Chapter 22

Bulk Electrolysis:
Electrogravimetry and Coulometry

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Oscar Statuette

Jewelry

Chromium Bumper

Electroplating: https://www.youtube.com/watch?v=OxhCU_jBiOA

How it Works: Rhodium Plating for Jewelry https://www.youtube.com/watch?v=Jfqjor_616Q

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Definition

- **Bulk Electrolysis deals with methods that involve electrolysis producing a quantitative change in oxidation state**
- **Example: In a mixture solution of Zn^{2+} and Cu^{2+}, convert all Cu^{2+} to Cu metal and leave Zn^{2+} in the solution.**

  → Hold the working electrode (e.g. Cu) potential at a certain value (positive than that for Zn reduction)

  $Cu^{2+}(aq) + 2e \rightarrow Cu(s)$

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Features of Bulk Electrolysis Cells

- Big working and counter electrodes—~100 times larger than normal electrodes (e.g., in CV)
- Large cell currents (mA vs μA-nA)
- Stirring Solution (mainly convection)
- working and counter electrode placed in two separated cell compartments (avoiding by-products produced at the counter electrode)

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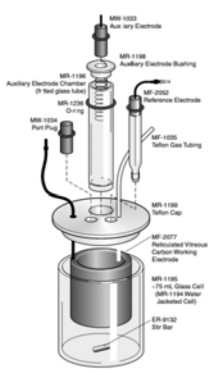
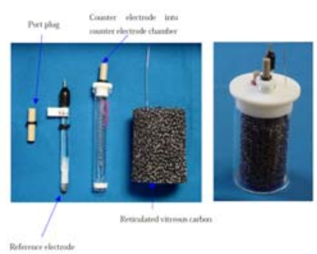
An example of bulk electrolysis cell produced by Bioanalytical System, Inc.





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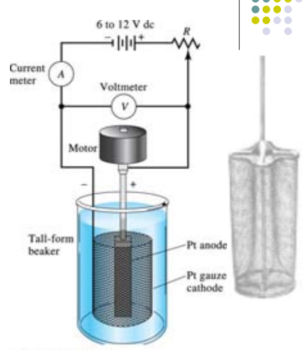
Electrogravimetric Methods

- Electrogravimetry without potential control.
- Electrogravimetry is potential-controlled—potentiostatic method.



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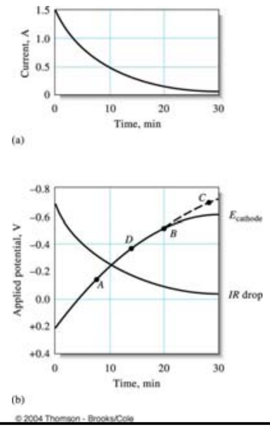

$Cu^{2+} \rightarrow Cu(s)$

$E_{cathode} = E^0 + (0.0592/2)\log[Cu^{2+}]$

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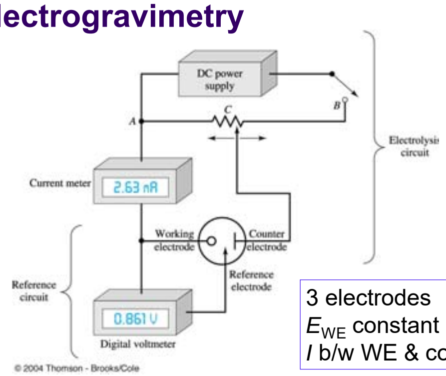
Controlled-Potential Electrogravimetry



3 electrodes
E_{WE} constant
I b/w WE & counter

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TABLE 22-2
Some Applications of Controlled-Potential Electrolysis*

Metal	Potential vs. SCE	Electrolyte	Other Elements That Can Be Present
Ag	+ 0.10	Acetic acid/acetate buffer	Cu and heavy metals
Cu	− 0.30	Tartrate + hydrazine + Cl^-	Bi, Sb, Pb, Sn, Ni, Cd, Zn
Bi	− 0.40	Tartrate + hydrazine + Cl^-	Pb, Zn, Sb, Cd, Sn
Sb	− 0.35	HCl + hydrazine at 70°C	Pb, Sn
Sn	− 0.60	HCl + hydroxylamine	Cd, Zn, Mn, Fe
Pb	− 0.60	Tartrate + hydrazine	Cd, Sn, Ni, Zn, Mn, Al, Fe
Cd	− 0.80	HCl + hydroxylamine	Zn
Ni	− 1.10	Ammoniacal tartrate + sodium sulfite	Zn, Al, Fe

*From J. J. Lingane, *Electroanalytical Chemistry*, 2nd ed., p. 413. New York: Interscience, 1958. This material is used by permission of John Wiley & Sons, Inc.

