

Unit 2 A
Coulometry and
Electrogravimetry

Dynamic Electrochemical Methods of analysis Electrolysis

Electrogravimetric and Coulometric Methods

- For a cell to do any useful work or for an electrolysis to occur, a significant current must flow.
- Whenever current flows, three factors act to decrease the output voltage of a galvanic cell or to increase the applied voltage needed for electrolysis.
- These factors are called the *ohmic potential*, *concentration overpotential (polarization)*, and *activation overpotential*.

Coulometry and Electrogravimetry

- A potential is applied forcing a nonspontaneous chemical reaction to take place
- How much voltage should be applied?
- $E_{\text{applied}} = E_{\text{back}} + iR$
- E_{back} = voltage require to cancel out the normal forward reaction (galvanic cell reaction)
- $iR = iR$ drop. The work applied to force the nonspontaneous reaction to take place. R is the cell resistance
- $E_{\text{back}} = E_{\text{reversible (galvanic)}} + \text{Overvoltage}$
- **Overvoltage:** it is the extra potential that must be applied beyond what we predict from the Nernst equation

Ohmic Potential

- The voltage needed to force current (ions) to flow through the cell is called the ohmic potential and is given by Ohm's law:

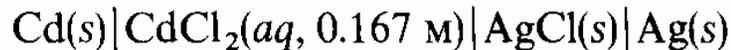
$$E_{\text{ohmic}} = IR$$

where I is the current and R is the resistance of the cell.

- In a galvanic cell at equilibrium, there is no ohmic potential because $I = 0$.
- If a current is drawn from the cell, the cell voltage decreases because part of the free energy released by the chemical reaction is needed to overcome the resistance of the cell itself.
- The voltage applied to an electrolysis cell must be great enough to provide the free energy for the chemical reaction and to overcome the cell resistance.
- In the absence of any other effects, *the voltage of a galvanic cell is decreased by IR , and the magnitude of the applied voltage in an electrolysis must be increased by IR in order for current to flow.*

EXAMPLE: Effect of Ohmic Potential

Consider the cell



in which the spontaneous chemical reaction is



In Equation 14-47, we calculated that the cell voltage should be 0.764 V. (a) If the cell has a resistance of 6.42 Ω and a current of 28.3 mA is drawn, what will be the cell voltage? (b) Suppose that the same cell is operated in reverse as an electrolysis. What voltage must be applied to reverse the reaction?

(a) In the absence of electron flow, the voltage (E_{eq} , where the subscript eq means equilibrium) is 0.764 V. With a current of 28.3 mA, the voltage will *decrease* to

$$E = E_{\text{eq}} - IR = 0.764 - (0.0283 \text{ A})(6.42 \Omega) = 0.582 \text{ V}$$

(b) By convention, the voltage applied to an electrolysis cell is given a negative sign. The voltage needed to reverse the spontaneous reaction will be

$$E = -E_{\text{eq}} - IR = -0.764 - (0.0283 \text{ A})(6.42 \Omega) = -0.946 \text{ V}$$

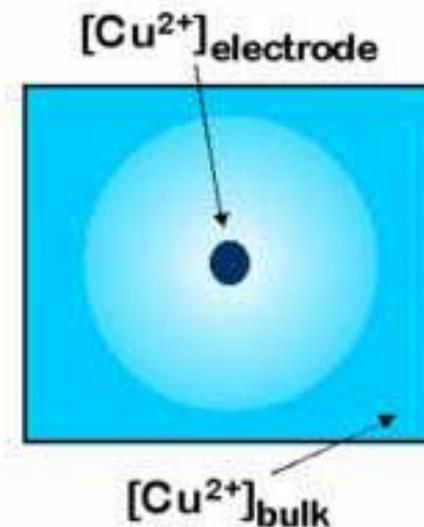
Notice that the magnitude of any galvanic cell voltage is *decreased* by the ohmic potential. The magnitude of the voltage that must be applied to any electrolysis cell is *increased* by the ohmic potential.

Overvoltage or overpotential

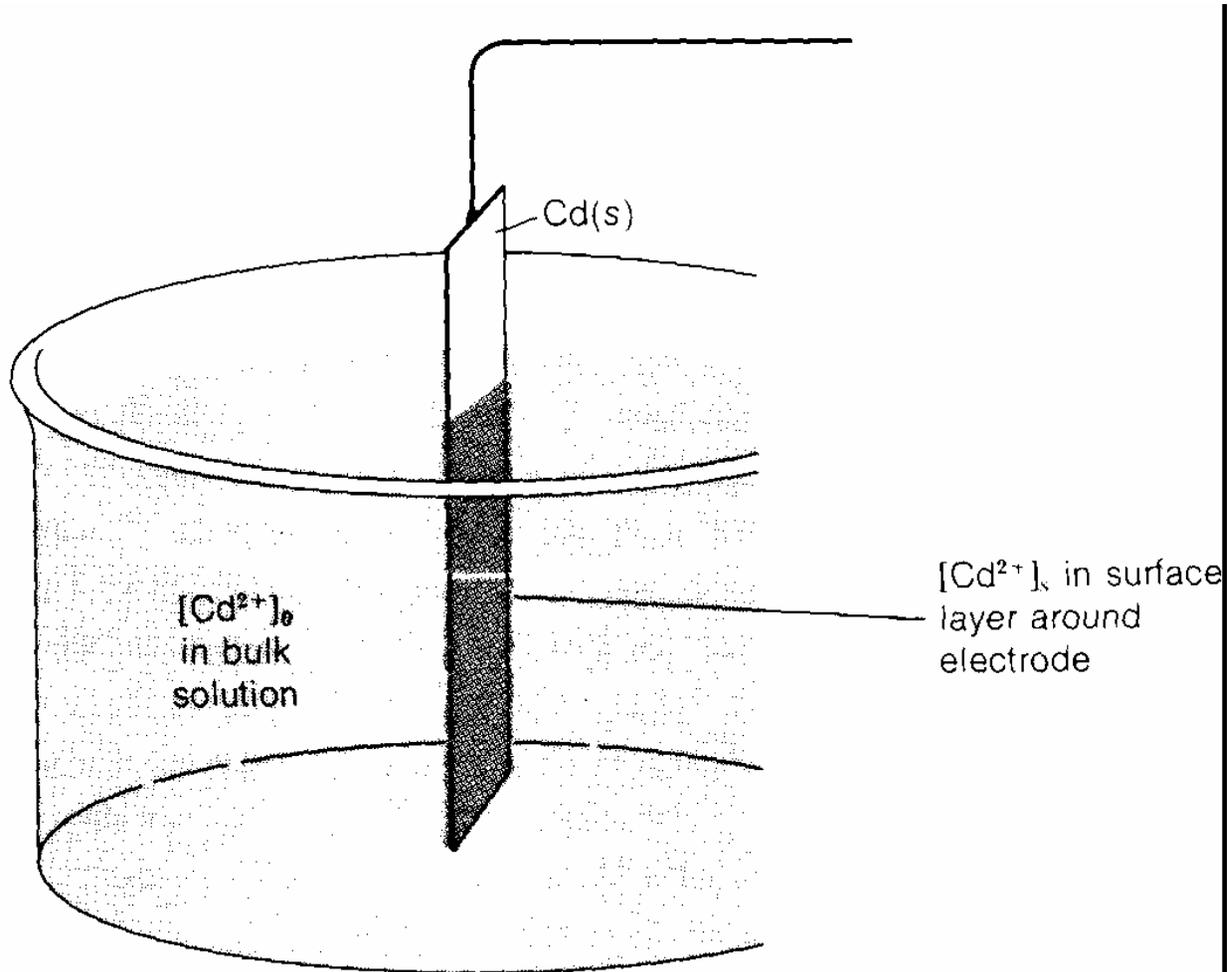
- The electrochemical cell is polarized if its actual potential is different than that expected according to Nernst equation.
- The extent of polarization is measured as overpotential η
- $\eta = E_{\text{applied}} - E_{\text{reversible(equilib)}}$
- What are the sources of overpotential?

