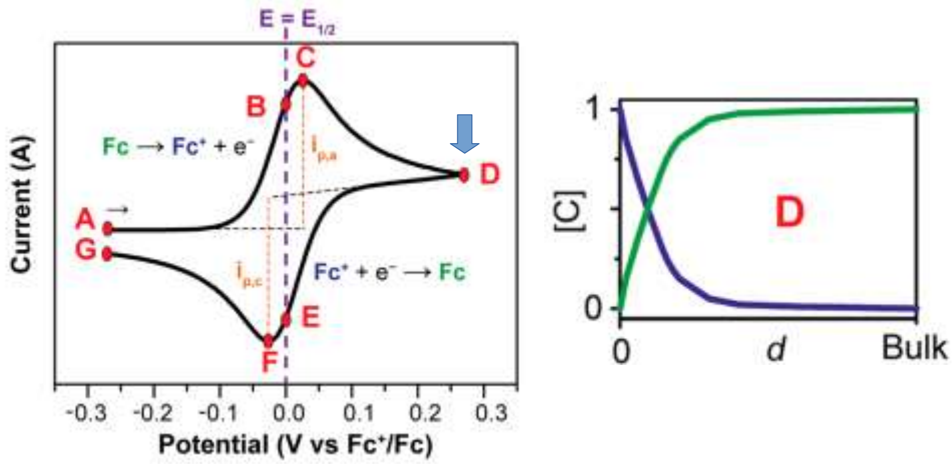


$$E = E^{0\prime} + \frac{RT}{F}\ln\frac{[Fc^+]}{[Fc]}$$

Voltammetry



Voltammetry



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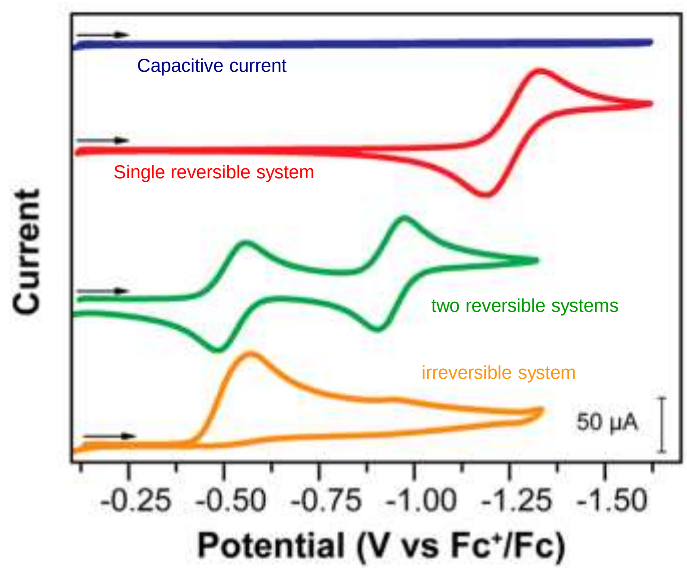
Voltammetry



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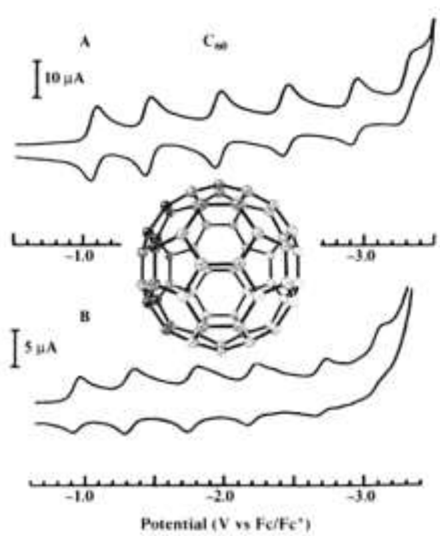
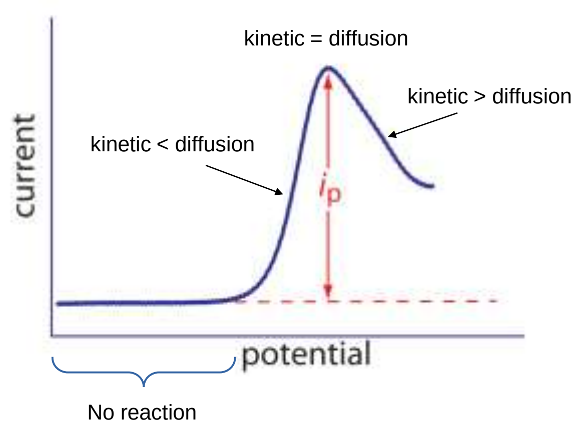
Voltammetry