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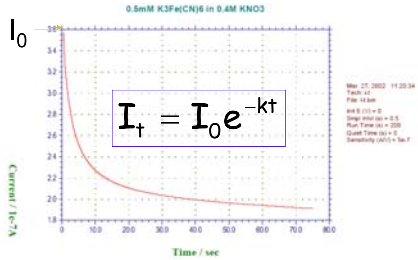
Current ~ Time Behavior



$$I_t = I_0 e^{-kt}$$

Electrochemical cell current decays exponentially as a function of time

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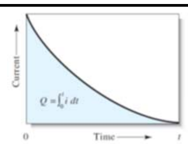
$$Q = \int_0^t I_t dt = \int_0^t I_0 e^{-kt} dt$$



- The quantity of electricity is obtained by integrating the current-time function
- *k* can be determined by a regression analysis of the I_t-t behavior
- *Q* may be determined by using a Mechanical or electronic coulometer: a current-time integrator
- *Q* may also be determined by using a chemical coulometer

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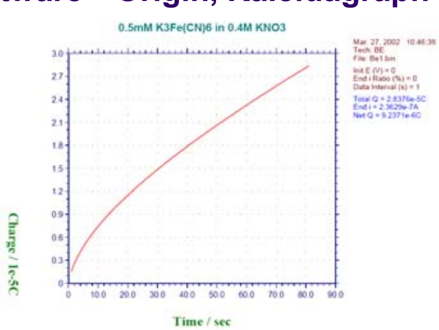
Integrate the I_t-t curve with software—Origin, Kaleidagraph etc



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Once *Q* is determined, Faraday's law can be used to determine the mass of analyte that underwent electrolysis

$$Q = nFN_A = nF \bullet (W / M.W.) = nF \bullet (CV)_A$$

n = number of electron transfer involved

F = Fraraday's constant $(96,487 \frac{coul}{mol\ e^-})$

N_A = number of analyte moles reacted

W = Weight (mass) of analyte (gram)

$M.W.$ = Molecular weight of analyte (grams/mol)

$$W = \frac{Q \bullet M.W.}{nF}$$

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Constant Current Coulometry

sometimes referred to as **coulometric titration** in which the titrant is electrons

- The electrons may let an analyte reduced or oxidized
- The electrons may also produce a species that reacts with the analyte
- The calculation of quantity of electricity involved is straight forward
  - **Q = I x t**

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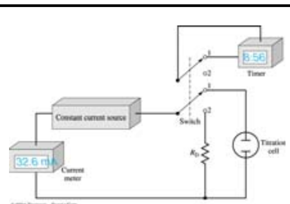

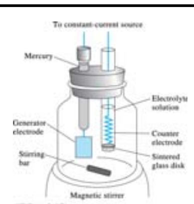

Titration of halides (X^-) in solution:

Ag (anode) -e = Ag^+ (quantatively)

$Ag^+ + X^- \rightleftharpoons AgX\downarrow$ (precipitation titration)

Coulometric Titration Apparatus

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Exercise

To analyze a brass alloy, a 0.442-g sample is dissolved in acid and diluted to volume in a 500-mL volumetric flask. Electrolysis of a 10.00-mL sample at –0.3 V versus a SCE reduces Cu^{2+} to Cu, requiring a total charge of 16.11 C. Adjusting the potential to –0.6 V versus a SCE and completing the electrolysis requires 0.442 C to reduce Pb^{2+} to Pb. Report the %w/w Cu and Pb in the alloy.

Solution

$$N_{Cu} = \frac{Q}{nF} = \frac{16.11\ \mathrm{C}}{\frac{2\ \mathrm{mol\ e^-}}{\mathrm{mol\ Cu}} \times \frac{96487\ \mathrm{C}}{\mathrm{mol\ e^-}}} = 8.348 \times 10^{-5}\ \mathrm{mol\ Cu}$$

$$8.348 \times 10^{-5}\ \mathrm{mol\ Cu} \times \frac{63.55\ \mathrm{g\ Cu}}{\mathrm{mol\ Cu}} = 5.301 \times 10^{-3}\ \mathrm{g\ Cu}$$

$$N_{Pb} = \frac{Q}{nF} = \frac{0.422\ \mathrm{C}}{\frac{2\ \mathrm{mol\ e^-}}{\mathrm{mol\ Pb}} \times \frac{96487\ \mathrm{C}}{\mathrm{mol\ e^-}}} = 2.19 \times 10^{-6}\ \mathrm{mol\ Pb}$$

$$2.19 \times 10^{-6}\ \mathrm{mol\ Pb} \times \frac{207.2\ \mathrm{g\ Pb}}{\mathrm{mol\ Cu}} = 4.53 \times 10^{-4}\ \mathrm{g\ Pb}$$

Cu% = 60.0%

Pb% = 5.12%

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Chapter 22 Summary

- Transport of ions by diffusion, migration, and convection
- Selectivity of electrolysis
- Controlled-potential electrolysis
- Electrogravimetry
- Coulometry
- Determination of charge
- Coulometric titrations

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Important Equations

$Q = It$ For constant current I

$Q = \int_0^t i\,dt$ For variable current i

$n_A = \dfrac{Q}{nF} = \dfrac{mass}{F.W.}$ Faraday's law

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