Chapter 24

Electrogravimetry and Coulometry

Electrochemical Techniques

- The simplest division of electrochemical techniques is between
 - bulk techniques,

in which we measure a property of the solution in the electrochemical cell,

- interfacial techniques,

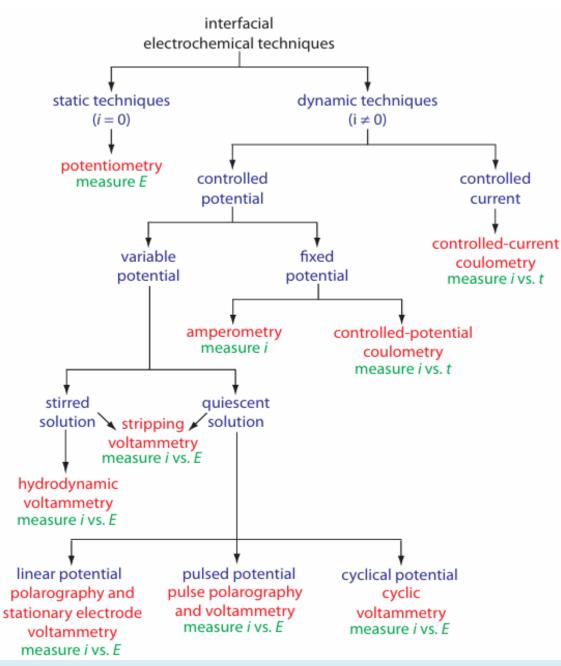
in which the potential, charge, or current depends on the species present at the interface between an electrode and the solution in which it sits.

- The measurement of a solution's conductivity, which is proportional to the total concentration of dissolved ions, is one example of a bulk technique.
- A determination of pH using a pH electrode is an example of an interfacial electrochemical technique.

- At the first level, we divide interfacial electrochemical techniques into static techniques and dynamic techniques.

In a static technique, we do not allow current to pass through the analyte's solution. (potentiometry)

In dynamic techniques, we allow current flow through the analyte solution (coulometry, amperometry and voltammetry)



Potentiometry, in which we measure the potential of an electrochemical cell under static conditions, is one of the most important quantitative electrochemical methods, Dynamic techniques, in which we allow current to flow through the analyte's solution, comprise the largest group of interfacial electrochemical techniques. Coulometry, in which we measure current as a function of time. Amperometry and voltammetry, in which we measure current as a function of a fixed or variable potential.

Family tree highlighting a number of interfacial electrochemical techniques. The specific techniques are shown in red, the experimental conditions are shown in blue, and the analytical signals are shown in green.

Dynamic Electrochemical Methods of analysis: Electrolysis, Electrogravimetric and Coulometric Methods

- Electrolysis is the decomposition of electrolyte as a result of the impact of direct current flowing through the electrolyzer. This term encompasses the actual electrochemical reaction taking place on the metallic electrodes, which is associated with the transport of charge, transport of ions to and from the electrode surface, and secondary chemical reactions taking place near the electrode. In *electrolysis*, an electric current is sent through an electrolyte and into a solution to stimulate the flow of ions necessary to run an otherwise nonspontaneous reaction.
- Electrogravimetry is electroanalytical method based on gravimetric determination of metallic elements, which are isolated on the cathode in form of metal or on the anode in form of metal oxide during *electrolysis*. This method employs two or three electrodes, and either a constant current or a constant potential is applied to the *pre-weighed* working electrode.
- Coulometry, is an electrochemical method in which the total charge (the number of coulombs) consumed in the redox conversion of an analyte at an electrode is measured and based on Faraday's law of electrolysis, which states that the mass of a substance produced or consumed during an electrolytic reaction is directly proportional to the amount of electricity that flows through the system

Electrogravimetry and Coulometry

- Electroanalytical methods based on electrolytic oxidation or reduction of an analyte for a sufficient period to assure its quantitative conversion to a new oxidation state
 - Electrogravimetry
 - Coulometry
 - Constant Potential Coulometry
 - Constant Current Coulometry (Coulometric titrations)
- In electrogravimetric methods, the product of the electrolysis is weighed as a deposit on one of the electrodes.
- In the two coulometric procedures, on the other hand, the quantity of electricity needed to complete the electrolysis is a measure of the amount of analyte present.
- These methods have moderate selectivity, sensitivity, and speed;
- They are among the most accurate and precise methods available,
- These require no calibration against standards; that is, the functional relationship between the quantity measured and the mass of analyte can be calculated from theory.