Redox system with several oxidation states

Voltammetry



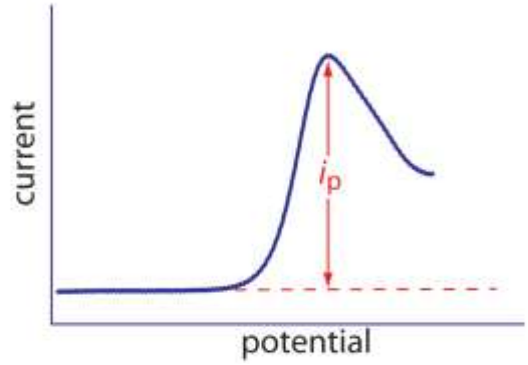
Kinetic: Butler-Volmer equation

Diffusion: Fick equation

$$i_p = 0.446nFAC_o\left(\frac{nFvD_o}{RT}\right)^{\frac{1}{2}}$$

Randles–Sevcik equation

Voltammetry



$$i_{peak} = 2.69 \times 10^5\, n^{3/2} A\, c_o \sqrt{D\, v}$$

Randles–Sevcik equation at 25 °C

i_{peak}: peak current (A)
A: surface area of the electrode (cm^2)
C_o: concentration of the species in solution (mol/cm^3)
D: diffusion coefficient (cm^2/s)
v: scan rate (V/s)

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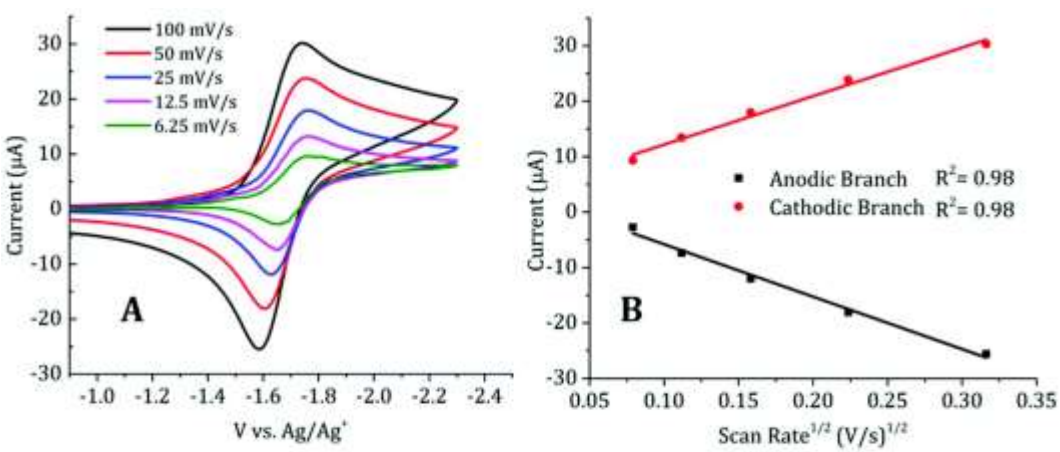
Voltammetry

