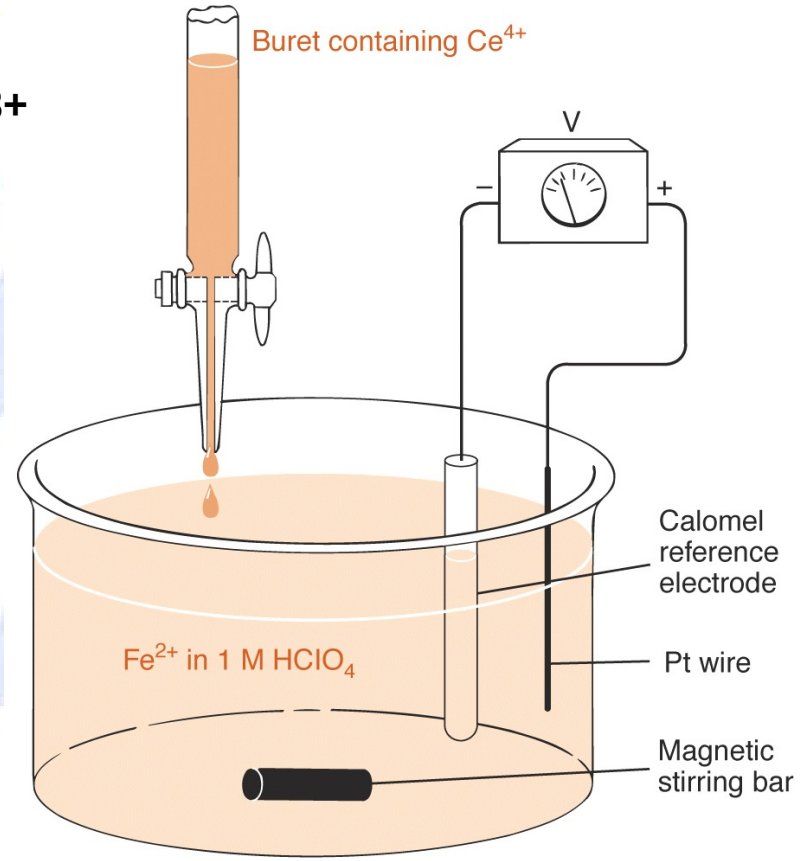
Redox Titration

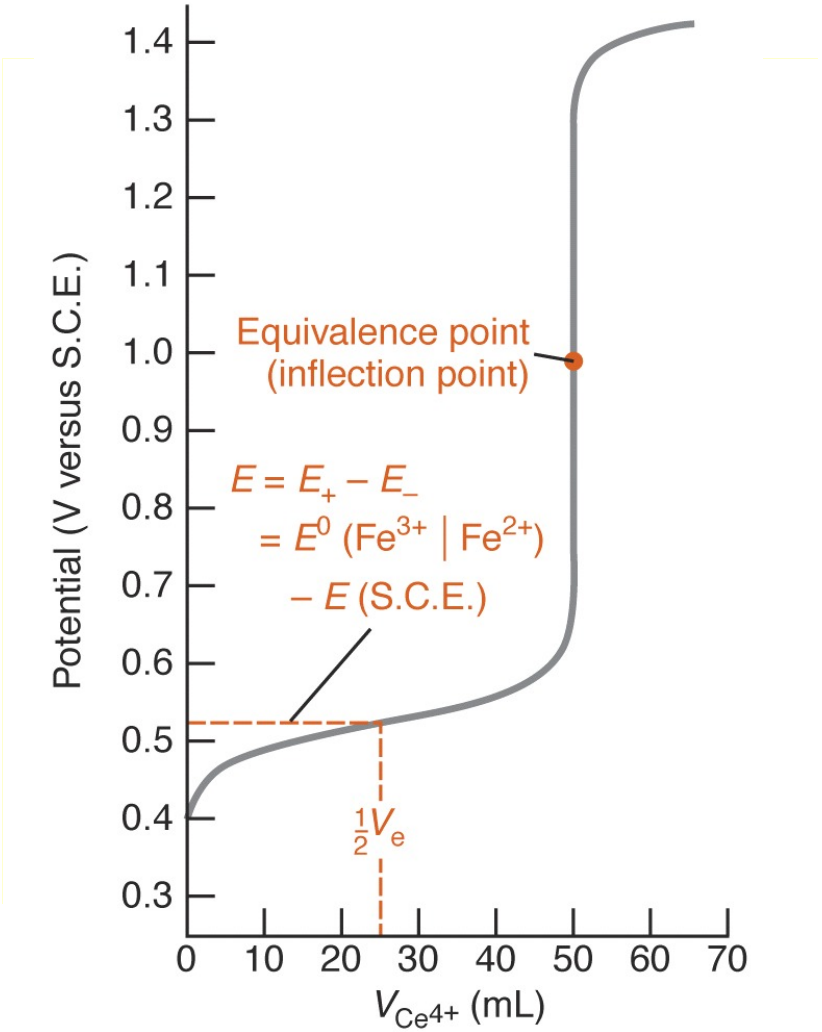
Redox Titration

$$Ce^{4+} + Fe^{2+} \rightarrow Ce^{3+} + Fe^{3+}$$

- Redox titration is based on the redox reaction (oxidation-reduction) between analyte and titrant.



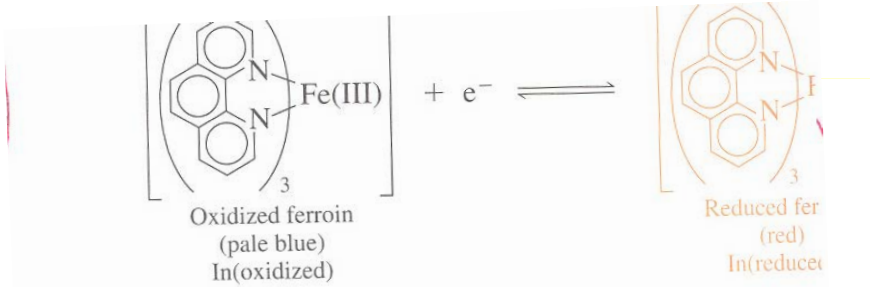
Position of the end point



Determine the end point

- Indicator electrode
- Redox indicators – the indicator has different color at reduction and oxidation state.
- Non redox indicator – change color when excess amount of titrant exists, e.g. Starch changes to deep blue color when excess amount I_2 remains

Redox indicator



To predict the potential range over which the indicator color w
write a Nernst equation for the indicator.

$$\text{In(oxidized)} + ne^- \rightleftharpoons \text{In(reduced)}$$

$$E = E^\circ - \frac{0.059\ 16}{n} \log\left(\frac{[\text{In(reduced)}]}{[\text{In(oxidized)}]}\right)$$

