Bulk Electrolysis:
Electrogravimetry and Coulometry

Potentiometric measurements are made in the absence of current flow. The measured potential is that of a **galvanic or voltaic cell**.

Chemical analyses can also be based on using a cell in an **electrolytic** fashion (i.e., driving a reaction with an applied voltage). In these cases, current flows in the cell.

Note that an electrochemical cell has a resistance to current flow, in analogy with resistance to current flow in any conductor. The relationship between voltage, current, and resistance is **ohm's Law**:

$$E = IR$$, where E is potential (voltage), I is current (in amperes) and R is resistance (in ohms)

To drive an endothermic electrochemical reaction, the applied voltage, $E_{applied}$, must overcome the cell potential and the IR drop:

$$E_{applied} = E_{cathode} - E_{anode} - IR$$

where $E_{cathode} - E_{anode} = E_{cell}$ as determined by the Nernst equation
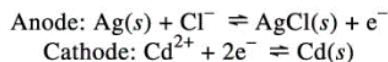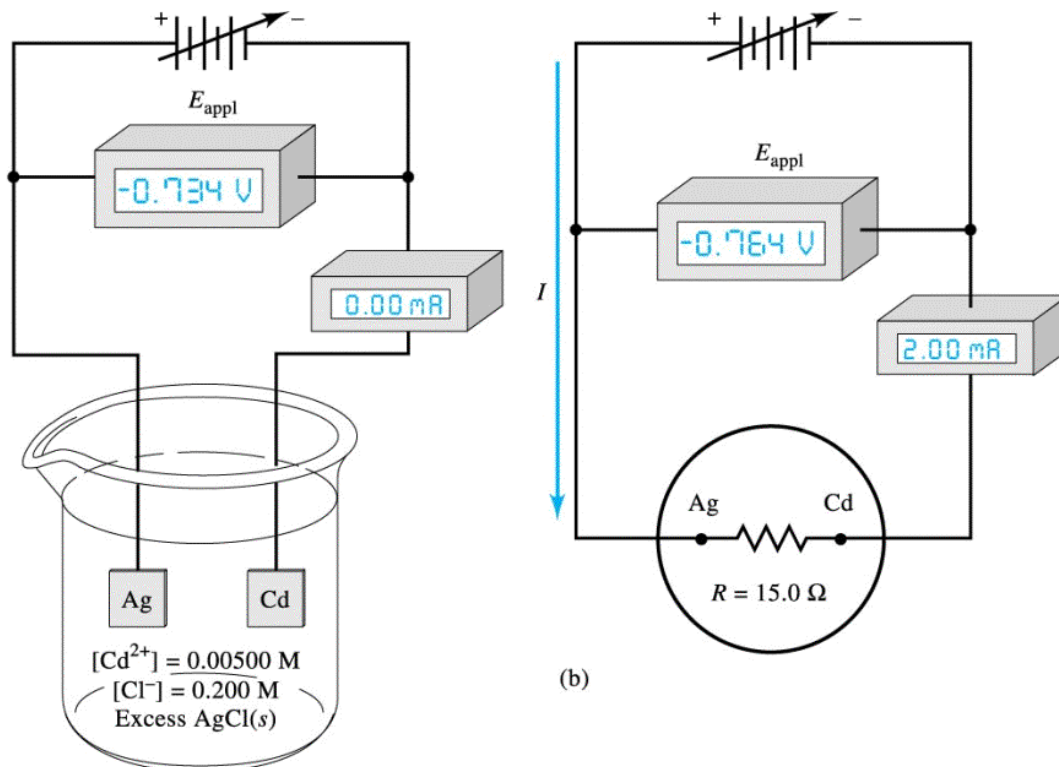
$E_{applied}$ must be $-IR$ volts more negative than the thermodynamic potential of the cell:

$$E_{applied} = E_{cell} - IR$$
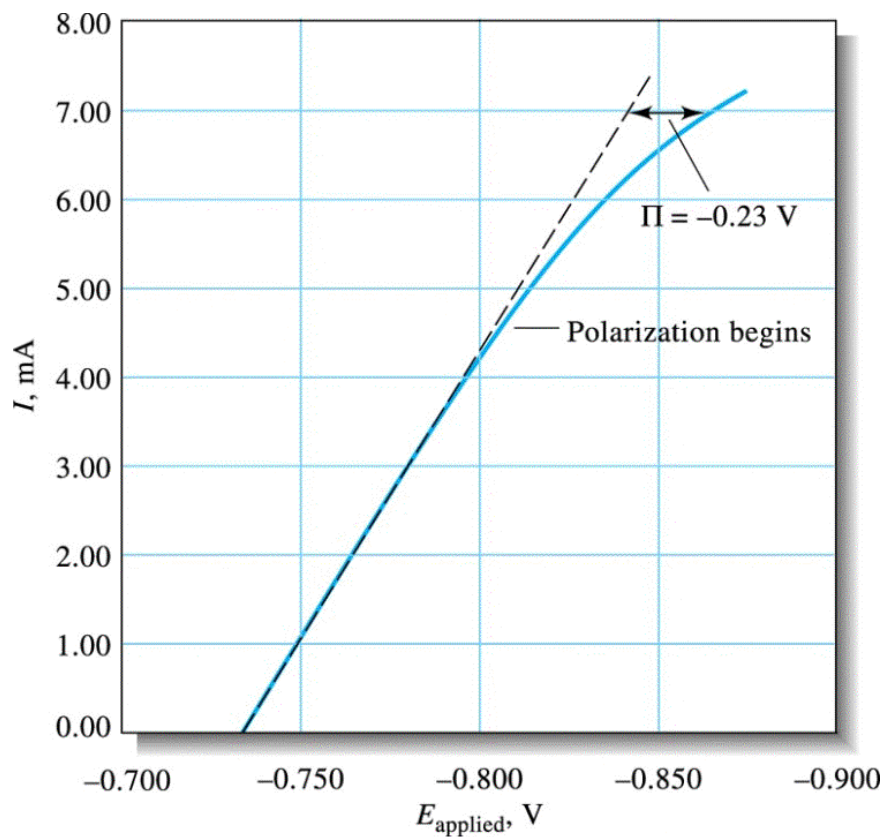
$$I = \frac{-E_{applied} + (E_{cell})}{R} = \frac{-E_{applied}}{R} + \frac{E_{cell}}{R}$$

$I=0$ when $-E_{applied} = E_{cell}$

A plot of I vs. $E_{applied}$ is linear with an intercept of E_{cell}/R and a slope of $-1/R$.
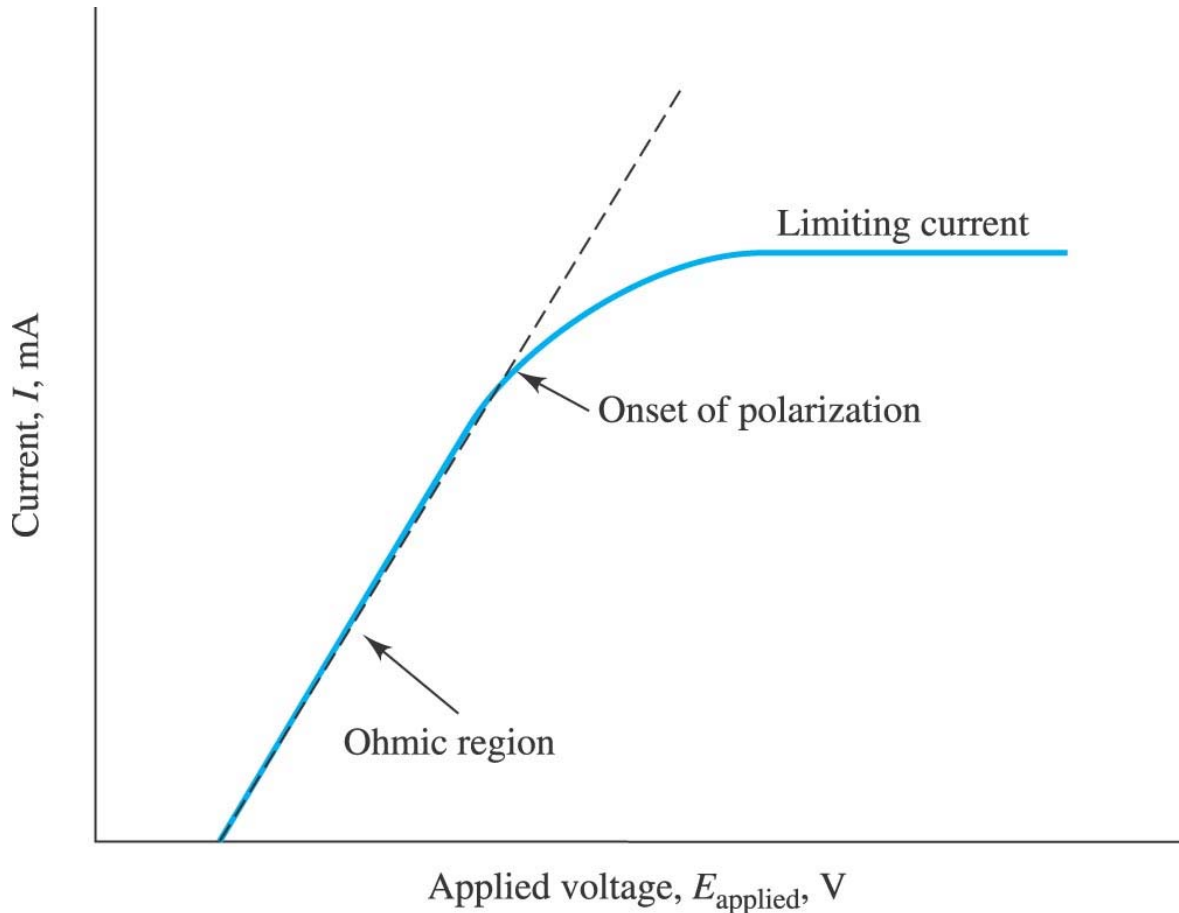
As $E_{applied}$ is more negative, the current, I, increases linearly until the cell becomes **polarized** as an **overvoltage** or **overpotential**, Π, arises.