♦ What is the difference between potentiometry and electrogravimetry? The potentiometric method measures the voltage without drawing appreciable current. On the other hand, the electrogravimetric and coulometric methods are electrolytic in nature with a net cell reaction and a net current.

What is the difference between electrogravimetry and coulometry?

In electrogravimetry, the product is weighed as a deposit on one of the electrodes. In coulometry, the quantity of electricity needed to complete the electrolysis is measured as coulombs.

- 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
 - ohmic potential,
 - concentration polarization (overpotential), and
 - Kinetic polarizaton (overpotential)

24A Current-Voltage relationships during an electrolysis

- An electrolysis can be performed in one of three ways:
 - (1) with constant applied cell voltage,
 - (2) with constant electrolysis current, or
 - (3) with constant working electrode potential.

It is useful to consider the consequences of each of these modes of operation. For all three modes, the behavior of the cell is governed by an equation

$$E_{\text{appl}} = (E_{\text{r}} - E_{\text{l}}) + (\boldsymbol{\eta}_{\text{rc}} + \boldsymbol{\eta}_{\text{rk}}) - (\boldsymbol{\eta}_{\text{lc}} + \boldsymbol{\eta}_{\text{lk}}) - IR$$

- Here, η_{rc} and η_{rk} are overvoltages resulting from concentration polarization and kinetic polarization at the right-hand electrode; η_{lc} and η_{lk} are the corresponding overvoltages at the left-hand electrode
- The values for E_r and E_l can be calculated from standard potentials using the Nernst equation.
- In many cases, only the right-hand electrode is polarizable because the lefthand electrode is a nonpolarizable reference electrode. The overvoltage is the extra voltage, above the thermodynamic potential, required to drive the electrode reaction at a certain rate and thus produce current in the cell.

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:

 $E_{ohmic} = IR$

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 Pontential

Consider the cell

r 4,

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Cd(s) | CdCl_2(aq, 0.167 \text{ m}) | AgCl(s) | Ag(s)
```

in which the spontaneous chemical reaction is

 $Cd(s) + 2AgCl(s) \rightarrow Cd^{2+} + 2Ag(s) + 2Cl^{-}$

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

$$E = E_{eq} - IR = 0.764 - (0.028 \text{ 3 A})(6.42 \Omega) = 0.582 \text{ V}$$

(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

$$E = -E_{eg} - IR = -0.764 - (0.028 \text{ 3 A})(6.42 \Omega) = -0.946 \text{ V}$$

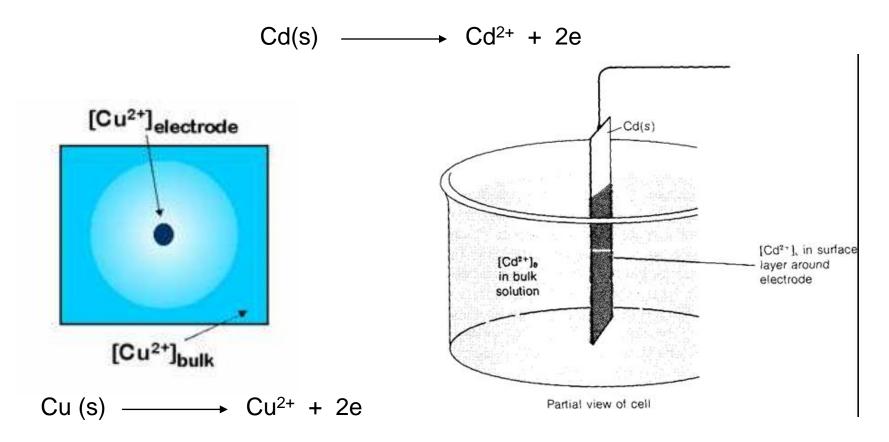
Notice that the magnitude of any galvanic cell voltage is *decreased* by the ohmic potential. The magnitude of the voltage that must be applied to any electrolysis cell is *increased* by the ohmic potential.

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
- $E_{applied} = E_{reversible(equilib)} + \eta$
- The overvoltage η is the extra voltage, above the thermodynamic potential, required to drive the electrode reaction at a certain rate and thus produce current in the cell
- What are the sources of overpotential? R
 - Overpotential results from concentration polarization and kinetic polarization at the electrodes

1. Concentration polarization (overpotential)

- 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



•The anode potential depends on $[Cd^2 +]_s$, not $[Cd^2 +]_o$, because $[Cd^2 +]_s$ 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

 $E_{(anode)} = E^{\circ}_{(anode)} - (0.05916/2) \log [Cd^{2+}]_{s}$

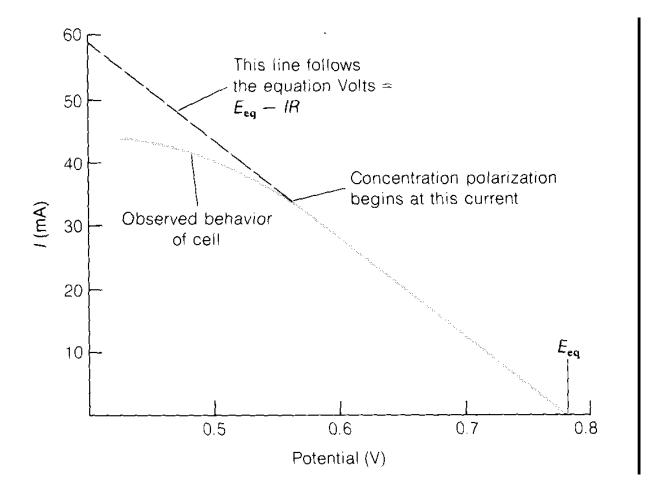
•If $[Cd^2 +]_s = [Cd^{2+}]_o$, the anode potential will be that expected from the bulk Cd^{2+} concentration.

•If the current is flowing so fast that Cd^{2+} cannot escape from the region around the electrode as fast as it is made, $[Cd^{2} +]_{s}$ will be greater than $[Cd^{2} +]_{o}$. •When $[Cd^{2} +]_{s}$ does not equal $[Cd^{2} +]_{o}$, we say that concentration polarization exists.

•The anode will become more positive and the

Cell voltage = E $_{(cathode)}$ -E $_{(anode)}$ 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 [Mⁿ⁺] gets smaller.

Example on Concentration overpotential

Assun	ne:				
[Cu ²⁺] _{bulk}		10 ⁻² M			
[Cu ²⁺] _{electro}	e =	104 M			
then					
Ebulk	= 0.337		592 2	log(10 ⁻²)	= 0.278
E _{electrode}	= 0.337	• <u>0.0</u>) <u>592</u> 2	log(10-4)	= 0.219
η_{conc}	= E _{eledrode}	- E _{bulk} =	-0.05	7V	

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 polarization?

- 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.

Example 1: on electrolysis

Can Pb²⁺ be quantitatively separated from Cu²⁺ 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:	Cu ²⁺ + 2e = Cu E = 0.33	7V
	Pb ²⁺ + 2e = Pb E = -0.126	V

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 - 10⁵M Cu²⁺

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

E = 0.189 V

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

E = -0.156 V

The separation is possible but our calculations neglect any overpotential.

Example 2:

Suppose that a solution containing 0.20 M Cu²⁺ and 1.0 M H⁺ is electrolyzed to deposit Cu(s) on a Pt cathode and to liberate O₂ 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.