1. Concentration overpotential (polarization)

- This takes place when the concentration at the electrode surface is different than that in the bulk solution.
- This behavior is observed when the rate of electrochemical reaction at the electrode surface is fast compared to the rate of diffusion of electroactive species from the solution bulk to the electrode surface



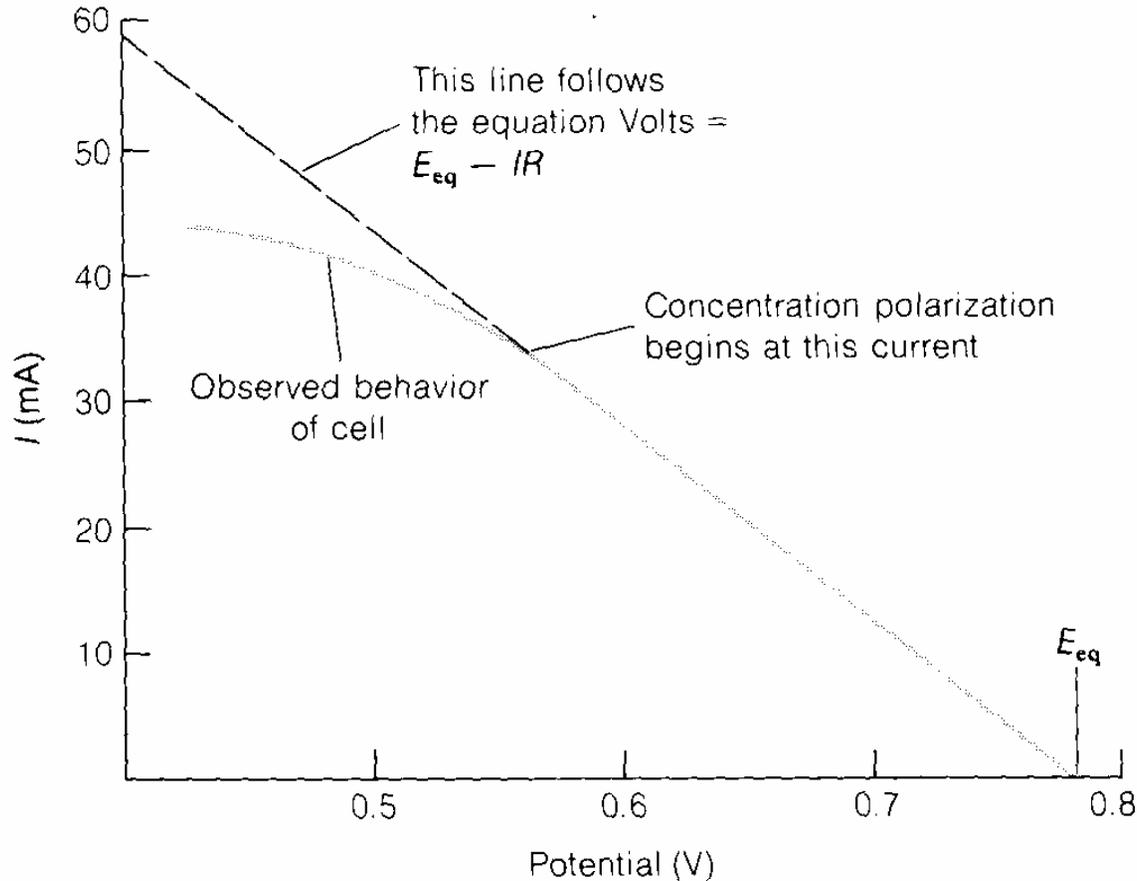
Example on concentration polarization



Partial view of cell

- The anode potential depends on $[\text{Cd}^{2+}]_s$, not $[\text{Cd}^{2+}]_o$, because $[\text{Cd}^{2+}]_s$ is the actual concentration at the electrode surface.
- Reversing the electrode reaction to write it as a reduction, the anode potential is given by the equation
- $$E_{(\text{anode})} = E^{\circ}_{(\text{anode})} - (0.05916/2) \log [\text{Cd}^{2+}]_s$$
- If $[\text{Cd}^{2+}]_s = [\text{Cd}^{2+}]_o$, the anode potential will be that expected from the bulk Cd^{2+} concentration.
- If the current is flowing so fast that Cd^{2+} cannot escape from the region around the electrode as fast as it is made, $[\text{Cd}^{2+}]_s$ will be greater than $[\text{Cd}^{2+}]_o$.
- When $[\text{Cd}^{2+}]_s$ does not equal $[\text{Cd}^{2+}]_o$, we say that concentration polarization exists.
- The anode will become more positive and the Cell voltage = $E_{(\text{cathode})} - E_{(\text{anode})}$ will decrease.

the straight line shows the behavior expected. When ions are **not transported** to or from an electrode as rapidly as they are consumed or created, we say that **concentration polarization** exists if only the ohmic potential (IR) affects the net cell voltage.



- **The deviation of the curve from the straight line at high currents is due to concentration polarization.**
- **In a galvanic cell, concentration polarization decreases the voltage below the value expected in the absence of concentration polarization.**
- **In electrolysis cells, the situation is reversed; reactant is depleted and product accumulates. Therefore the concentration polarization requires us to apply a voltage of greater magnitude (more negative) than that expected in the absence of polarization.**
- **Concentration polarization gets worse as $[M^{n+}]$ gets smaller.**

Example on Concentration overpotential

Assume:

$$[\text{Cu}^{2+}]_{\text{bulk}} = 10^{-2} \text{ M}$$

$$[\text{Cu}^{2+}]_{\text{electrode}} = 10^{-4} \text{ M}$$

then

$$E_{\text{bulk}} = 0.337 + \frac{0.0592}{2} \log(10^{-2}) = 0.278$$

$$E_{\text{electrode}} = 0.337 + \frac{0.0592}{2} \log(10^{-4}) = 0.219$$

$$\eta_{\text{conc}} = E_{\text{electrode}} - E_{\text{bulk}} = -0.059 \text{ V}$$