$\Pi = -0.23$ V

Polarization begins

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$$E_{applied} = (E_{cathode} - E_{anode}) - IR - \Pi$$

As $E_{applied}$ is increased further, current becomes independent of $E_{applied}$. This gives rise to a limiting current:
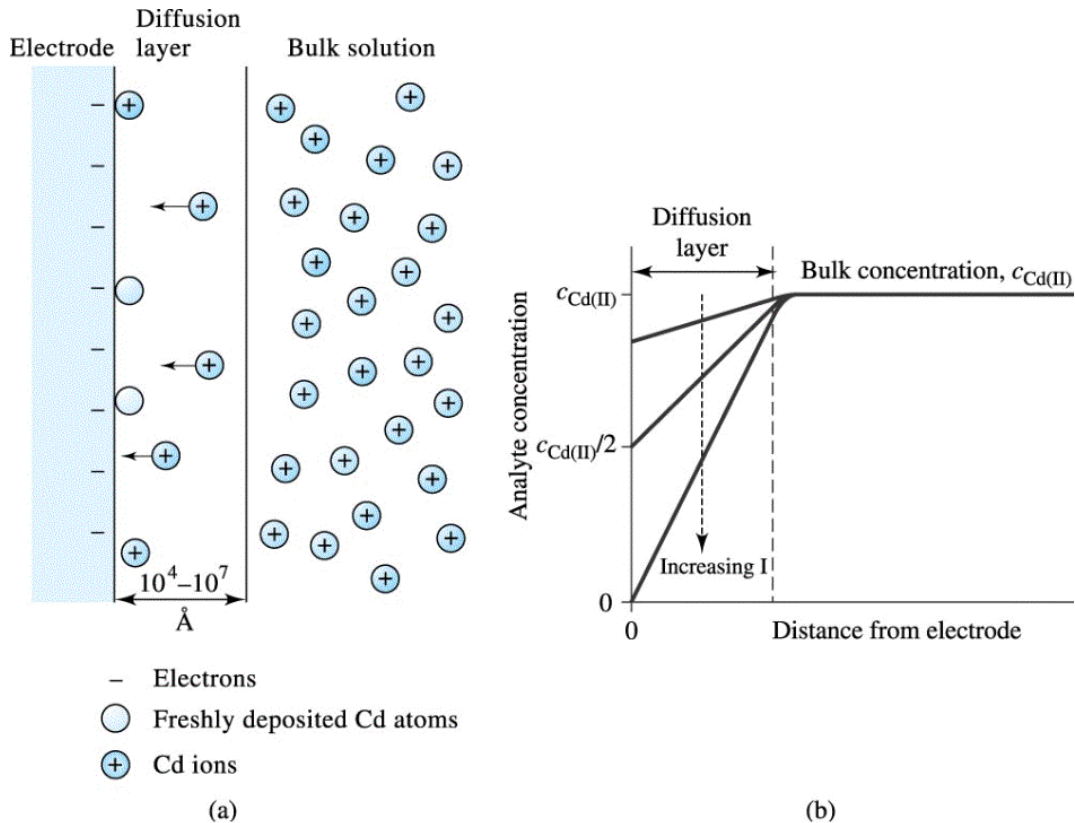

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What gives rise to polarization?

Rate-limiting (i.e., current limiting) phenomena are categorized in terms of **concentration polarization** and **kinetic polarization**.

Concentration polarization: due to a limited rate of mass transport from the bulk solution to the surface of the electrode.