As with acid-base indicators, the color of In(reduced) will be observ

$$\frac{[\text{In(reduced)}]}{[\text{In(oxidized)}]} \gtrsim \frac{10}{1}$$

and the color of In(oxidized) will be observed when

$$\frac{[\text{In(reduced)}]}{[\text{In(oxidized)}]} \lesssim \frac{1}{10}$$

Putting these quotients into Equation 16-14 tells us that the color
over the range

$$E = \left(E^\circ \pm \frac{0.059\ 16}{n}\right) \text{volts}$$

Redox indicators

Table 16-2 **Redox indicators**

Indicator	Color		E°
	Oxidized	Reduced	
Phenosafranine	Red	Colorless	0.28
Indigo tetrasulfonate	Blue	Colorless	0.36
Methylene blue	Blue	Colorless	0.53
Diphenylamine	Violet	Colorless	0.75
4′-Ethoxy-2,4-diaminoazobenzene	Yellow	Red	0.76
Diphenylamine sulfonic acid	Red-violet	Colorless	0.85
Diphenylbenzidine sulfonic acid	Violet	Colorless	0.87
Tris(2,2′-bipyridine)iron	Pale blue	Red	1.120
Tris(1,10-phenanthroline)iron (ferroin)	Pale blue	Red	1.147
Tris(5-nitro-1,10-phenanthroline)iron	Pale blue	Red-violet	1.25
Tris(2,2′-bipyridine)ruthenium	Pale blue	Yellow	1.29

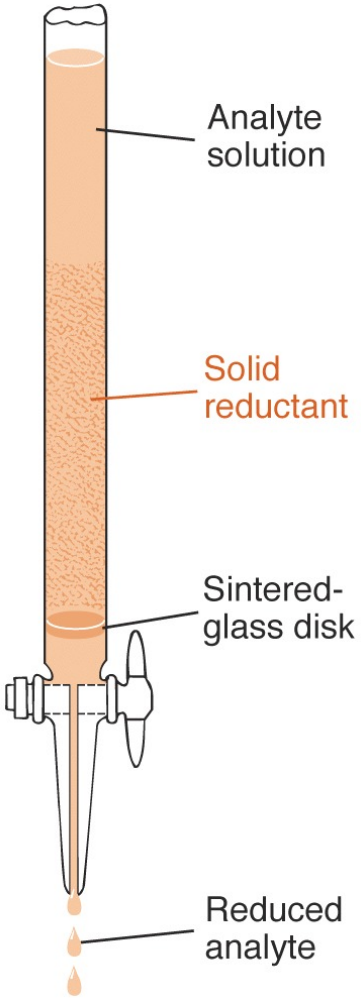
The indicator potential transition range should overlap the steep part of the titration curve

Adjustment of oxidation state

- Sometimes the oxidation states of analytes need to be adjusted before titration – oxidants need to be removed.
  - Pre-oxidation:
    - $S_2O_8^{2-}$ (peroxydisulfate, persulfate):
      $S_2O_8^{2-} + 2e \leftrightarrows 2SO_4^{2-}$
      $S_2O_8^{2-} + 2H_2O \rightarrow 4SO_4^{2-} + O_2 + 4H^+$ (boiling)
      sometime, Ag^+ is needed as catalyst
      $S_2O_8^{2-} + Ag^+ \rightarrow SO_4^{2-} + SO_4^- + 4Ag^{2+}$
    - H_2O_2

Adjustment of oxidation state

– Pre-reduction
  - $SnCl_2$, etc
  - Reductor:
    Jones reductor: Zn-Zn amalgam
    Walden reductor: Ag/AgCl



Example of typical oxidants

- Potassium Permanganate ($KMnO_4$)
  $MnO_4^- + 8H^+ + 5e \rightarrow Mn^{2+} + 4H_2O$ $E^o = 1.507V$ (pH<1)
  $MnO_4^- + 4H^+ + 3e \rightarrow MnO_2(s) + 2H_2O$ $E^o = 1.692V$ (pH≈7)
  In alkaline solution: $MnO_4^- + e \rightarrow MnO_4^{2-}$
- Preparation, standardization and storage
  - Not a primary standard, MnO_2 impurity
  - To prepare, dissolve $KMnO_4$ in DI water, boil in a hour to make sure oxidize all organics, filter through sintered glass filter (why?), store in dark glass.
  - Use either Fe^{2+} or sodium oxalate ($Na_2C_2O_4$) for standardization

Table 16-3 Analytical applications of permanganate titrations

Species analyzed	Oxidation reaction	Notes
Fe^{2+}	$Fe^{2+} \rightleftharpoons Fe^{3+} + e^-$	Fe^{3+} is reduced to Fe^{2+} with Sn^{2+} or a Jones reductor. Titration is carried out in 1 M H_2SO_4 or 1 M HCl containing Mn^{2+}, H_3PO_4, and H_2SO_4. Mn^{2+} inhibits oxidation of Cl^- by MnO_4^-. H_3PO_4 complexes Fe^{3+} to prevent formation of yellow Fe^{3+}-chloride complexes.
$H_2C_2O_4$	$H_2C_2O_4 \rightleftharpoons 2CO_2 + 2H^+ + 2e^-$	Add 95% of titrant at 25°C, then complete titration at 55°–60°C.
Br^-	$Br^- \rightleftharpoons \frac{1}{2}Br_2(g) + e^-$	Titrate in boiling 2 M H_2SO_4 to remove $Br_2(g)$.
H_2O_2	$H_2O_2 \rightleftharpoons O_2(g) + 2H^+ + 2e^-$	Titrate in 1 M H_2SO_4.
HNO_2	$HNO_2 + H_2O \rightleftharpoons NO_3^- + 3H^+ + 2e^-$	Add excess standard $KMnO_4$ and back-titrate after 15 min at 40°C with Fe^{2+}.
As^{3+}	$H_3AsO_3 + H_2O \rightleftharpoons H_3AsO_4 + 2H^+ + 2e^-$	Titrate in 1 M HCl with KI or ICl catalyst.
Sb^{3+}	$H_3SbO_3 + H_2O \rightleftharpoons H_3SbO_4 + 2H^+ + 2e^-$	Titrate in 2 M HCl.
Mo^{3+}	$Mo^{3+} + 2H_2O \rightleftharpoons MoO_2^{2+} + 4H^+ + 3e^-$	Reduce Mo in a Jones reductor, and run the Mo^{3+} into excess Fe^{3+} in 1 M H_2SO_4. Titrate the Fe^{2+} formed.