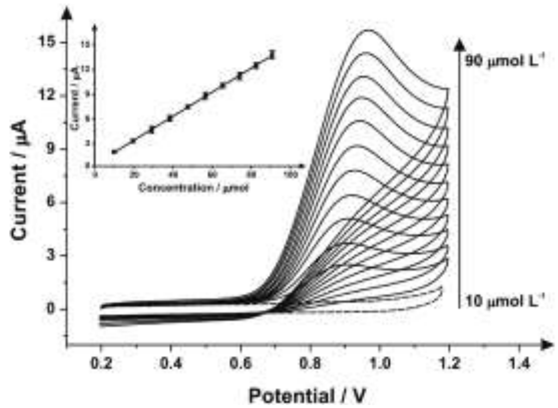


$$i_{peak} = 2.69 \times 10^5\, n^{3/2} A\, c_o \sqrt{D\, v}$$

To check for linear diffusion

At 25 ºC

Voltammetry

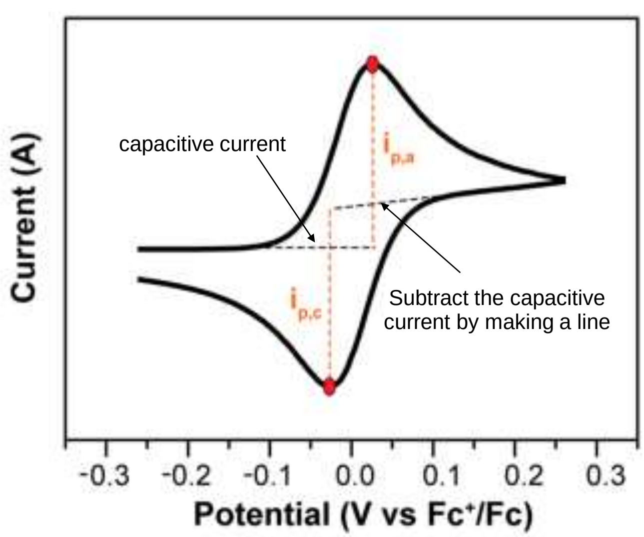


$$i_{peak} = 2.69 \times 10^5 \, n^{3/2} \, A \, c_o \sqrt{D \, v}$$

The peaks of current with different concentrations of a given molecule in a CV experiment. J. Braz. Chem. Soc., Vol. 26, No. 5, 1034-1042, 2015.