Diffusion
Electrode layer   Bulk solution

10^4–10^7
Å

−   Electrons

◯   Freshly deposited Cd atoms

⊕   Cd ions

(a)

Diffusion layer

Bulk concentration, $c_{Cd(II)}$

$c_{Cd(II)}$

$c_{Cd(II)}/2$

Analyte concentration

Increasing I

0

0   Distance from electrode

(b)

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Once the rate at which reactants are consumed in the diffusion layer faster than they can be replaced from the bulk solution, the diffusion layer becomes relatively depleted in reactants. The transfer of electrons at the surface can be no faster than the rate at which the reactants interact with the surface.

(Likewise, polarization can occur when the rate at which products are removed from the surface is less than the rate at which they are produced.)

What determines the rate of mass transport?

Mass transport processes:

1. Diffusion – Motion arising due to a concentration gradient. A net motion occurs because species move from regions of higher concentration to regions of lower concentration. Once equilibrium is reached, no net motion occurs although species continue to move.

For a reactant approaching a surface:

net rate of diffusion = k([bulk]-[surface]), where k is a rate constant.

2. Migration – Motion arising due to the influence of an external field.
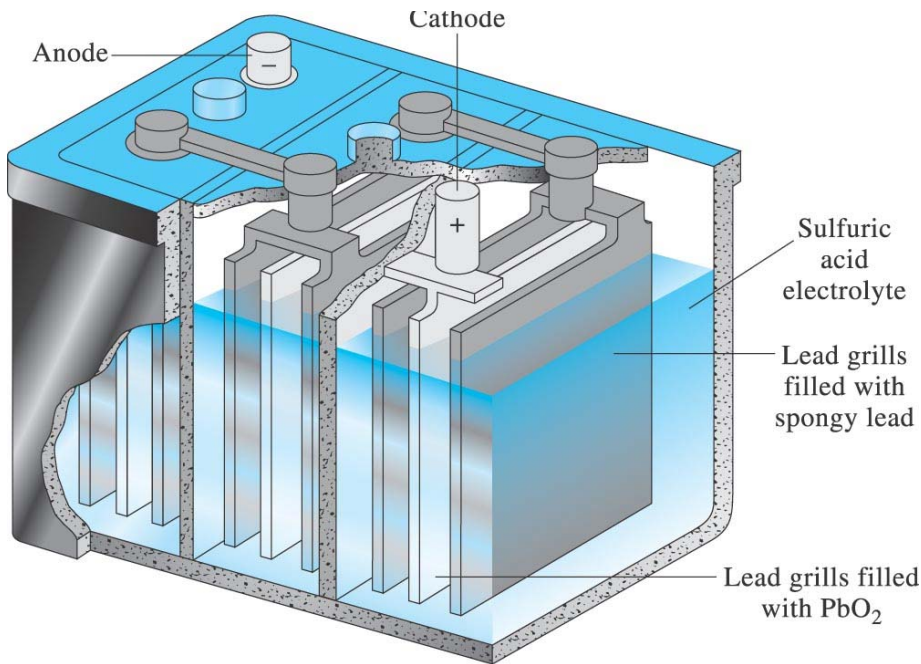

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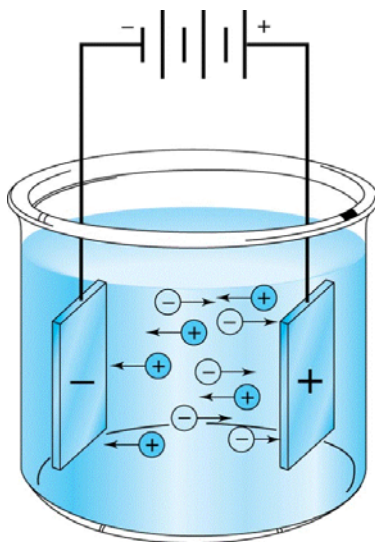
Migration is generally undesirable for analytical applications. Therefore, a relatively high concentration of electrolyte is used both to minimize the IR drop of the solution and to allow for the electrolyte to undergo most of the migration that arises from the electric field in the cell.

3. Convection – Motion due to mechanical forces such as stirring or shaking.

Note that concentration polarization can either be desirable or undesirable, depending upon the application (as we shall see).