Table 16-3 Analytical applications of permanganate titrations

Species analyzed	Oxidation reaction	Notes
W^{3+}	$W^{3+} + 2H_2O \rightleftharpoons WO_2^{2+} + 4H^+ + 3e^-$	Reduce W with Pb(Hg) at 50°C and titrate in 1 M HCl.
U^{4+}	$U^{4+} + 2H_2O \rightleftharpoons UO_2^{2+} + 4H^+ + 2e^-$	Reduce U to U^{3+} with a Jones reductor. Expose to air to produce U^{4+}, which is titrated in 1 M H_2SO_4.
Ti^{3+}	$Ti^{3+} + H_2O \rightleftharpoons TiO^{2+} + 2H^+ + e^-$	Reduce Ti to Ti^{3+} with a Jones reductor, and run the Ti^{3+} into excess Fe^{3+} in 1 M H_2SO_4. Titrate the Fe^{2+} that is formed.
Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Co^{2+}, La^{3+}, Th^{4+}, Pb^{2+}, Ce^{3+}, BiO^+, Ag^+	$H_2C_2O_4 \rightleftharpoons 2CO_2 + 2H^+ + 2e^-$	Precipitate the metal oxalate. Dissolve in acid and titrate the $H_2C_2O_4$.
$S_2O_8^{2-}$	$S_2O_8^{2-} + 2Fe^{2+} + 2H^+ \rightleftharpoons 2Fe^{3+} + 2HSO_4^-$	Peroxydisulfate is added to excess standard Fe^{2+} containing H_3PO_4. Unreacted Fe^{2+} is titrated with MnO_4^-.
PO_4^{3-}	$Mo^{3+} + 2H_2O \rightleftharpoons MoO_2^{2+} + 4H^+ + 3e^-$	$(NH_4)_3PO_4 \cdot 12MoO_3$ is precipitated and dissolved in H_2SO_4. The Mo(VI) is reduced (as above) and titrated.

Methods involving Iodine

- Iodine is hardly soluble in water, but very soluble in Iodide solution
  $I_2 + I^- \rightleftarrows I_3^-$ (triiodide)
- Iodimetry: I_3^- as titrant
  Iodometry: I_3^- is produced by adding oxidating analytes into excess amount of Iodide (I^-)
- Indicator starch, added near the end point (Iodometry), but at the beginning for Iodimetry.
- Standardization (pure enough for primary standard, but evaporates during weighting)
  - Weight and dissolve in I^-
  - Use Arsenious Oxide (As_4O_6) or Soduim Thiosulfate ($Na_2S_2O_4$) for standardization
- Storage, no light, no oxygen

Table 16-4 Titrations with standard triiodide (iodimetric titrations)

Species analyzed	Oxidation reaction	Notes
As^{3+}	$H_3AsO_3 + H_2O \rightleftharpoons H_3AsO_4 + 2H^+ + 2e^-$	Titrate directly in $NaHCO_3$ solution with I_3^-.
Sn^{2+}	$SnCl_4^{2-} + 2Cl^- \rightleftharpoons SnCl_6^{2-} + 2e^-$	Sn(IV) is reduced to Sn(II) with granular Pb or Ni in 1 M HCl and titrated in the absence of oxygen.
N_2H_4	$N_2H_4 \rightleftharpoons N_2 + 4H^+ + 4e^-$	Titrate in $NaHCO_3$ solution.
SO_2	$SO_2 + H_2O \rightleftharpoons H_2SO_3$ $H_2SO_3 + H_2O \rightleftharpoons SO_4^{2-} + 4H^+ + 2e^-$	Add SO_2 (or H_2SO_3 or HSO_3^- or SO_3^{2-}) to excess standard I_3^- in dilute acid and back-titrate unreacted I_3^- with standard thiosulfate.
H_2S	$H_2S \rightleftharpoons S(s) + 2H^+ + 2e^-$	Add H_2S to excess I_3^- in 1 M HCl and back-titrate with thiosulfate.
Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}	$M^{2+} + H_2S \rightarrow MS(s) + 2H^+$ $MS(s) \rightleftharpoons M^{2+} + S + 2e^-$	Precipitate and wash metal sulfide. Dissolve in 3 M HCl with excess standard I_3^- and back-titrate with thiosulfate.
Cysteine, glutathione, thioglycolic acid, mercaptoethanol	$2RSH \rightleftharpoons RSSR + 2H^+ + 2e^-$	Titrate the sulfhydryl compound at pH 4–5 with I_3^-.
HCN	$I_2 + HCN \rightleftharpoons ICN + I^- + H^+$	Titrate in carbonate-bicarbonate buffer, using *p*-xylene as an extraction indicator.
$H_2C{=}O$	$H_2CO + 3OH^- \rightleftharpoons HCO_2^- + 2H_2O + 2e^-$	Add excess I_3^- plus NaOH to the unknown. After 5 min, add HCl and back-titrate with thiosulfate.
Glucose (and other reducing sugars)	$\begin{matrix} O \\ \| \\ RCH \end{matrix} + 3OH^- \rightleftharpoons RCO_2^- + 2H_2O + 2e^-$	Add excess I_3^- plus NaOH to the sample. After 5 min, add HCl and back-titrate with thiosulfate.
Ascorbic acid (vitamin C)	Ascorbate + $H_2O \rightleftharpoons$ dehydroascorbate + $2H^+ + 2e^-$	Titrate directly with I_3^-.
H_3PO_3	$H_3PO_3 + H_2O \rightleftharpoons H_3PO_4 + 2H^+ + 2e^-$	Titrate in $NaHCO_3$ solution.

Table 16-5 Titration of I_3^- produced by analyte (iodometric titrations)

Species analyzed	Reaction	Notes
Cl_2	$Cl_2 + 3I^- \rightleftharpoons 2Cl^- + I_3^-$	Reaction in dilute acid.
$HOCl$	$HOCl + H^+ + 3I^- \rightleftharpoons Cl^- + I_3^- + H_2O$	Reaction in 0.5 M H_2SO_4.
Br_2	$Br_2 + 3I^- \rightleftharpoons 2Br^- + I_3^-$	Reaction in dilute acid.
BrO_3^-	$BrO_3^- + 6H^+ + 9I^- \rightleftharpoons Br^- + 3I_3^- + 3H_2O$	Reaction in 0.5 M H_2SO_4.
IO_3^-	$2IO_3^- + 16I^- + 12H^+ \rightleftharpoons 6I_3^- + 6H_2O$	Reaction in 0.5 M HCl.
IO_4^-	$2IO_4^- + 22I^- + 16H^+ \rightleftharpoons 8I_3^- + 8H_2O$	Reaction in 0.5 M HCl.
O_2	$O_2 + 4Mn(OH)_2 + 2H_2O \rightleftharpoons 4Mn(OH)_3$ $2Mn(OH)_3 + 6H^+ + 6I^- \rightleftharpoons 2Mn^{2+} + 2I_3^- + 6H_2O$	The sample is treated with Mn^{2+}, NaOH, and KI. After 1 min, it is acidified with H_2SO_4, and the I_3^- is titrated.
H_2O_2	$H_2O_2 + 3I^- + 2H^+ \rightleftharpoons I_3^- + 2H_2O$	Reaction in 1 M H_2SO_4 with NH_4MoO_3 catalyst.
O_3[a]	$O_3 + 3I^- + 2H^+ \rightleftharpoons O_2 + I_3^- + H_2O$	O_3 is passed through neutral 2 wt % KI solution. Add H_2SO_4 and titrate.
NO_2^-	$2HNO_2 + 2H^+ + 3I^- \rightleftharpoons 2NO + I_3^- + 2H_2O$	The nitric oxide is removed (by bubbling CO_2 generated in situ) prior to titration of I_3^-.
As^{5+}	$H_3AsO_4 + 2H^+ + 3I^- \rightleftharpoons H_3AsO_3 + I_3^- + H_2O$	Reaction in 5 M HCl.
$S_2O_8^{2-}$	$S_2O_8^{2-} + 3I^- \rightleftharpoons 2SO_4^{2-} + I_3^-$	Reaction in neutral solution. Then acidify and titrate.
Cu^{2+}	$2Cu^{2+} + 5I^- \rightleftharpoons 2CuI(s) + I_3^-$	NH_4HF_2 is used as a buffer.
$Fe(CN)_6^{3-}$	$2Fe(CN)_6^{3-} + 3I^- \rightleftharpoons 2Fe(CN)_6^{4-} + I_3^-$	Reaction in 1 M HCl.
MnO_4^-	$2MnO_4^- + 16H^+ + 15I^- \rightleftharpoons 2Mn^{2+} + 5I_3^- + 8H_2O$	Reaction in 0.1 M HCl.
MnO_2	$MnO_2(s) + 4H^+ + 3I^- \rightleftharpoons Mn^{2+} + I_3^- + 2H_2O$	Reaction in 0.5 M H_3PO_4 or HCl.
$Cr_2O_7^{2-}$	$Cr_2O_7^{2-} + 14H^+ + 9I^- \rightleftharpoons 2Cr^{3+} + 3I_3^- + 7H_2O$	Reaction in 0.4 M HCl requires 5 min for completion and is particularly sensitive to air oxidation.
Ce^{4+}	$2Ce^{4+} + 3I^- \rightleftharpoons 2Ce^{3+} + I_3^-$	Reaction in 1 M H_2SO_4.