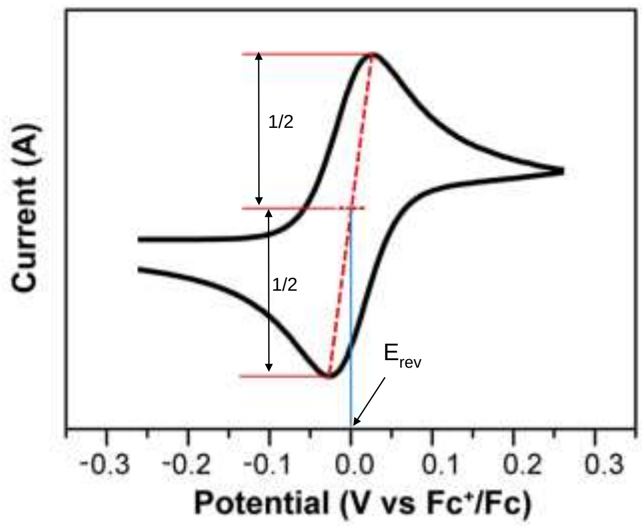
Voltammetry

To find i_{peak} cathodic and anodic



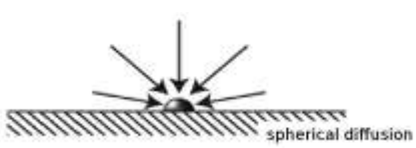
Voltammetry

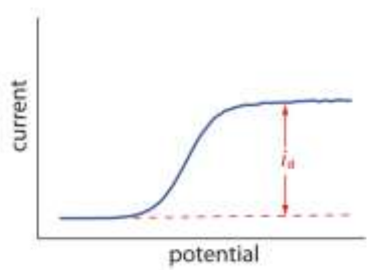
To find the reversible potential



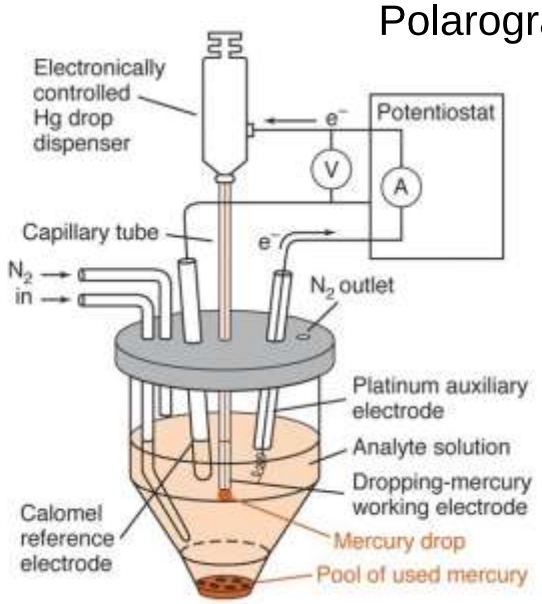
Polarography

Jaroslav Heyrovský
Invented in 1922
Nobel prize in 1959



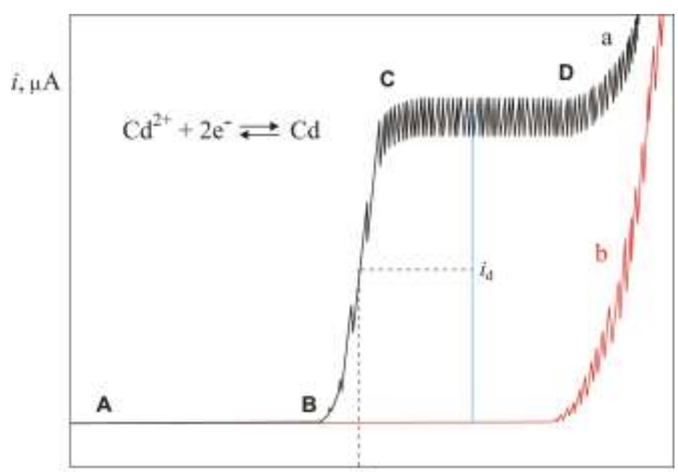


Polarography



Polarography apparatus featuring a dropping- mercury working electrode.

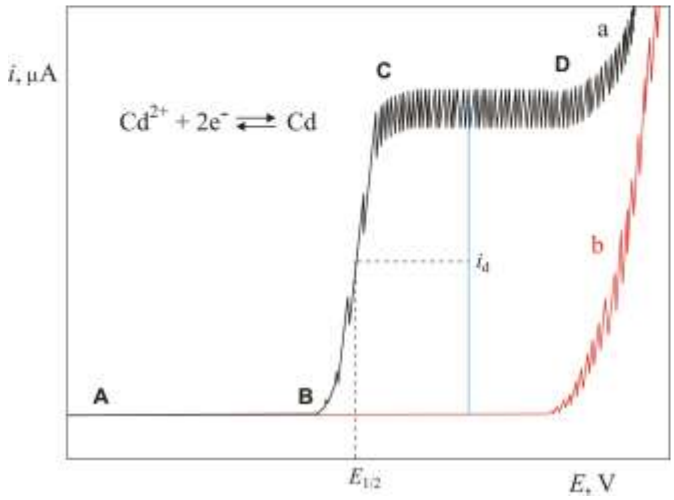
Polarography



Polarograms for (a) 0.5 mM $Cd(II)(OH_2)_6^{2+}$ in 1 M HCl and (b) 1 M HCl.

$$E = E_{1/2} + \frac{RT}{nF} \ln \frac{i_d - i}{i}$$

Polarography



Polarograms for (a) 0.5 mM $Cd(II)(OH_2)_6^{2+}$ in 1 M HCl and (b) 1 M HCl.

Ilkovic equations

$$i_{avg} = 607nD^{1/2}m^{2/3}t^{1/6}C$$

m = mercury flow rate (cm^3/s)
t = drop lifetime (s)