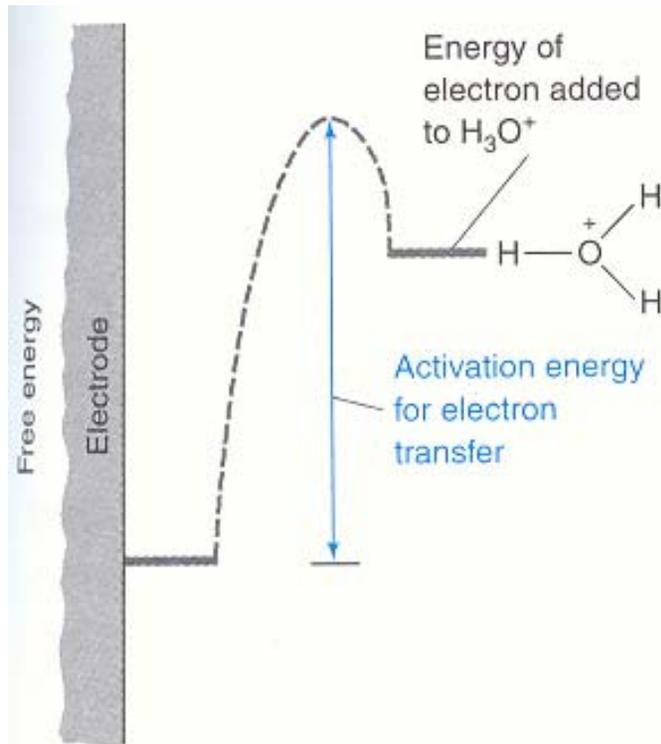
Factors that affect concentration polarization

- **Among the factors causing ions to move toward or away from the electrode are**
 - diffusion,
 - convection,
 - electrostatic attraction or repulsion.
- **Raising the temperature increases the rate of diffusion and thereby decreases concentration polarization.**
- **Mechanical stirring is very effective in transporting species through the cell.**
- **Increasing ionic strength decreases the electrostatic forces between ions and the electrode.**
- **These factors can all be used to affect the degree of polarization.**
- **Also, the greater the electrode surface area, the more current can be passed without polarization.**

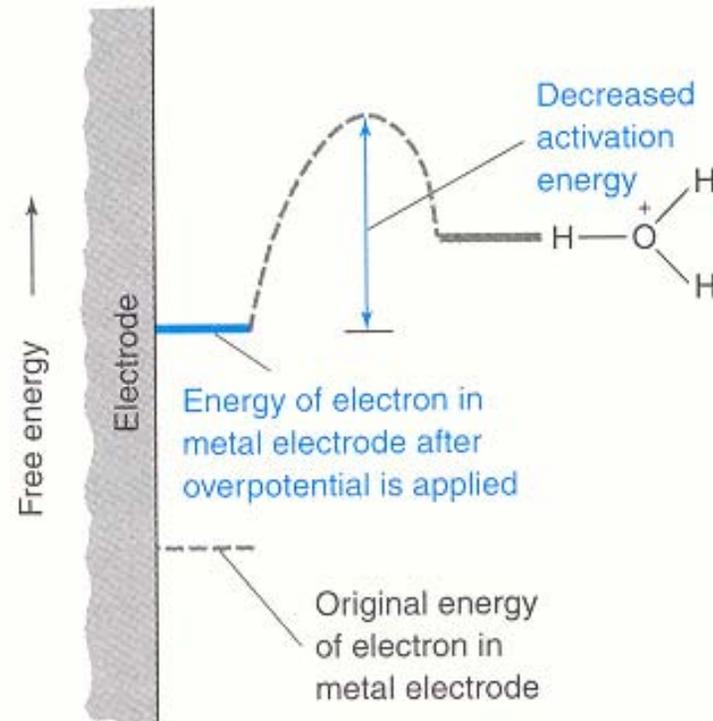
- **How can we reduce the concentration overpotential?**
 - **Increase T**
 - **Increase stirring**
 - **Increase electrode surface area: more reaction takes place**
 - **Change ionic strength to increase or decrease attraction between electrode and reactive ion.**

Activation Overpotential

- **Activation overpotential is a result of the activation energy barrier for the electrode reaction.**
- ***The faster you wish to drive an electrode reaction, the greater the overpotential that must be applied.***
 - **More overpotential is required to speed up an electrode reaction.**



(a)



(b)

How to calculate the potential required to reverse a reaction

$$E_{\text{app}} = (E_{\text{anode}} + \eta_{\text{ac}} + \eta_{\text{aa}}) - (E_{\text{cathode}} + \eta_{\text{cc}} + \eta_{\text{ca}})$$

η_{ac} = concentration overpotential at anode

η_{aa} = activation overpotential at anode

η_{cc} = concentration overpotential at cathode

η_{ca} = activation overpotential at cathode

This explains why many reactions do not proceed as expected or will not occur at all.

Example 1 on electrolysis

Can Pb^{2+} be quantitatively separated from Cu^{2+} by electrodeposition?

Assume that our solution starts with 0.1M of each metal ion.

Assume that 99.99% of each will be quantitatively deposited
Then 0.01% (10^{-5} M) will be left in the solution

Given that:



Copper

We start with 0.1 M and begin our deposition. We don't want any lead to deposit until at least 99.99% of the copper has been removed - $10^{-5}M$ Cu^{2+}

$$E = 0.337 - \frac{0.0592}{2} \log \frac{1}{10^{-5}}$$

$$E = 0.189 \text{ V}$$

Lead

It would start depositing at:

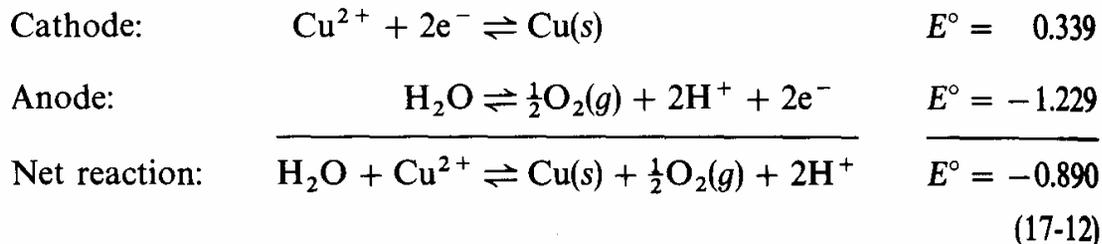
$$E = -0.126 - \frac{0.0592}{2} \log \frac{1}{0.1}$$

$$E = -0.156 \text{ V}$$

The separation is possible but our calculations neglect any overpotential

Example 2

- **Suppose that a solution containing 0.20 M Cu^{2+} and 1.0 M H^+ is electrolyzed to deposit Cu(s) on a Pt cathode and to liberate O_2 at a Pt anode. Calculate the voltage needed for electrolysis. If the resistance of this cell is 0.44 ohm. Estimate the voltage needed to maintain a current of 2.0 A. Assume that the anode overpotential is 1.28 V and there is no concentration polarization.**



Assuming that O_2 is liberated at a pressure of 0.20 atm, we naively calculate the voltage needed for the electrolysis as follows:

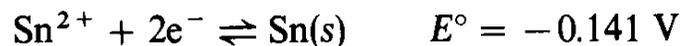
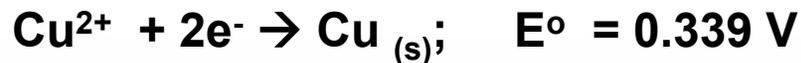
$$\begin{aligned}
 E &= E^\circ - \frac{0.05916}{n} \log \frac{P_{\text{O}_2}^{1/2} [\text{H}^+]^2}{[\text{Cu}^{2+}]} \\
 &= -0.890 - \frac{0.05916}{2} \log \frac{(0.20)^{1/2} (1.0)^2}{(0.20)} = -0.900 \text{ V} \quad (17-13)
 \end{aligned}$$