a. The pH must be ≥7 when O_3 is added to I^-. In acidic solution each O_3 produces 1.25 I_3^-, not 1 I_3^-.

[N. V. Klassen, D. Marchington, and H. C. E. McGowan, *Anal. Chem.* **1994**, *66*, 2921.]

Can be used to analyze oxidants and reductants

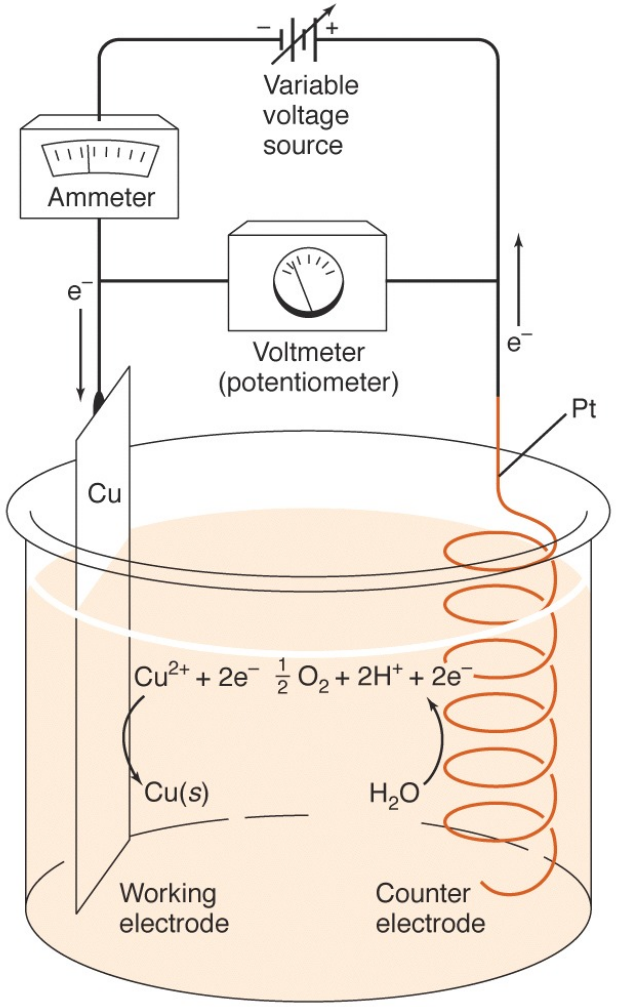
Electroanalysis

Thermodynamic and Kinetic

- If there is no net current passing through the electrochemical cell, the system is at thermodynamically equilibrium state. The potential can be calculated by Nernst equation.
- If there is net current passing through, the system is away from the thermodynamic equilibrium state, thus the potential can not be calculated by Nernst equation

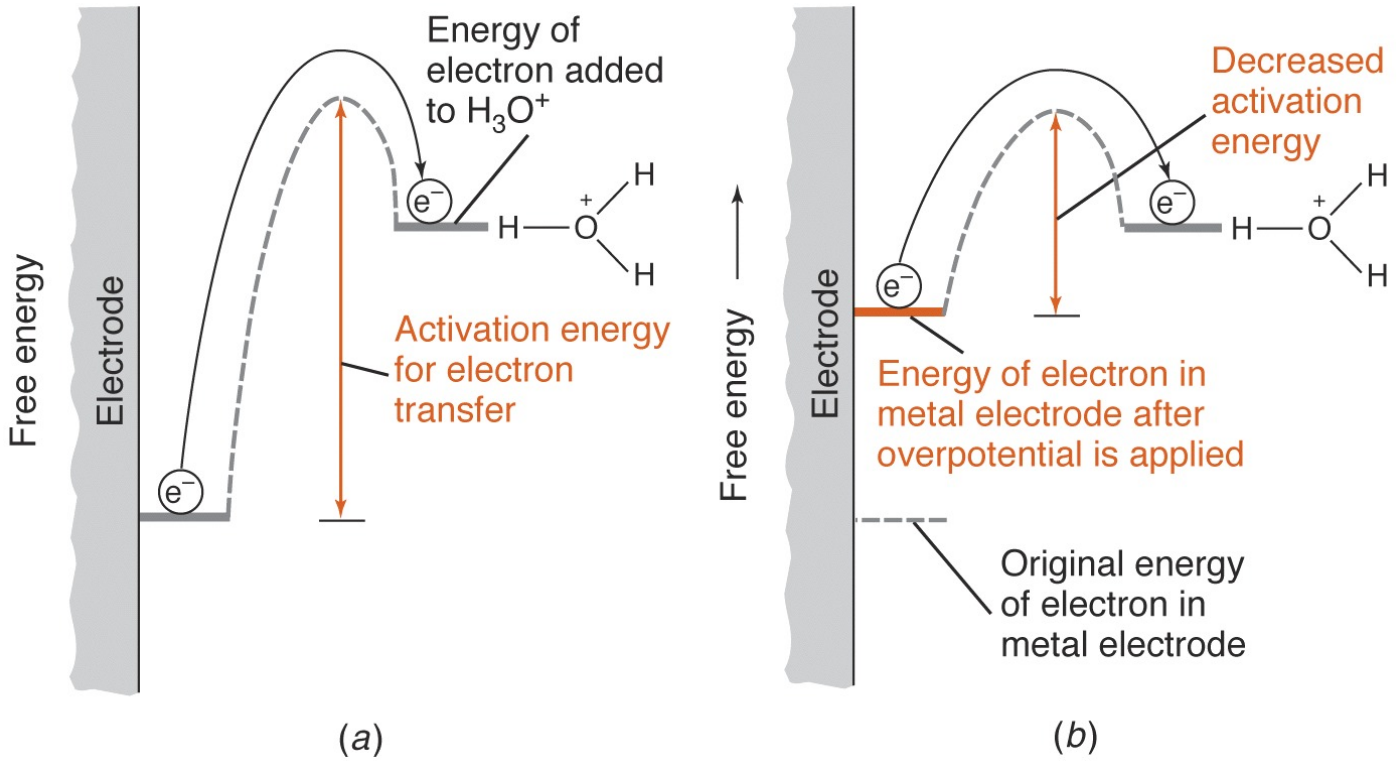
Kinetics of electrochemical system

- When Current passing through the system, the potential will move away from that of equilibrium state for three reasons
  - Overpotential
  - IR drop
  - Concentration polarization