Polarography

For the analysis of electroactive compounds

Organic compounds:
- Carbonyl
- carboxylic acid
- C=C compounds

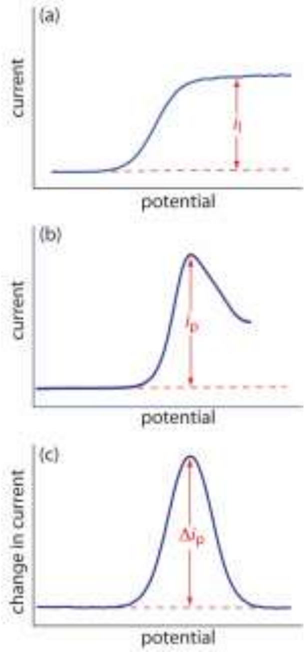
metal ions :
- Lead, tin, cadmium, iron

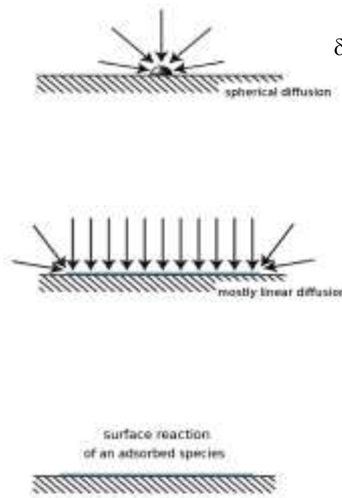
inorganic anions,
- IO_3^- and nitrate

Voltammetry

$\delta=\sqrt{2Dt}$ (diffusion layer)

disk electrode





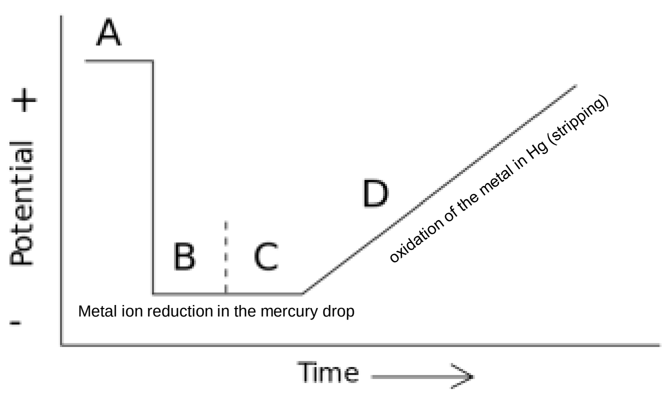
$\delta >> r_{\text{electrode}}$

$\delta << r_{\text{electrode}}$

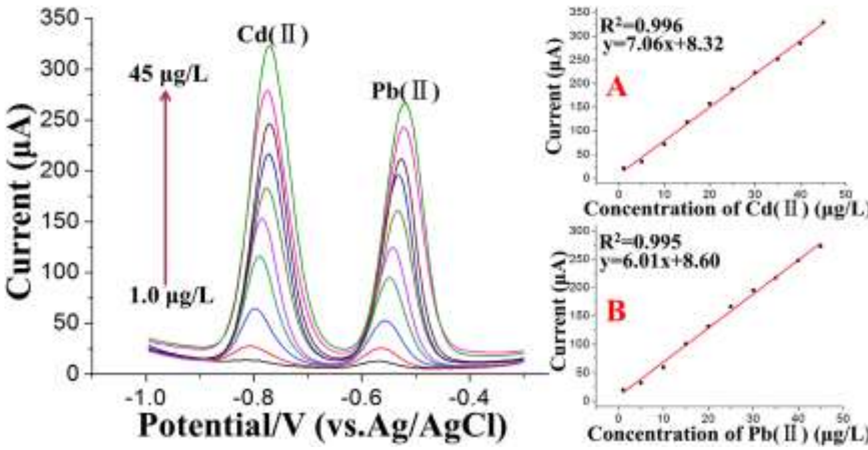
No diffusion

Anodic stripping voltammetry

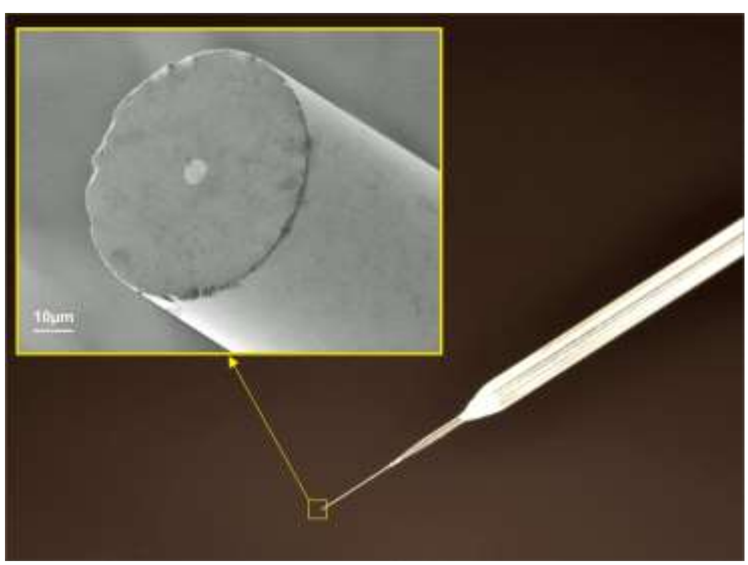
Potential profile imposed to the electrode with time