Cathode:
Cu²⁺ + 2e⁻
$$\rightleftharpoons$$
 Cu(s)
Anode:
Net reaction:

$$\begin{array}{c}
Cu^{2+} + 2e^{-} \rightleftharpoons Cu(s) \\
H_2O \rightleftharpoons \frac{1}{2}O_2(g) + 2H^+ + 2e^{-} \\
H_2O + Cu^{2+} \rightleftharpoons Cu(s) + \frac{1}{2}O_2(g) + 2H^+ \\
\end{array}$$

$$\begin{array}{c}
E^{\circ} = & 0.339 \\
E^{\circ} = & -1.229 \\
\hline
E^{\circ} = & -0.890 \\
(17-12)
\end{array}$$

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

$$E = E^{\circ} - \frac{0.059 \ 16}{n} \log \frac{P_{0_2}^{1/2} [\mathrm{H}^+]^2}{[\mathrm{Cu}^{2+}]}$$
$$= -0.890 - \frac{0.059 \ 16}{2} \log \frac{(0.20)^{1/2} (1.0)^2}{(0.20)} = -0.900 \ \mathrm{V} \qquad (17-13)$$

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 O₂ to occur.

- 4,

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

Example 3:

- A solution containing 0.1M Cu²⁺ and 0.1 M Sn²⁺ calculate:
 - the potential at which Cu^{2+} starts deposition.
 - The potential ate which Cu²⁺ is completely deposited (99.99% deposition).
 - The potential at which Sn²⁺ starts deposition.
- Would Sn²⁺ be reduced before the copper is completely deposited?
- From the standard potentials given below we expect that Cu²⁺ be reduced more easily than Sn²⁺

Cu²⁺ + 2e⁻ → Cu_(s); E^o = 0.339 V
Sn²⁺ + 2e⁻
$$\rightleftharpoons$$
 Sn(s) $E^{\circ} = -0.141$ V

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

$$E(\text{cathode}) = 0.339 - \frac{0.059\,16}{2}\log\frac{1}{0.1} = 0.31\,\text{V}$$
 (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

$$E(\text{cathode}) = 0.339 - \frac{0.059\ 16}{2}\log\frac{1}{10^{-5}} = 0.19\ \text{V}$$
 (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 Sn(s) from a solution containing 0.1 M Sn^{2+} , a cathode potential of -0.17 V is required:

E(cathode, for reduction of
$$\text{Sn}^{2+}$$
) = $-0.141 - \frac{0.059 \ 16}{2} \log \frac{1}{[\text{Sn}^{2+}]}$

$$= -0.141 - \frac{0.059\ 16}{2}\log\frac{1}{0.1} = -0.17\ V \tag{17-20}$$

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

Example 4

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

$$Cu^{2+} + 2e^{-} \iff Cu(s)$$
 $E^{0} = 0.337 V$
 $Pb^{2+} + 2e^{-} \iff Pb(s)$ $E^{0} = -0.126 V$

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.

2. Kinetic polarization

- Kinetic polarization is a condition in which the current is limited by the rate at which electrons transfer between the electrode surfaces and the reactants in the solution.
- Kinetic polarization can be described as the change of the static permittivity of the solution with respect to that of the pure solvent.

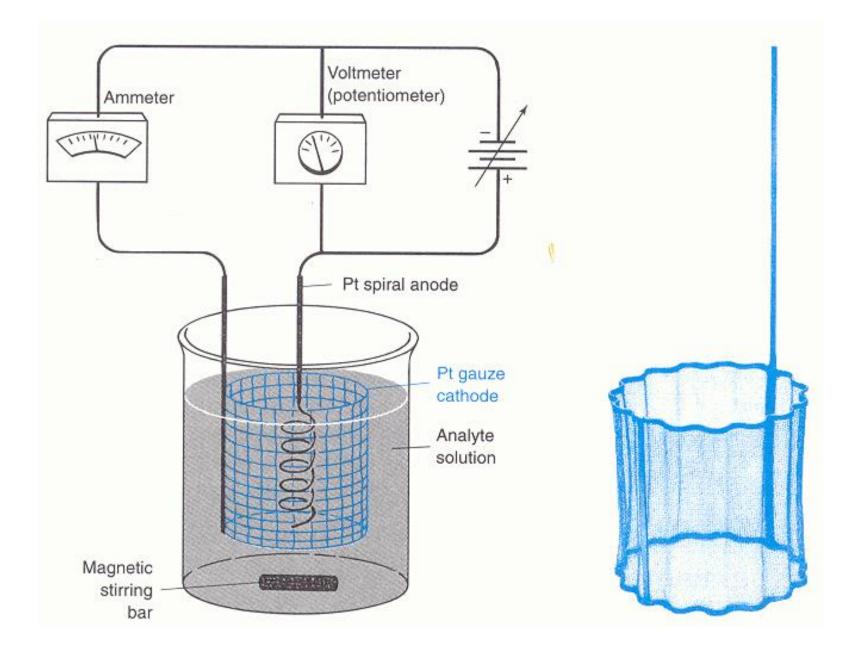
What is the Difference Between Concentration Polarization and Kinetic Polarization?

Concentration polarization and kinetic polarization can be described as the contributions to the overpotential of a system. The key difference between concentration polarization and kinetic polarization is that concentration polarization comes from the changes in the concentration of the electrolyte, whereas kinetic polarization is the change in static permittivity.