Overpotential

- Overpotential is to overcome the activation of energy barrier of the reaction



IR drop

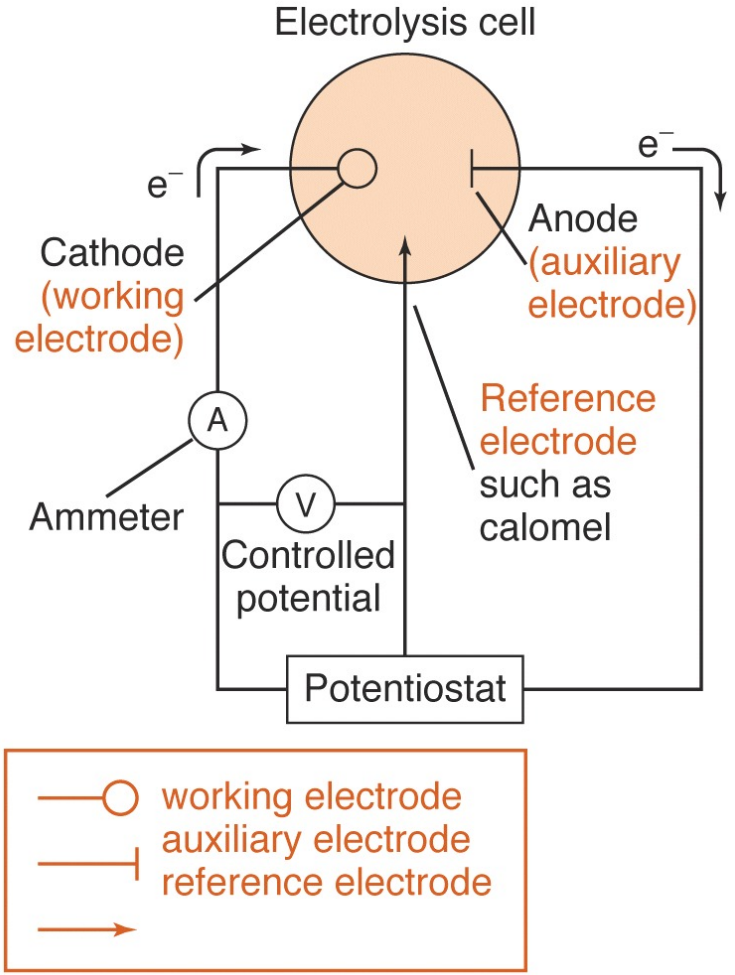
- Inevitably, the electrochemical system will have ohimic resistance, when the current runs through the system, the voltage will drop due the ohmic resistance:
  $\Delta V = IR$

Concentration Overpotential

- Due to the concentration gradient from the surface of the electrode to the bulk of the solution.

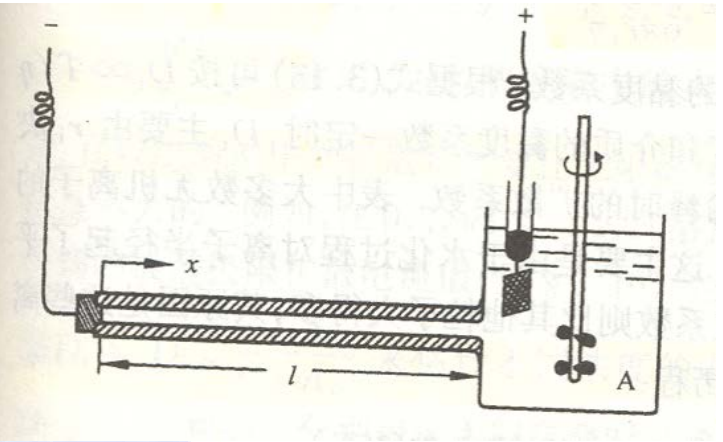
Three electrode system

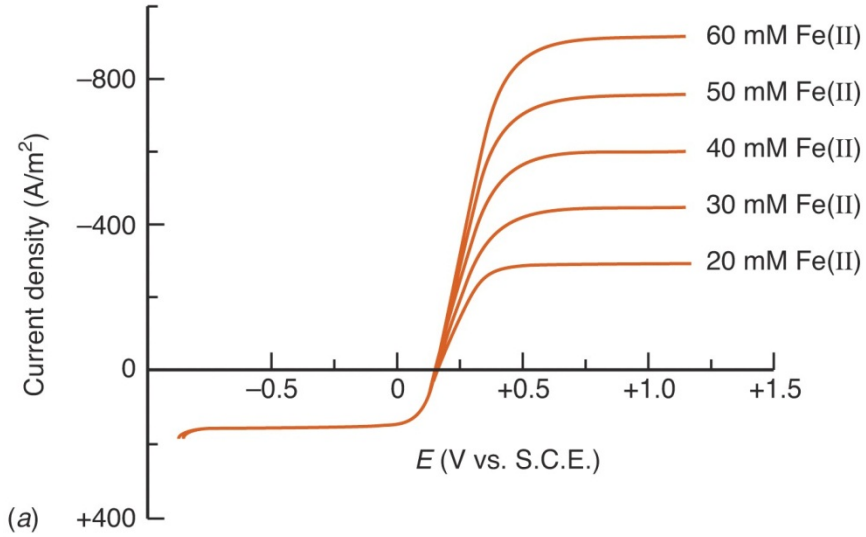
- Working electrode: where the analytical reaction happens
- Counter electrode: for the current to flow and make a close circuit.
- Reference electrode: no current pass through and serve as a reference point for potential measurement
- Why three electrode system is needed??