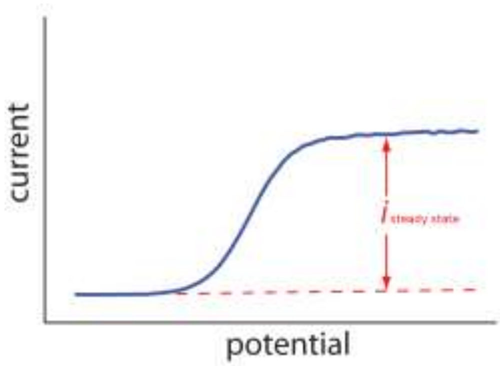
Anodic stripping voltammetry



Voltammetry ultra micro electrode



Voltammetry ultra micro electrode



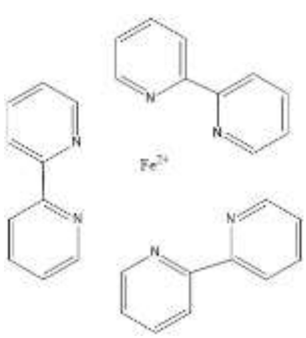
$$I_{steady\ state} = 4\ n\ F\ D\ r\ C_o$$

Exercise

Use a voltammetric analysis to calculate the diffusion coefficient D of iron−2,2′−bipyridine at 25 °C.

Reaction: $[Fe(bipy)_3]^{2+} \rightleftharpoons [Fe(bipy)_3]^{3+} + 1e^-$

$c =$ 1.003 mM,
i_{peak} (ox) = 209 nA,
scan rate = 2.00 V/s,
$A_{electrode}$ = 0.500cm²



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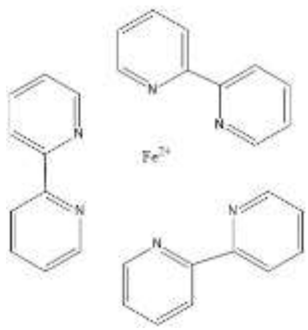

$$i_{peak} = 2.69 \times 10^5\, n^{3/2} A\, c_o \sqrt{D\, v}$$

Randles–Sevcik equation at 25 °C

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$$i_{peak} = 2.69 \times 10^5\, n^{3/2} A\, c_o \sqrt{D\, v}$$

$$D = \left(\frac{i_{peak}}{2.69 \times 10^5\, n^{3/2} A\, c_o\, v^{1/2}} \right)^2$$

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Exercise

Use a voltammetric analysis to calculate the diffusion coefficient D of iron−2,2′−bipyridine at 25 °C.

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scan rate = 2.00 V/s,
$A_{electrode}$ = 0.500cm²

$$i_{peak} = 2.69 \times 10^5\, n^{3/2}\, A\, c_o \sqrt{D\, v}$$

$$D = \left(\frac{209\times10^{-9}\,A}{2.69\times10^5\,(1)^{3/2}\,(0.500\,cm^2)(1.003\times10^{-3}\,mol/1000\,cm^3)(2.00\,V/s)^{1/2}} \right)^2$$

Exercise

Use a voltammetric analysis to calculate the diffusion coefficient D of iron−2,2′−bipyridine at 25 °C.

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scan rate = 2.00 V/s,
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$$i_{peak} = 2.69 \times 10^5\, n^{3/2}\, A\, c_o \sqrt{D\, v}$$

$$D = 1.2\times10^{-12}\ cm^2/s$$

Migration current

Migration current vs. Diffusion current

The “active species” concentration should be less than 5% than the one of the electrolyte to prevent any migration current