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 $H_2 + \frac{1}{2}O_2$ 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.,
- Pb²⁺ as PbO₂ and Mn²⁺ as MnO₂

- 24B An introduction To Coulometric Methods of Analysis
 Potentiometry: Electrochemical cells under static conditions
 Coulometry, electrogravimetry, voltammetry: Electrochemical cells under dynamic methods (current passes through the cell)
 Coulometry: an electrochemical method based on the measurement of the quantity of electricity (in coulombs) needed to convert the analyte
- quantitatively to a different oxidation state
- •A potential is applied from an external source forcing a non-spontaneous chemical reaction to take place :Electrolytic method
- measured quantity and the mass of analyte can be computed from known physical constants : standardization is not usually necessary
- as accurate as gravimetric and volumetric procedures
- faster and more convenient than gravimetric measurements

24B-1 Units for Quantity of Electricity

- The quantity of electricity or charge is measured in units of coulombs (C).
- A coulomb is the quantity of charge transported in one second by a constant current of one ampere.
- Thus, for a constant current of I amperes for t seconds, the charge in coulombs Q is given by the expression O = It
- For a variable current i, the charge is given by the integral $Q = \int_0^t i \, dt$
- * The faraday F is the charge in coulombs of one mole of electrons. The charge of the electron is 1.60218 x 10⁻¹⁹ C, so we may therefore write

$$F = 6.02214 \times 10^{23} \frac{e^{-}}{\text{mol } e^{-}} \times 1.60218 \times 10^{-19} \frac{C}{e^{-}}$$
$$= 96,485 \frac{C}{\text{mol } e^{-}}$$

Faraday's law relates the number of moles of the analyte n_A to the charge

$$n_{\rm A} = \frac{Q}{nF}$$

n = #moles of electrons transferred in the half-cell rxn F = Faradays constant = 96487 C mol-1 n_A = number of moles of analyte

Example 24-1

A constant current of 0.800 A was used to deposit copper at the cathode and oxygen at the anode of an electrolytic cell. Calculate the mass of each product that was formed in 15.2 min, assuming that no other redox reactions occur.

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

 $2H_2O \rightarrow 4e^- + O_2(g) + 4H^+$

Thus, 1 mol of copper is equivalent to 2 mol of electrons and 1 mol of oxygen corresponds to 4 mol of electrons.

$$Q = 0.800 \text{ A} \times 15.2 \text{ min} \times 60 \text{ s/min}$$

= 729.6 A · s = 729.6 C

We can find the number of moles of Cu and O_2

$$n_{\rm Cu} = \frac{Q}{nF} = \frac{729.6 \ C}{2 \ \text{mol} \ e^{-/\text{mol} \ Cu} \times 96,485 \ C/\text{mol} \ e^{-}}$$

= 3.781 × 10⁻³ mol Cu
$$n_{\rm O_2} = \frac{Q}{nF} = \frac{729.6 \ C}{4 \ \text{mol} \ e^{-/\text{mol} \ O_2} \times 96,485 \ C/\text{mol} \ e^{-}}$$

= 1.890 × 10⁻³ mol O₂

The masses of Cu and O2 are given by

-

$$m_{\rm Cu} = n_{\rm Cu} \mathcal{M}_{\rm Cu} = 3.781 \times 10^{-3} \, \text{mol Cu} \times \frac{63.55 \, \text{g Cu}}{1 \, \text{mol Cu}}$$
$$= 0.240 \, \text{g Cu}$$
$$m_{\rm O_2} = n_{\rm O_2} \mathcal{M}_{\rm O_2} = 1.890 \times 10^{-3} \, \text{mol O}_2 \times \frac{32.00 \, \text{g O}_2}{1 \, \text{mol O}_2}$$

 $n_{\rm A} = \frac{Q}{nF}$

 $= 0.0605 \text{ g O}_2$