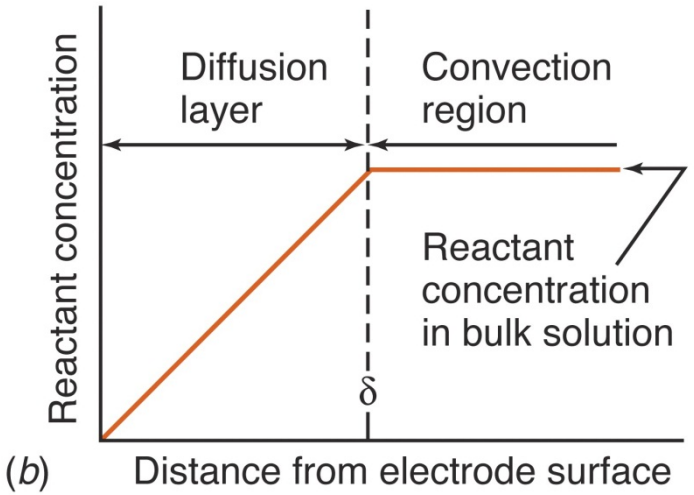


Amperometry

- Diffusion limited current







Three electrode system

- Working electrode: where the analytical reaction happens
- Counter electrode: for the current to flow and make a close circuit.
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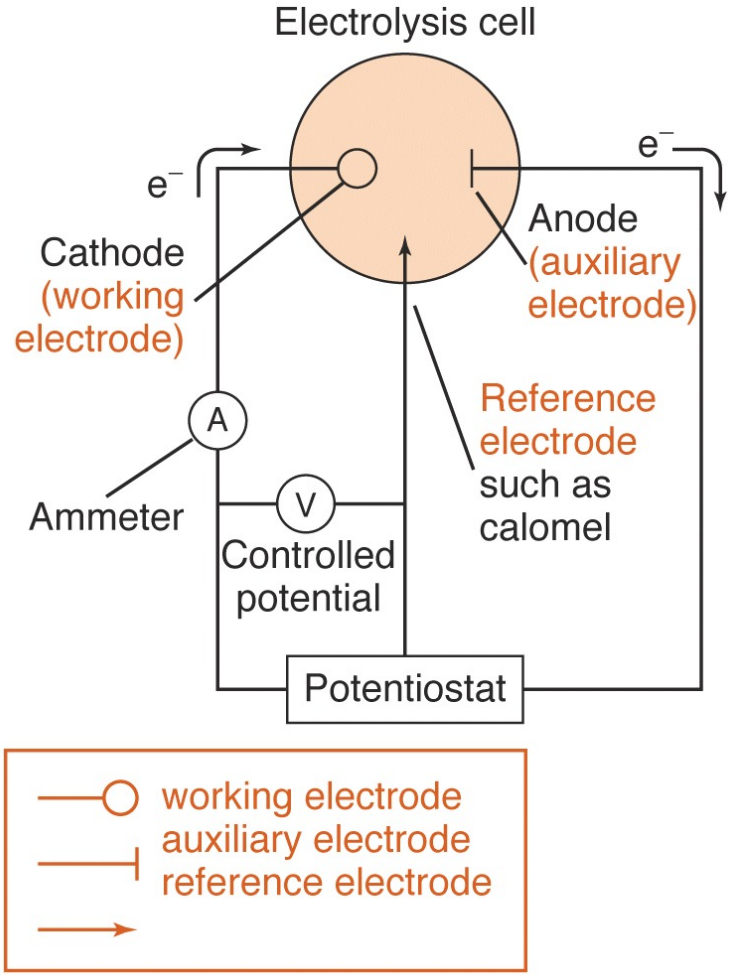
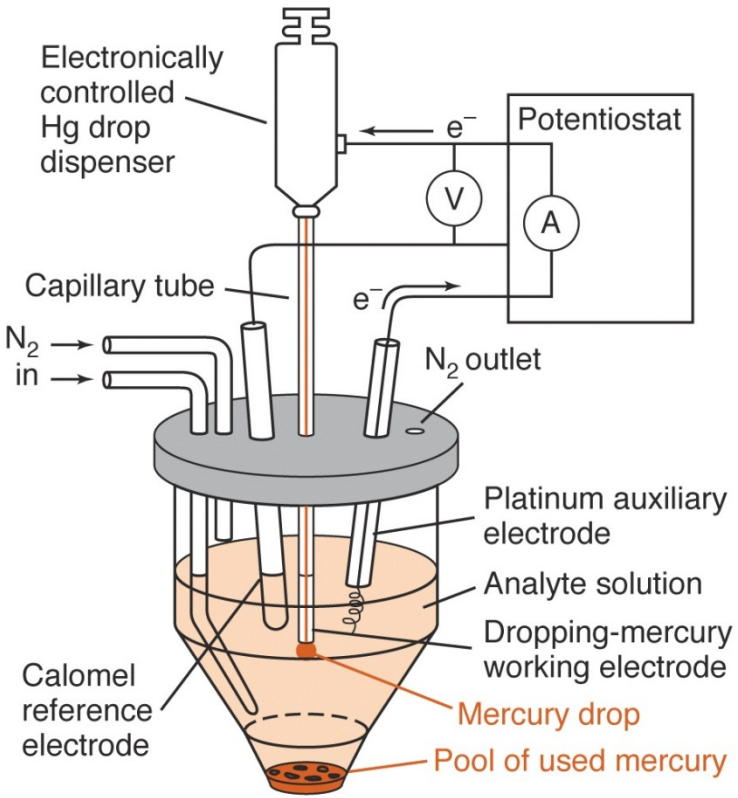
- Why three electrode system is needed??

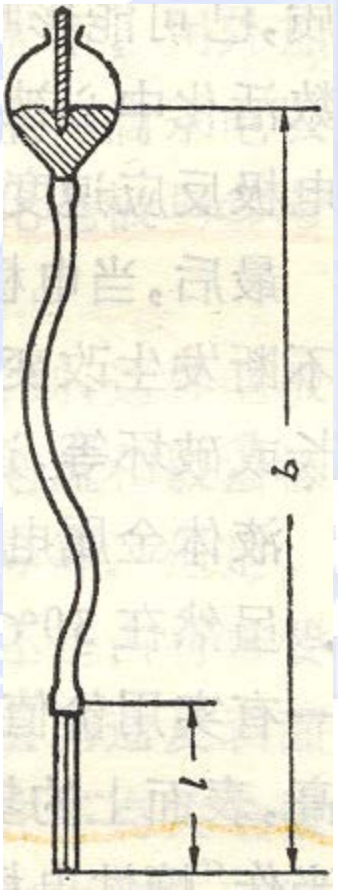


Polarography: Historical Significance

- Polarograph developed by Jaroslav Heyrovsky in 1922.
- Heyrovsky won Nobel Prize
- Polarograph is THE most widely used electro analytical method
- Still one of the most reliable analytical method for ppm level impurities.