In the absence of any polarization effects, we expect that no reaction should occur if the applied voltage is more positive than -0.900 V . When the voltage is more negative than -0.900 V , we expect deposition of Cu and liberation of O_2 to occur.

$$\begin{aligned}
 E(\text{applied}) &= \underbrace{E(\text{cathode}) - E(\text{anode})}_{E_{\text{eq}}} - IR - \underbrace{\text{overpotential}}_{1.28 \text{ V}} \\
 &= 0.900 \text{ V} \quad \text{(from Table 17-1)} \\
 &\quad \text{(from Equation 17-13)} \\
 &= -0.900 - (2.0 \text{ A})(0.44 \ \Omega) - 1.28 \text{ V} \\
 &= -0.900 - 0.88 - 1.28 = -3.04 \text{ V}
 \end{aligned}$$

Example 2

- **A solution containing 0.1M Cu^{2+} and 0.1 M Sn^{2+} calculate:**
 - the potential at which Cu^{2+} starts deposition.
 - The potential at which Cu^{2+} is completely deposited (99.99% deposition).
 - The potential at which Sn^{2+} starts deposition.
- **Would Sn^{2+} be reduced before the copper is completely deposited?**
- **From the standard potentials given below we expect that Cu^{2+} be reduced more easily than Sn^{2+}**



The cathode potential at which Cu^{2+} ought to be reduced is calculated as

$$E(\text{cathode}) = 0.339 - \frac{0.05916}{2} \log \frac{1}{0.1} = 0.31 \text{ V} \quad (17-18)$$

If 99.99% of the Cu^{2+} were deposited, the concentration of Cu^{2+} remaining in solution would be 10^{-5} M , and the cathode potential required to continue reduction would be

$$E(\text{cathode}) = 0.339 - \frac{0.05916}{2} \log \frac{1}{10^{-5}} = 0.19 \text{ V} \quad (17-19)$$

At a cathode potential of 0.19 V, then, rather complete deposition of copper is expected. Would Sn^{2+} be reduced at this potential? To deposit $\text{Sn}(s)$ from a solution containing 0.1 M Sn^{2+} , a cathode potential of -0.17 V is required:

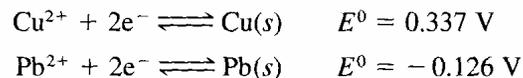
$$\begin{aligned} E(\text{cathode, for reduction of } \text{Sn}^{2+}) &= -0.141 - \frac{0.05916}{2} \log \frac{1}{[\text{Sn}^{2+}]} \\ &= -0.141 - \frac{0.05916}{2} \log \frac{1}{0.1} = -0.17 \text{ V} \end{aligned} \quad (17-20)$$

We do not expect significant reduction of Sn^{2+} at a cathode potential more

Example 3

Is a quantitative separation of Cu^{2+} and Pb^{2+} by electrolytic deposition feasible in principle? If so, what range of cathode potentials (vs. SCE) can be used? Assume that the sample solution is initially 0.1000 M in each ion and that quantitative removal of an ion is realized when only 1 part in 10,000 remains undeposited.

In Appendix 5, we find



It is apparent that copper will begin to deposit before lead because the electrode potential for Cu^{2+} is larger than that for Pb^{2+} . Let us first calculate the cathode potential required to reduce the Cu^{2+} concentration to 10^{-4} of its original concentration (that is, to 1.00×10^{-5} M). Substituting into the Nernst equation, we obtain

$$E = 0.337 - \frac{0.0592}{2} \log \frac{1}{1.00 \times 10^{-5}} = 0.189 \text{ V}$$

Similarly, we can derive the cathode potential at which lead begins to deposit:

$$E = -0.126 - \frac{0.0592}{2} \log \frac{1}{0.100} = -0.156 \text{ V}$$

Therefore, if the cathode potential is maintained between 0.189 V and -0.156 V (vs. SHE), a quantitative separation should in theory occur. To convert these potentials to potentials relative to a saturated calomel electrode, we treat the reference electrode as the anode and write

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{SCE}} = 0.189 - 0.244 = -0.055 \text{ V}$$

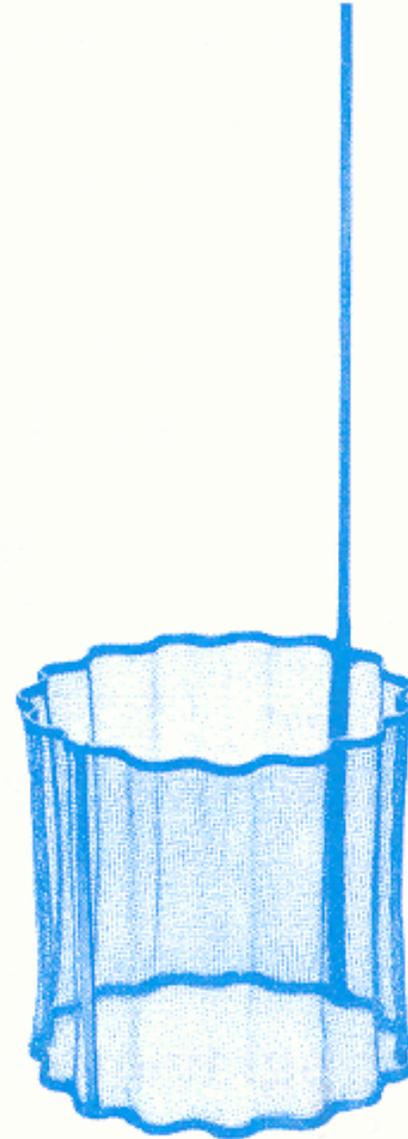
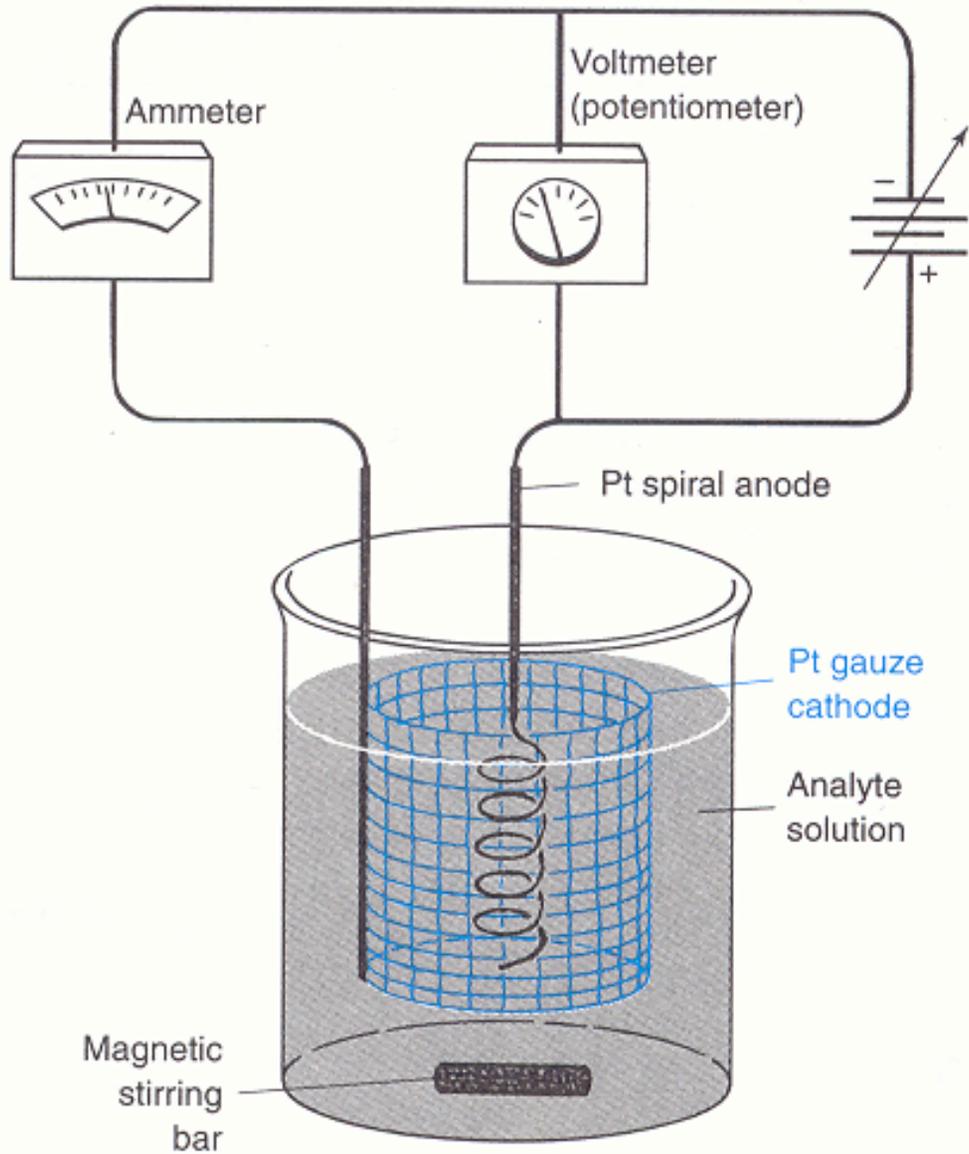
and