24B-2 Types of Coulometric Methods:

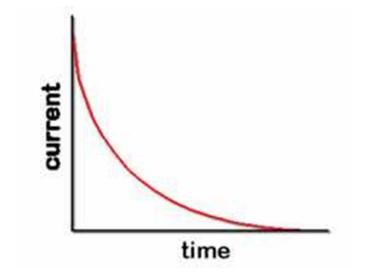
- 1. Controlled potential coulometry:
- 2. Controlled current coulometry:

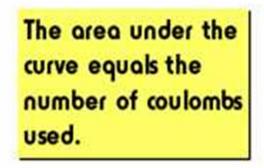
Fundamental requirement for both methods is 100% current efficiency

- all e⁻ go to participate in the desired electrochemical process
- If not, then takes more current \rightarrow over-estimate amount of analyte
- Current efficiency of 100% does not, however, imply that the analyte must necessarily participate directly in the electron-transfer process at the electrode. Indeed, more often than not, the analyte participates, at least in part, in a reaction that is secondary to the electrode reaction.

24C- Controlled potential (Potentiostatic) coulometry):

- The working electrode *(the electrode at which the analytical rxn occurs)* will be kept at the constant potential that the analyte's quantitative reduction or oxidation occurs without simultaneously reducing or oxidizing other species in the solution
- The current flowing through the cell is proportional to the analyte's concentration. As the reactants are consumed, the current decreases. When the reaction is complete, the current is negligible.
- The quantity of electricity is usually measured with an electronic integrator.





Controlled potential coulometry

- An analysis of this kind has all the advantages of an electrogravimetric method, but it is not necessary to weigh a product. The technique can therefore be applied to systems that yield deposits with poor physical properties as well as to reactions that yield no solid product at all. For example, arsenic may be determined coulometrically by the electrolytic oxidation of arsenous acid (H₃AsO₃,) to arsenic acid (H₃AsO₄) at a platinum anode. Similarly, the analytical conversion of iron(II) to iron(III) can be accomplished with suitable control of the anode potential.
- controlled-potential coulometry is carried out in
 - ✓ small-volume electrochemical cells,
 - $\checkmark\,$ using electrodes with large surface areas
 - \checkmark with high stirring rates.

24C-1 Instrumentation:

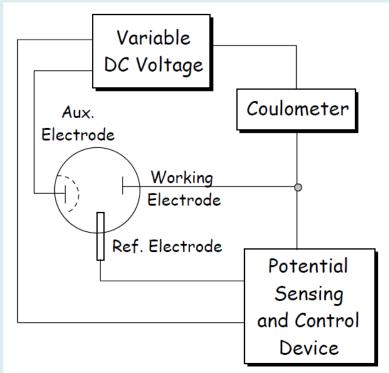
•The instrumentation for potentiostatic coulometry consists of an:

-electrolysis cell,

-a potentiostat and

-an electronic integrator for determining the charge consumed.

* *Potentiostat* is an electronic device that maintains the potential of a working electrode at a constant level relative to reference electrode with a feedback circuitry which adjusts the potential of the variable DC voltage source to maintain $E_w - E_{ref}$ constant



Electrolysis Cell:

Consisted of three electrode system:

1) Working electrode, 2) counter(auxiliary) electrode, 3) refrence electrode

Working electrode where the electrolysis takes place. E_w is fixed vs the E_{ref}

- 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
- Auxiliary electrode is part of the other half-cell and it is often made from the same material as the working electrode
- Usually separated from the solution in contact with the working electrode to prevent reaction between species produced at Aux. Electr. and species in the bulk of solution