Setup Polarograph





- Dropping Hg electrode (DME)
- Working under limited diffusion current

Polarography curve

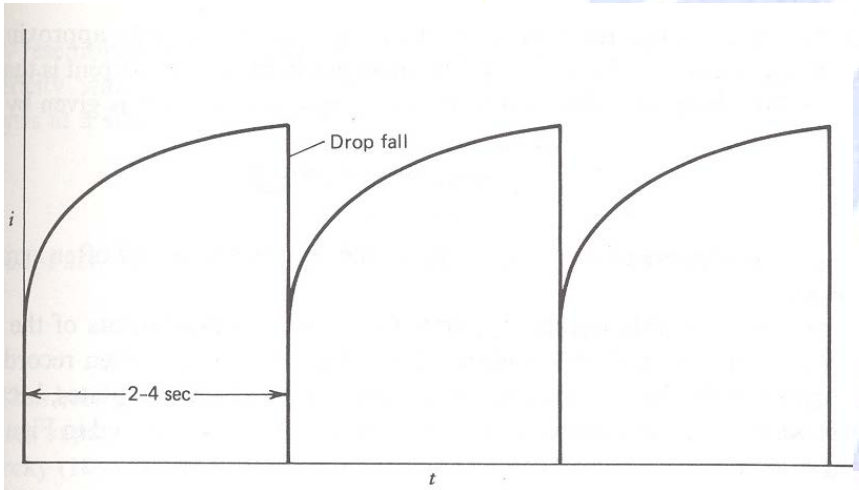
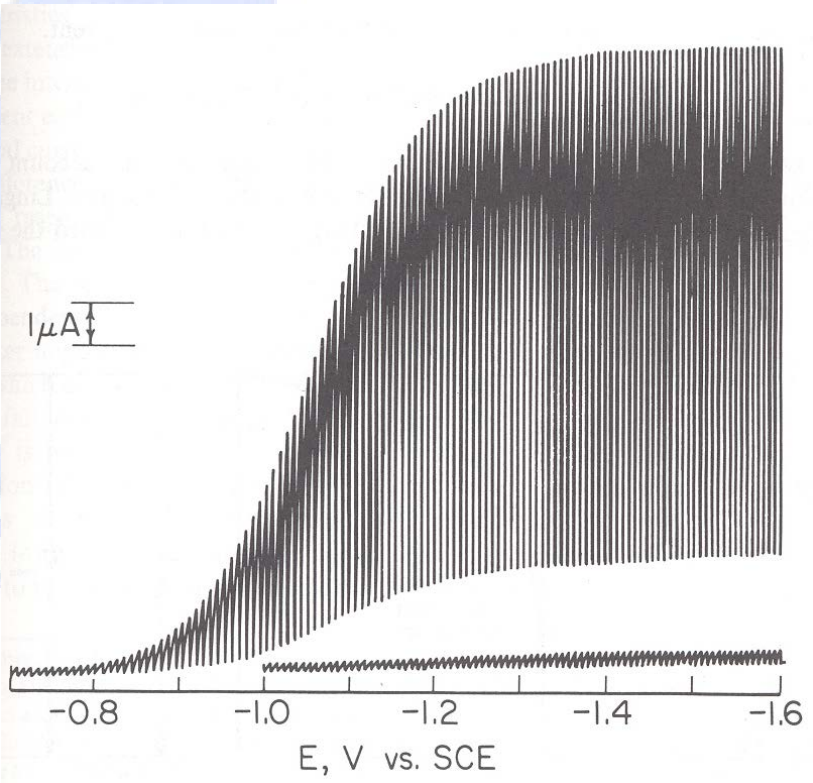


Figure 5.3.2
Current growth during three successive drops of a DME.

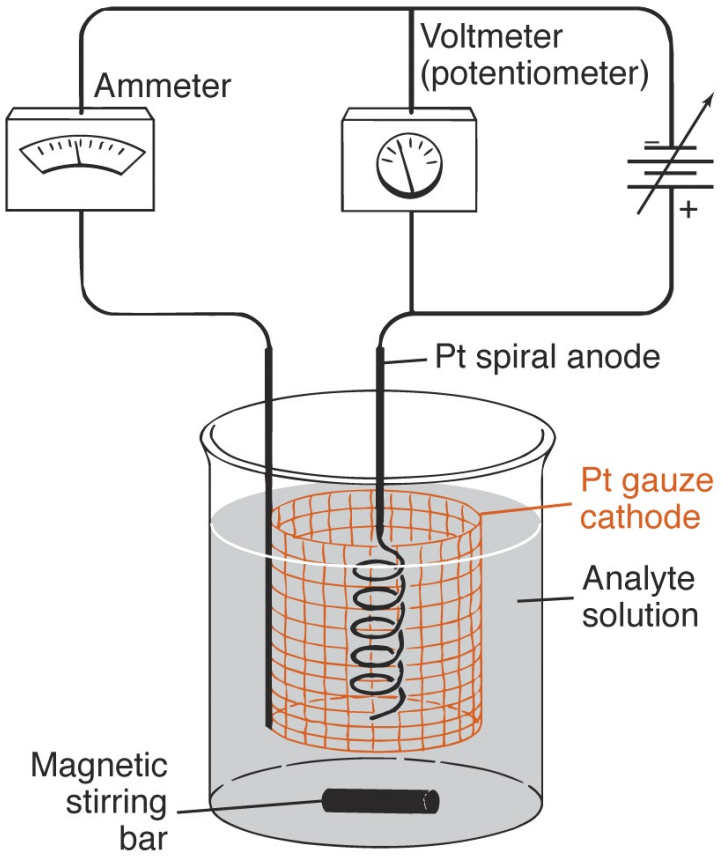


Example

- $Cd^{2+}+2e \rightarrow Cd$ E (vs SCE)=-0.64 V
  $Zn^{2+}+2e \rightarrow Zn$ E (vs SCE)=-1.10 V

Electrogravimetric Analysis

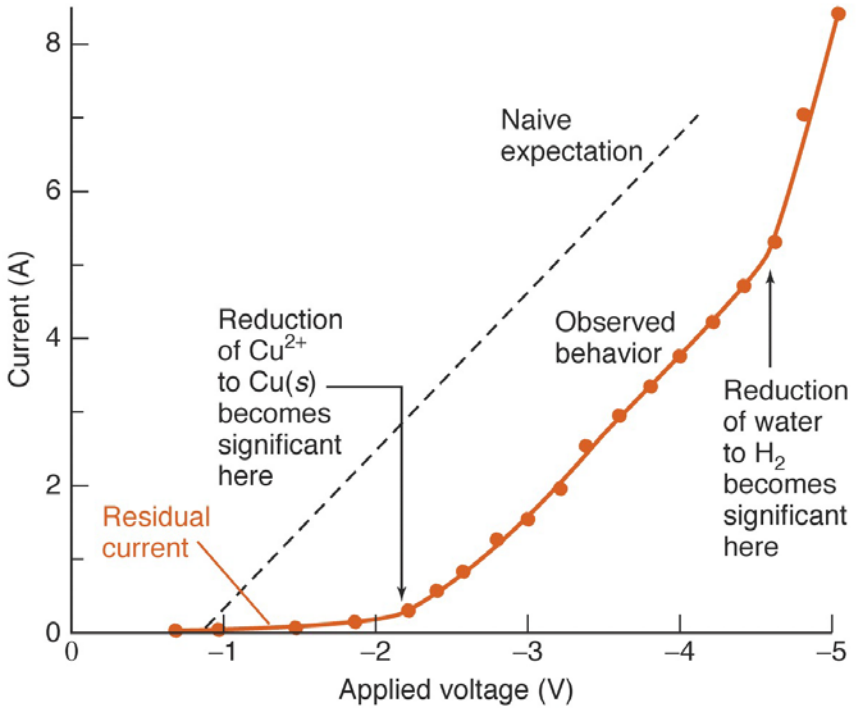
- Quantitatively electrochemically deposit analyte onto electrode, the amount of analyte can be measured by measure the weight change of the electrode.
- The end point determination
  - Color change e.g. $Cu^{2+} + 2e \rightarrow Cu$
  - Deposition on fresh electrode surface.