$$E_{\text{cell}} = -0.156 - 0.244 = -0.400 \text{ V}$$

Therefore, the cathode potential should be kept between -0.055 V and -0.400 V versus the SCE.

Electrogravimetry

- **In an electrogravimetric analysis, the analyte is quantitatively deposited as a solid on the cathode or anode.**
 - **The mass of the electrode directly measures the amount of analyte.**
 - **Not always practical because numerous materials can be reduced or oxidized and still not plated out on an electrode.**
- **Electrogravimetry can be conducted with or without a controlled potential**
- **When No control**
 - **A fixed potential is set and the electrodeposition is carried out**
 - **The starting potential must be initially high to ensure complete deposition**
 - **The deposition will slow down as the reaction proceeds**



- **In practice, there may be other electroactive species that interfere by codeposition with the desired analyte.**
- **Even the solvent (water) is electroactive, since it decomposes to $\text{H}_2 + 1/2\text{O}_2$ at a sufficiently high voltage.**
- **Although these gases are liberated from the solution, their presence at the electrode surface interferes with deposition of solids.**
- **Because of these complications, control of the electrode potential is an important feature of a successful electrogravimetric analysis.**

Examples on electrogravimetry

- **Cu: is deposited from acidic solution using a Pt cathode**
- **Ni : is deposited from a basic solution**
- **Zn: is deposited from acidic citrate solution**
- **Some metals can be deposited as metal complexes e.g., Ag, Cd, Au**
- **Some metals are deposited as oxides on the anode e.g.,**
- **Pb^{2+} as PbO_2 and Mn^{2+} as MnO_2**

Coulometric Methods of Analysis

- **Potentiometry:** Electrochemical cells under static conditions
- **Coulometry, electrogravimetry, voltammetry and amperometry:** Electrochemical cells under dynamic methods (current passes through the cell)
- Coulometric methods are based on exhaustive electrolysis of the analyte: that is quantitative reduction or oxidation of the analyte at the working electrode or the analyte reacts quantitatively with a reagent generated at the working electrode
- A potential is applied from an external source forcing a nonspontaneous chemical reaction to take place (Electrolytic cell)

Types of Coulometry

1. **Controlled potential coulometry: constant potential is applied to electrochemical cell**
2. **Controlled current coulometry: constant current is passed through the electrochemical cell**

Faraday's law:

Total charge, Q, in coulombs passed during electrolysis is related to the absolute amount of analyte:

$$Q = nFN$$

n = #moles of electrons transferred per mole of analyte

F = Faradays constant = 96487 C mol⁻¹

N = number of moles of analyte

Coulomb = C = Ampere X sec = A.s

- For a constant current, i :
 $Q = it_e$; (t_e = electrolysis time)
- For controlled potential coulometry: the current varies with time:

$$Q = \int_{t=0}^{t=t_e} i(t) dt$$

What do we measure in coulometry?

Current and time. Q & N are then calculated according to one of the above equations

- Coulometry requires **100% current efficiency**. What does this mean?
 - All the current must result in the analyte's oxidation or reduction

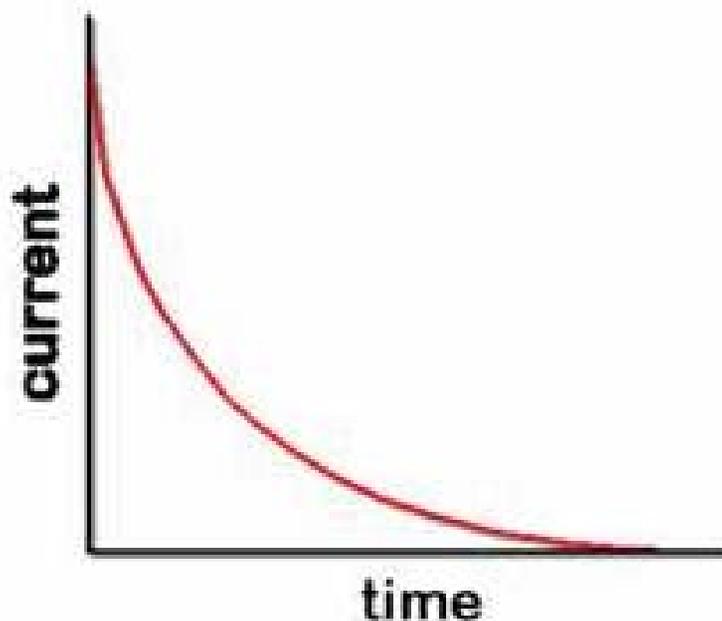
Controlled potential coulometry (Potentiostatic coulometry)

- **The working electrode will be kept at constant potential that allows for the analyt's reduction or oxidation without simultaneously reducing or oxidizing other species in the solution**
- **The current flowing through the cell is proportional to the analyt's concentration**
- **With time the analyte's concentration as well as the current will decrease**
- **The quantity of electricity is measured with an electronic integrator.**

Controlled potential coulometry

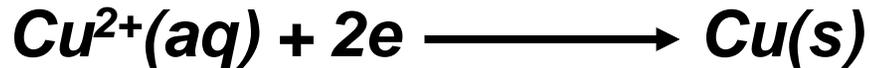
As the reactants are consumed, the current decreases. When the reaction is complete, the current is negligible.

The area under the curve equals the number of coulombs used.