Ref. electrode is often either SCE or Ag/AgCI connected to bulk solution by a salt bridge

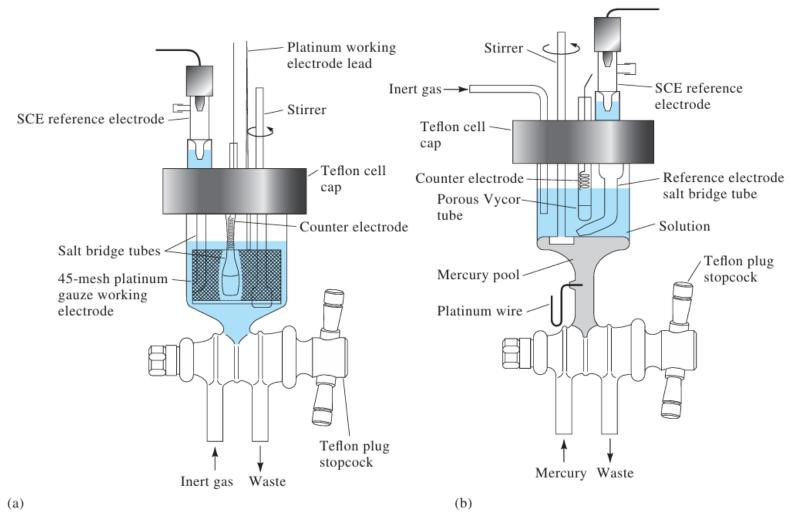


FIGURE 24-5 Electrolysis cells for potentiostatic coulometry. Working electrode: (a) platinum gauze and (b) mercury pool. (Reprinted with permission from J. E. Harrar and C. L. Pomernacki, *Anal. Chem.*, **1973**, *45*, 57, **DOI**: 10.1021/

A mercury pool type cell is useful for determination of metal ions and certain types of organic compounds. Easily reduced elements like copper, nickel, cobalt, silver, and cadmium are readily separated from ions such as aluminum, titanium, alkali metals, and phosphates as a preliminary step in an analysis.

- 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/AgCI 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

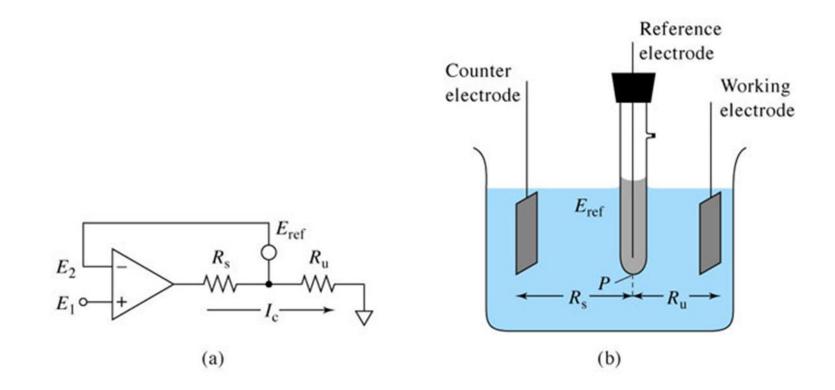


FIGURE 24-6 Schematic of a system for controlled-potential coulometry. (a) Equivalent circuit. (b)Resistances within the cell. The cell current *Ic* passes to the integrator readout module, which provides a number proportional to the total quantity of charge that passes through the cell.

 R_s : cell resistance between counter electrode and tip of the reference electrode R_u : uncompansated cell resistance between the ref. Elec. And working electr.

Controlled-Current (amperostatic) Coulometry:

- The current is kept constant until an indicator signals completion of the analytical reaction.
- The quantity of charge required to attain the end point is calculated from the magnitude of the current and the time of its passage. Q=i x t
- Controlled-current coulometry, also known as amperostatic coulometry or coulometric titrimetry
 - When called coulometric titration, electrons serve as the titrant.
 - An example is the titration of halides by silver ions produced at a silver anode.
- The current in a coulometric titration is carefully maintained at a constant and accurately known level by means of an amperostat.

- 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.

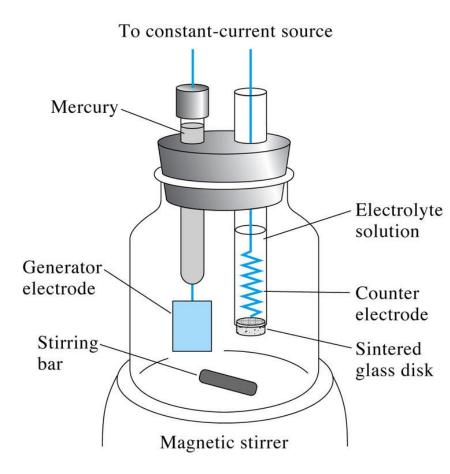
Experimental problems with constant current coulometry

1) as electrolysis occurs the analyte's concentration and, therefore, the current due to its oxidation or reduction steadily decreases.

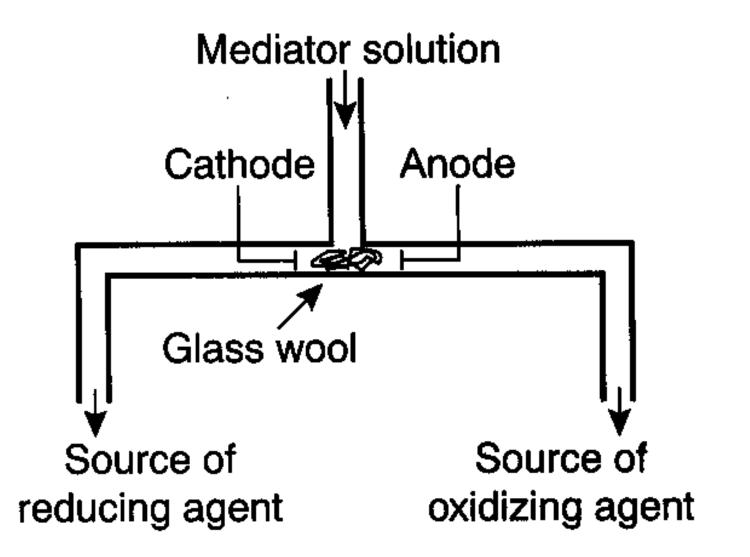
- To maintain a constant current the cell potential must change until another oxidation or reduction reaction can occur at the working electrode.
- Unless the system is carefully designed, these secondary reactions will produce a current efficiency of less than 100%.
- Second problem is the need for 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, is needed. Most of the end-point detection methods applicable to volumetricanalysis are equally satisfactory here. Visual observations of color changes of indicators, as well as potentiometric, amperometric, and photometric measurements have all been used successfully.

Instrumentation

- Controlled-current coulometry normally is carried out using a amperostat 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. Should have a large surface area
- 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.