(*a*)

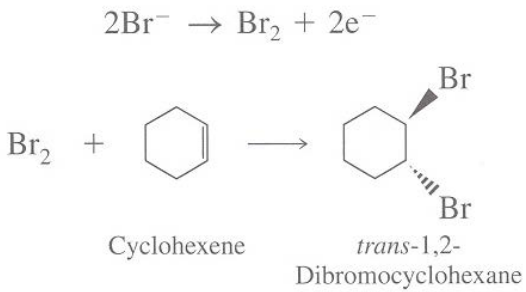
Electrogravimetric Analysis

- Current-Voltage relationship
- Interference of other ions
- To limit the potential, depolarizer is added to prevent hydrogen or oxygen evolution.
  e.g.
  $NO_3^- + 10H^+ + 8e \rightarrow NH_4^+ + 3H_2O$
  Prevent hydrogen evolution

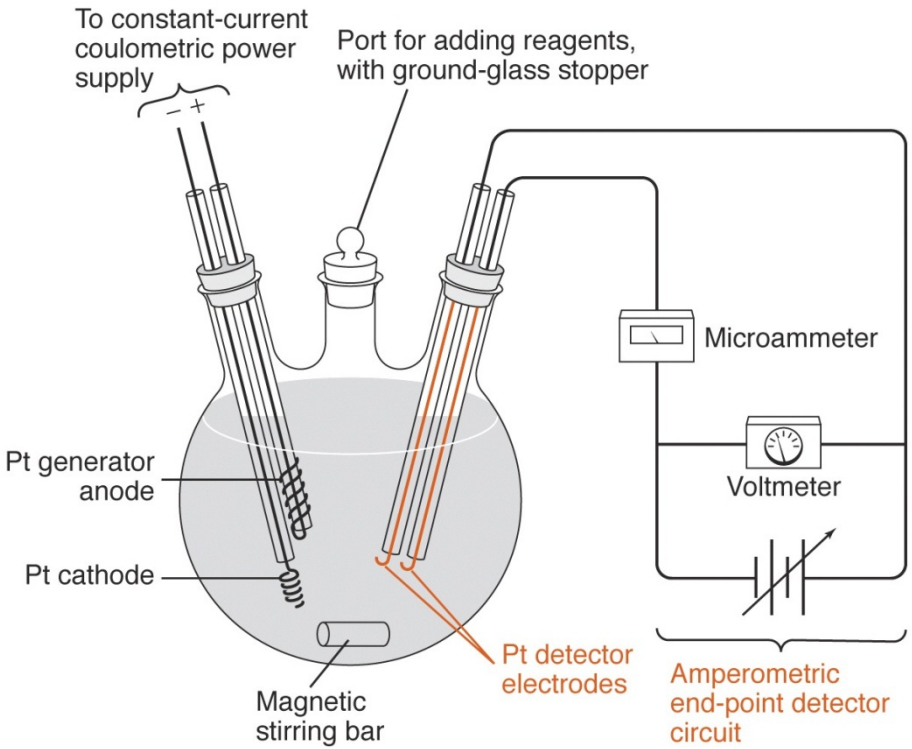


Coulometry

- Generating titrate electrochemically, the amount of titrate generated can be measured by counting electrons.



- Detector anode $2Br^- \rightarrow Br_2 + 2e$
- Detector cathode $Br_2 + 2e \rightarrow Br^-$

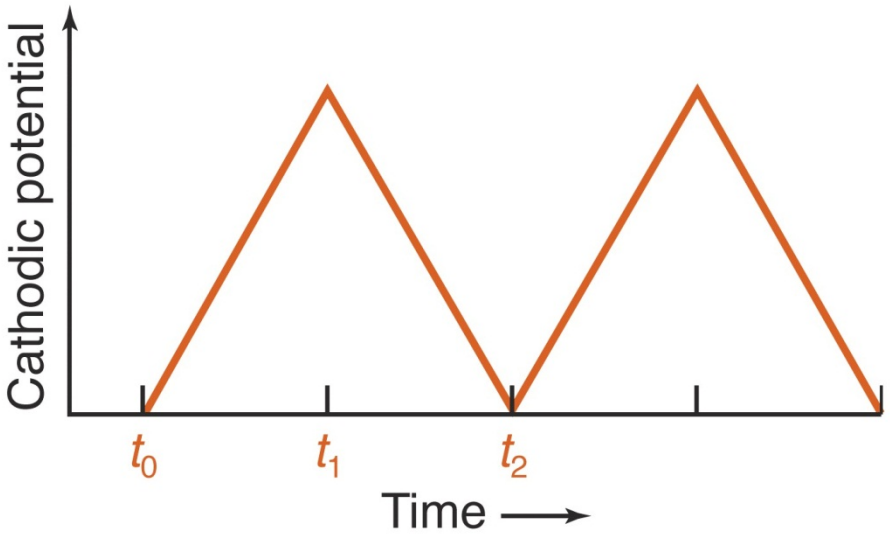


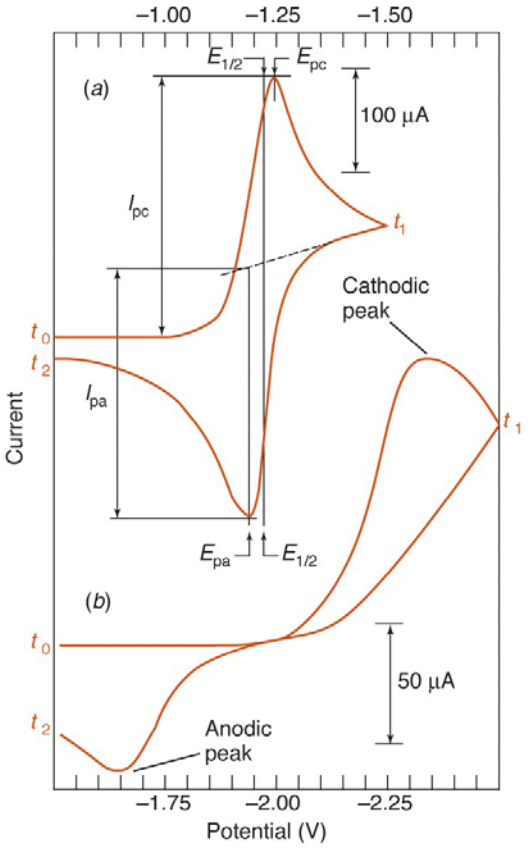
Coulometry

- Advantage of Coulometry titration
  - Precision
  - Sensitivity
  - Generating otherwise unstable titrant in-site
- Constant current $Q = I \times t$
- Constant potential
  - 3-electrode system
  - $Q = \int I \times t$
  - More sensitive and selective

Cyclic voltammetry

- Linear Sweep Voltammetry (LSV)
- Cyclic Voltammetry (CV)-good for the study of reaction mechanism
  - Initial potential
  - End potential
  - Sweep rate (mV/s)





Karl Fischer Titration of H_2O

- Detecting trace amount of water in organic solution.
- An example of coulometric titration