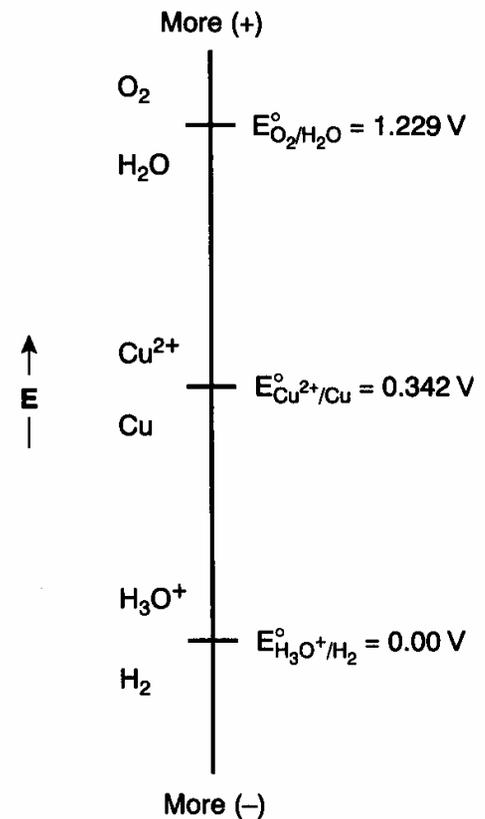


Selecting a Constant Potential

- The potential is selected so that the desired oxidation or reduction reaction goes to completion without interference from redox reactions involving other components of the sample matrix.



- This reaction is favored when the working electrode's potential is more negative than +0.342 V.
- To maintain a 100% current efficiency, the potential must be selected so that the reduction of H^+ to H_2 does not contribute significantly to the total charge passed at the electrode.



Calculation of the potential needed for quantitative reduction of Cu^{2+}

$$E = E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} - \frac{0.05916}{2} \log \frac{1}{[\text{Cu}^{2+}]}$$

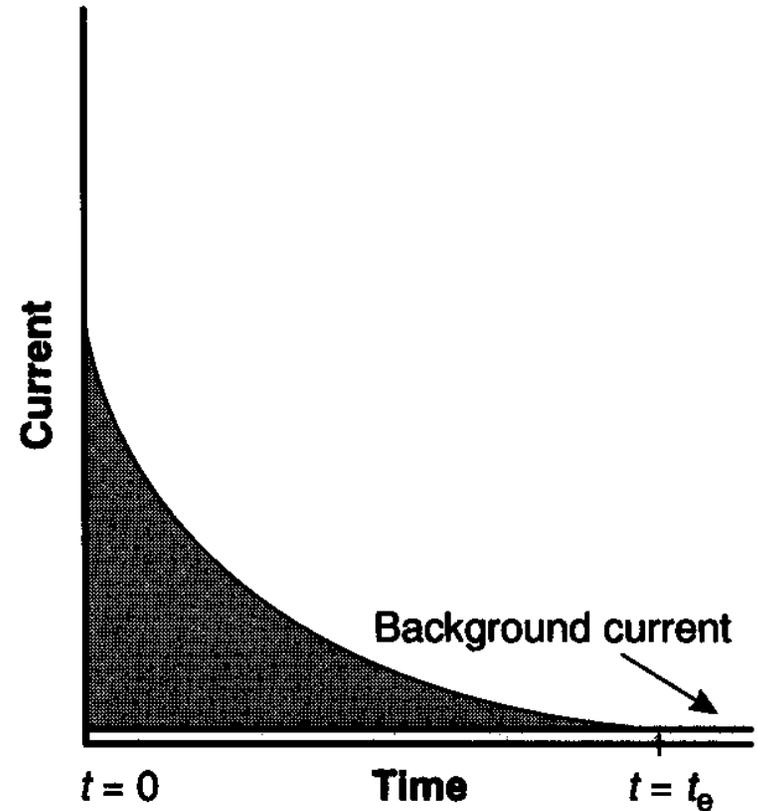
- Cu^{2+} would be considered completely reduced when 99.99% has been deposited.
- Then the concentration of Cu^{2+} left would be $\leq 1 \times 10^{-4} [\text{Cu}^{2+}]_0$

$$E = E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} - \frac{0.05916}{2} \log \frac{1}{10^{-4} [\text{Cu}^{2+}]_0}$$

- If $[\text{Cu}^{2+}]_0$ was $1 \times 10^{-4} \text{ M}$
then the cathode's potential must be more negative than $+0.105 \text{ V}$ versus the SHE (-0.139 V versus the SCE) to achieve a quantitative reduction of Cu^{2+} to Cu. At this potential H^+ will not be reduced to H_2 i.e., Current efficiency would be 100%
- Actually potential needed for Cu^{2+} are more negative than $+0.105$ due to the overpotential

Minimizing electrolysis time

- Current decreases continuous throughout electrolysis.
- An **exhaustive electrolysis**, therefore, may require a **longer time**
- The current at time t is
$$i = i_0 e^{-kt}$$
- i_0 is the initial current
- k is a constant that is **directly proportional** to the
 - area of the working electrode
 - rate of stirringand **inversely proportional** to
 - volume of the solution.



- For an exhaustive electrolysis in which 99.99% of the analyte is oxidized or reduced, the current at the end of the analysis, t_e , may be approximated

$$i \leq (10^{-4})i_0$$

Since $i = i_0 e^{-kt}$

$$t_e = 1/k \ln (1 \times 10^{-4}) = 9.21/k$$

- Thus, increasing k leads to a shorter analysis time.
- For this reason controlled-potential coulometry is carried out in
 - **small-volume electrochemical cells,**
 - **using electrodes with large surface areas**
 - **with high stirring rates.**
- A quantitative electrolysis typically requires approximately 30-60 min, although shorter or longer times are possible.

Instrumentation

- A three-electrode potentiostat system is used. Two types of working
- electrodes are commonly used: a Pt electrode manufactured from platinum-gauze and fashioned into a cylindrical tube, and an Hg pool electrode.
- The large overpotential for reducing H^+ at mercury makes it the electrode of choice for analytes requiring negative potentials. For example, potentials more negative than -1 V versus the SCE are feasible at an Hg electrode (but not at a Pt electrode), even in very acidic solutions.
- The ease with which mercury is oxidized prevents its use at potentials that are positive with respect to the SHE.
- Platinum working electrodes are used when positive potentials are required.

- The auxiliary electrode, which is often a Pt wire, is separated by a salt bridge from the solution containing the analyte.
- This is necessary to prevent electrolysis products generated at the auxiliary electrode from reacting with the analyte and interfering in the analysis.
- A saturated calomel or Ag/AgCl electrode serves as the reference electrode.
- A means of determining the total charge passed during electrolysis. One method is to **monitor the current as a function of time and determine the area under the curve.**
- Modern instruments, however, use **electronic integration** to monitor charge as a function of time. The total charge can be read directly from a digital readout or from a plot of charge versus time

Controlled-Current Coulometry (amperstatic)

- The current is kept constant until an **indicator signals completion** of the analytical reaction.
- The quantity of electricity required to attain the end point is calculated from the magnitude of the current and the time of its passage.
- Controlled-current coulometry, also known as **amperostatic coulometry** or **coulometric titrimetry**
 - When called coulometric titration, electrons serve as the titrant.