Method for the external generation of oxidizing and reducing agents in coulomtric 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.

Applications of Coulometric Titrations:

a) Can be used for Acid-Base(Neutralization) Titrations

b.) Can be used for Complexation Titrations (EDTA)

c.) Can be used for Redox Titrations

 $Ce^{3+} \leftrightarrow Ce^{4+} + e^{-}$

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

Comparison of Coulometric and Volumetric Titrations

- Both require a detectable end point and are subject to a titration error as a consequence
- regarding the apparatus and solutions employed:
 - The timer and switch correspond closely to the buret, the switch performing the same function as a stopcock.
- Coulometry, advantages is the elimination of problems associated with the preparation, standardization, and storage of standard solutions. (instability of Br, CI and Ti)
- With coulometry, by proper choice of current, microquantities of a substance can be introduced with ease and accuracy
- the coulometric method adapts easily to automatic titrations, because current can be controlled quite easily.

Coulometric titrations are subject to five potential sources of error:

- (1) variation in the current during electrolysis,
- (2) departure of the process from 100% current efficiency,
- (3) error in the current measurement,
- (4) Error in the measurement of time, and

(5) titration error due to the difference between the equivalence point and the end point.

The last of these difficulties is common to volumetric methods as well. For situations in which the indicator error is the limiting factor, the' two methods are likely to have comparable reliability.

Quantitative calculations: Example 1

• The purity of a sample of $Na_2S_2O_3$ was determined by a coulometric redox titration using I^{-} as a mediator, and 1_{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 $S_2O_3^{2-}$ with I_3^{-} is

$$2S_2O_3^{2-}(aq) + I_3^{-}(aq) \rightleftharpoons S_4O_6^{2-}(aq) + 3I^{-}(aq)$$

Oxidizing $S_2O_3^{2-}$ to $S_4O_6^{2-}$ requires one electron per $S_2O_3^{2-}$ (n = 1). Combining equations 11.23 and 11.24, and making an appropriate substitution for moles of Na₂S₂O₃ gives

$$\frac{nF(g \operatorname{Na}_2 S_2 O_3)}{FW \operatorname{Na}_2 S_2 O_3} = it_e$$

Solving for the grams of Na₂S₂O₃ gives

$$g \operatorname{Na}_{2} \operatorname{S}_{2} \operatorname{O}_{3} = \frac{it_{e} (\operatorname{FW} \operatorname{Na}_{2} \operatorname{S}_{2} \operatorname{O}_{3})}{nF}$$
$$= \frac{(0.03645 \text{ A})(221.8 \text{ s})(158.1 \text{ g/mol})}{(1 \text{ mol } e^{-})(96487 \text{ C/mol } e^{-})} = 0.01325 \text{ g} \operatorname{Na}_{2} \operatorname{S}_{2} \operatorname{O}_{3}$$

This represents the amount of $Na_2S_2O_3$ in a 10.00-mL portion of a 100-m sample, thus 0.1325 g of $Na_2S_2O_3$ is present in the original sample. The puri 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 $S_2O_3^{2-}$ is oxidized directly at t working electrode instead of in solution.

Example 2

A 0.3619-g sample of tetrachloropicolinic acid, C₆HNO₂Cl₄, 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

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

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