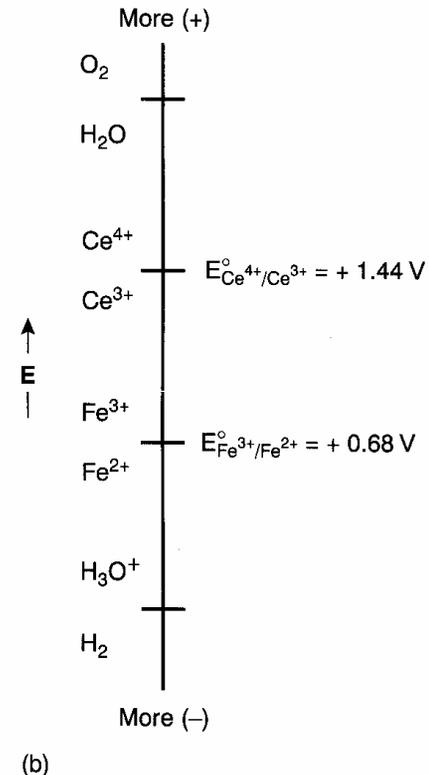
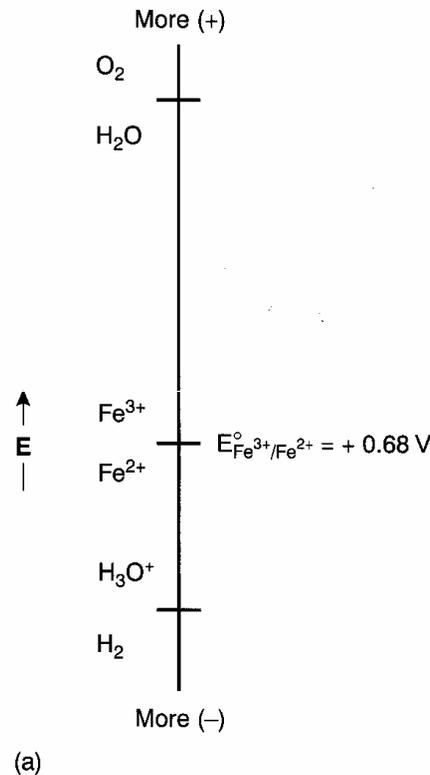
- **Controlled-current coulometry, has two advantages over controlled-potential coulometry.**
 - **First, using a constant current leads to more rapid analysis since the current does not decrease over time. Thus, a typical analysis time for controlled current coulometry is less than 10 min, as opposed to approximately 30-60 min for controlled-potential coulometry.**
 - **Second, with a constant current the total charge is simply the product of current and time. A method for integrating the current-time curve, therefore, is not necessary.**

Experimental problems with constant current coulometry

- Using a constant current does present two important experimental problems that must be solved if accurate results are to be obtained.
- First, as electrolysis occurs the analyte's concentration and, therefore, **the current due to its oxidation or reduction steadily decreases.**
 - To maintain a constant current the **cell potential must change until another oxidation or reduction** reaction can occur at the working electrode.
 - Unless the system is carefully designed, these secondary reactions will produce a current efficiency of less than 100%.
- Second problem is the need for a **method of determining when the analyte has been exhaustively electrolyzed.**
 - In controlled-potential coulometry this is signaled by a decrease in the current to a **constant background or residual current.**
 - In controlled-current coulometry, a constant current continues to flow even when the analyte has been completely oxidized or reduced. A suitable means of determining the end-point of the reaction, t_e , is needed.

Maintaining Current Efficiency

- Why changing the working electrode's potential can lead to less than 100% current efficiency?
- let's consider the coulometric analysis for Fe^{2+} based on its oxidation to Fe^{3+} at a Pt working electrode in 1 M H_2SO_4 .
- $\text{Fe}^{2+}(\text{aq}) = \text{Fe}^{3+}(\text{aq}) + \text{e}^-$
- The diagram for this system is shown. Initially the potential of the working electrode remains nearly constant at a level near the standard-state potential for the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple.
- As the concentration of Fe^{2+} decreases, the potential of the working electrode **shifts toward more positive** values until another oxidation reaction can provide the necessary current.
- Thus, in this case the potential eventually increases to a level at which the oxidation of H_2O occurs.
- $6\text{H}_2\text{O}(\text{l}) \rightarrow \text{O}_2(\text{g}) + 4\text{H}_3\text{O}^+(\text{aq}) + 4\text{e}^-$



- **Since the current due to the oxidation of H₂O does not contribute to the oxidation of Fe²⁺, the current efficiency of the analysis is less than 100%.**
- **To maintain a 100% current efficiency the products of any competing oxidation reactions must react both rapidly and quantitatively with the remaining Fe²⁺.**
- **This may be accomplished, for example, by adding an excess of Ce³⁺ to the analytical solution.**
- **When the potential of the working electrode shifts to a more positive potential, the first species to be oxidized is Ce³⁺.**
- **$\text{Ce}^{3+}(\text{aq}) = \text{Ce}^{4+}(\text{aq}) + \text{e}^-$**
- **The Ce⁴⁺ produced at the working electrode rapidly mixes with the solution, where it reacts with any available Fe²⁺.**

- $\text{Ce}^{4+}(\text{aq}) + \text{Fe}^{2+}(\text{aq}) = \text{Fe}^{3+}(\text{aq}) + \text{Ce}^{3+}(\text{aq})$
- Combining these reactions gives the desired overall reaction
- $\text{Fe}^{2+}(\text{aq}) = \text{Fe}^{3+}(\text{aq}) + \text{e}^-$
- Thus, a current efficiency of 100% is maintained.
- Since the concentration of Ce^{3+} remains at its initial level, the potential of the working electrode remains constant as long as any Fe^{2+} is present.
- This prevents other oxidation reactions, such as that for H_2O , from interfering with the analysis.
- A species, such as Ce^{3+} which is used to maintain 100% current efficiency is called a **Mediator**.

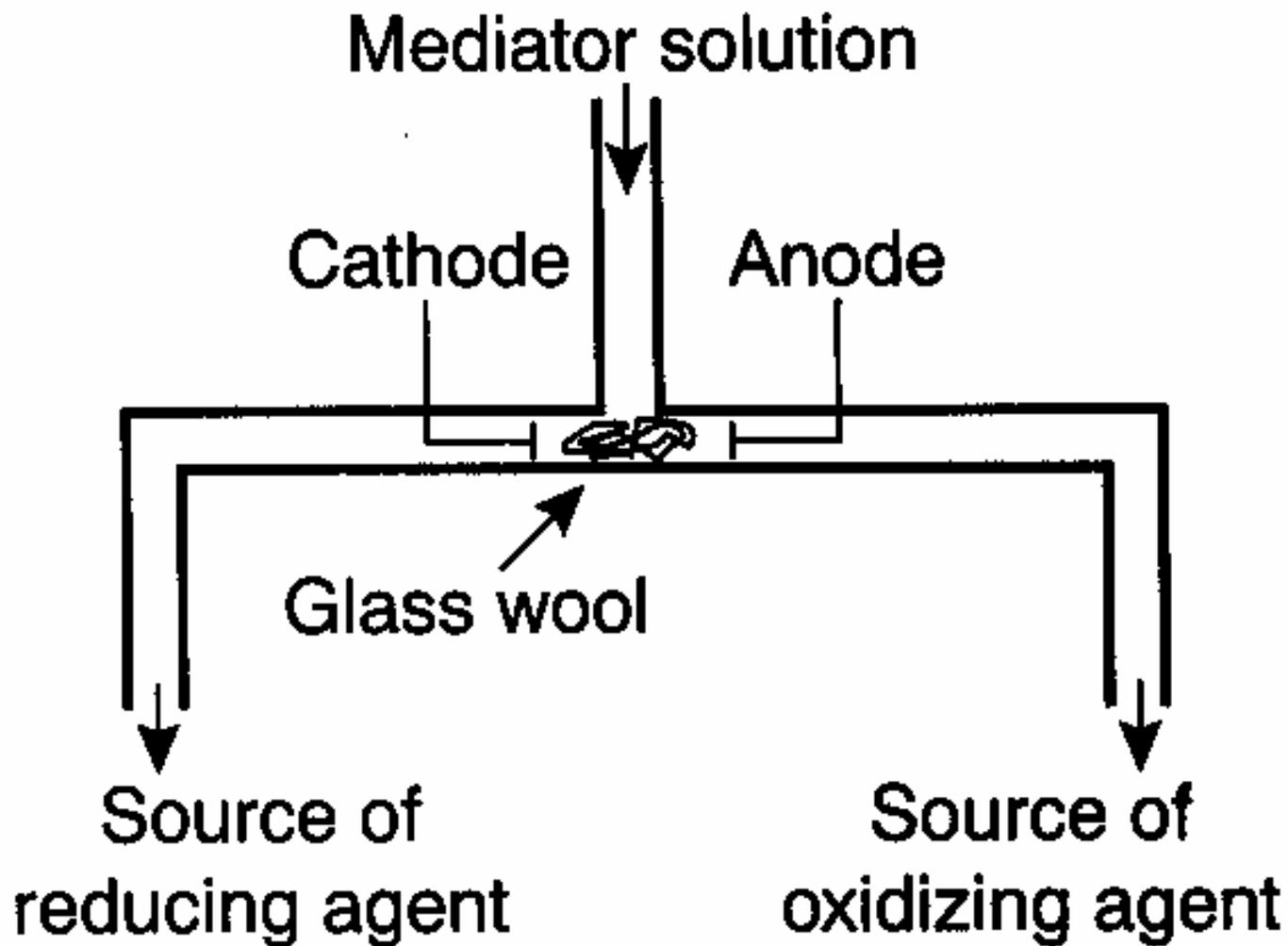
End Point Determination

- How do we judge that the analyte's electrolysis is complete?
- When all Fe^{2+} has been completely oxidized, electrolysis should be stopped; otherwise the current continues to flow as a result of the oxidation of Ce^{3+} and, eventually, the oxidation of H_2O .
- How do we know that the oxidation of Fe^{2+} is complete?
- We monitor the reaction of the rest of iron (II) with Ce (IV) by using visual indicators, and potentiometric and conductometric measurements.

Instrumentation

- **Controlled-current coulometry normally is carried out using a galvanostat and an electrochemical cell consisting of a working electrode and a counter electrode.**
- **The working electrode is constructed from Pt, is also called the generator electrode since it is where the mediator reacts to generate the species reacting with the analyte.**
- **The counter electrode is isolated from the analytical solution by a salt bridge or porous frit to prevent its electrolysis products from reacting with the analyte.**
- **Alternatively, oxidizing or reducing the mediator can be carried out externally, and the appropriate products flushed into the analytical solution.**

Method for the external generation of oxidizing and reducing agents in coulometric titration



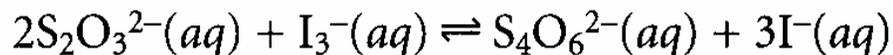
- The other necessary instrumental component for controlled-current coulometry is an **accurate clock for measuring the electrolysis time, t_e , and a switch for starting and stopping the electrolysis.**
- Analog clocks can read time to the nearest ± 0.01 s, but the need to frequently stop and start the electrolysis near the end point leads to a net uncertainty of ± 0.1 s.
- Digital clocks provide a more accurate measurement of time, with errors of ± 1 ms being possible.
- The switch must control the flow of current and the clock, so that an accurate determination of the electrolysis time is possible.

Quantitative calculations

Example 1

- The purity of a sample of $\text{Na}_2\text{S}_2\text{O}_3$ was determined by a coulometric redox titration using I^- as a mediator, and I_3^- as the "titrant". A sample weighing 0.1342 g is transferred to a 100-mL volumetric flask and diluted to volume with distilled water. A 10.00-mL portion is transferred to an electrochemical cell along with 25 ml, of 1 M KI, 75 mL of a pH 7.0 phosphate buffer, and several drops of a starch indicator solution. Electrolysis at a constant current of 36.45 mA required 221.8 s to reach the starch indicator end point. Determine the purity of the sample.

From Table 11.9 we see that the coulometric titration of $\text{S}_2\text{O}_3^{2-}$ with I_3^- is



Oxidizing $\text{S}_2\text{O}_3^{2-}$ to $\text{S}_4\text{O}_6^{2-}$ requires one electron per $\text{S}_2\text{O}_3^{2-}$ ($n = 1$). Combining equations 11.23 and 11.24, and making an appropriate substitution for moles of $\text{Na}_2\text{S}_2\text{O}_3$ gives

$$\frac{nF(\text{g Na}_2\text{S}_2\text{O}_3)}{\text{FW Na}_2\text{S}_2\text{O}_3} = it_e$$

Solving for the grams of $\text{Na}_2\text{S}_2\text{O}_3$ gives

$$\begin{aligned} \text{g Na}_2\text{S}_2\text{O}_3 &= \frac{it_e(\text{FW Na}_2\text{S}_2\text{O}_3)}{nF} \\ &= \frac{(0.03645 \text{ A})(221.8 \text{ s})(158.1 \text{ g/mol})}{(1 \text{ mol } e^-)(96487 \text{ C/mol } e^-)} = 0.01325 \text{ g Na}_2\text{S}_2\text{O}_3 \end{aligned}$$

This represents the amount of $\text{Na}_2\text{S}_2\text{O}_3$ in a 10.00-mL portion of a 100-mL sample, thus 0.1325 g of $\text{Na}_2\text{S}_2\text{O}_3$ is present in the original sample. The purity of the sample, therefore, is

$$\frac{0.1325 \text{ g Na}_2\text{S}_2\text{O}_3}{0.1342\text{-g sample}} \times 100 = 98.73\% \text{ w/w Na}_2\text{S}_2\text{O}_3$$

Note that the calculation is worked as if $\text{S}_2\text{O}_3^{2-}$ is oxidized directly at the working electrode instead of in solution.

Example 2

- A 0.3619-g sample of tetrachloropicolinic acid, $C_6HNO_2Cl_4$, is dissolved in distilled water, transferred to a 1000-ml, volumetric flask, and diluted to volume. An exhaustive controlled-potential electrolysis of a 10.00-mL portion of this solution at a spongy silver cathode requires 5.374 C of charge. What is the value of n for this reduction reaction?

The 10.00-mL portion of sample contains 3.619 mg, or 1.39×10^{-5} mol of tetrachloropicolinic acid. Solving equation 11.23 for n and making appropriate substitutions gives

$$n = \frac{Q}{FN} = \frac{5.374 \text{ C}}{(96478 \text{ C/mol } e^-)(1.39 \times 10^{-5} \text{ mol C}_6\text{HNO}_2\text{Cl}_4)} = 4.01$$

Thus, reducing a molecule of tetrachloropicolinic acid requires four electrons. The overall reaction, which results in the selective formation of 3,6-dichloropicolinic acid, is