Kinetic polarization – Due to inherently slow reaction at either the anode or cathode. (Remember kinetics – a thermodynamically favored reaction need not be fast.) An overpotential may be required to overcome an activation barrier (i.e., large $\Delta G^{\ddagger}$).
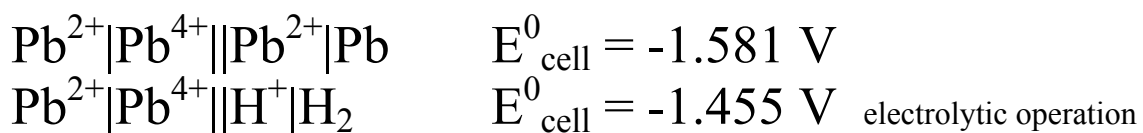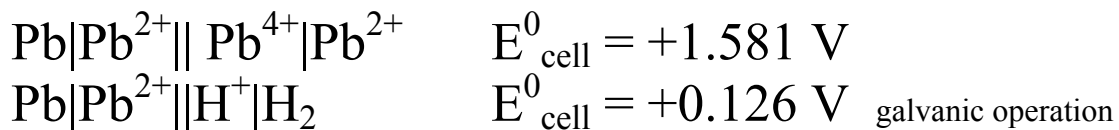
Ex. Reactions involving gas evolution, such as production of H_2 or O_2 (overpotentials as large as 1 V are often required).

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$$Pb(s) + PbO_2(s) + 2H_2SO_4 \rightleftharpoons 2PbSO_4 + 2H_2O$$

Thermodynamically, H_2 should form at the cathode during both galvanic and electrolytic operation but the overpotential on Pb and PbO_2 is sufficiently large that H_2 formation is minimal.

$Pb|Pb^{2+}|| Pb^{4+}|Pb^{2+}$ $\qquad E^0_{cell} = +1.581$ V

$Pb|Pb^{2+}||H^+|H_2$ $\qquad E^0_{cell} = +0.126$ V $\quad$ galvanic operation

$Pb^{2+}|Pb^{4+}||Pb^{2+}|Pb$ $\qquad E^0_{cell} = -1.581$ V

$Pb^{2+}|Pb^{4+}||H^+|H_2$ $\qquad E^0_{cell} = -1.455$ V $\quad$ electrolytic operation

Trace metals with lower overpotentials for H_2 formation can limit battery lifetime…

Analytical methods based on bulk electrolysis:

Electrogravimetry and Coulometric methods

Electrogravimetry: Electrolysis used to deposit a metal on a solid electrode so that its mass can be determined (gravimetry).

Two general approaches:

1. Constant applied potential
2. Variable applied potential to maintain constant cell potential

Ex. Deposition of copper (reduction) on a Pt gauze electrode from a $CuSO_4$ solution with oxidation of water at the anode.

cathode: $2(Cu^{2+} + 2e^- \rightarrow Cu(s))$
anode: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$
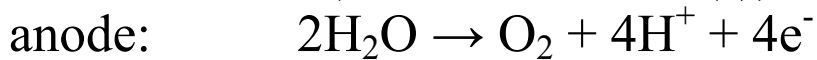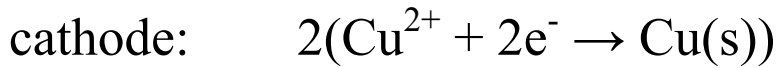
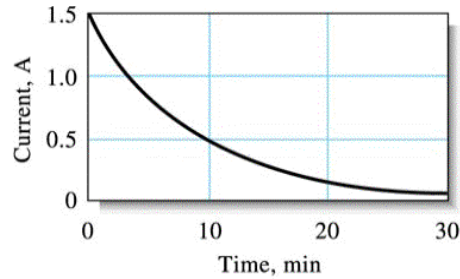$(E^0 = E^0_{cathode} - E^0_{anode} = +0.337 - 1.229 = -0.892$ V$)$

The current flow decreases as $[Cu^{2+}]$ is reduced, even in a well-stirred cell, as the copper ions are converted to copper metal at the cathode.
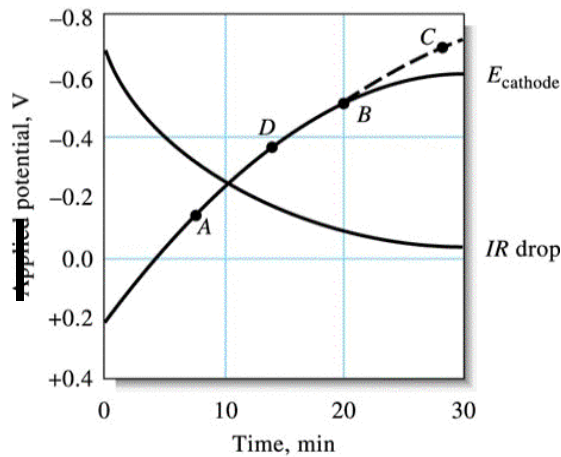

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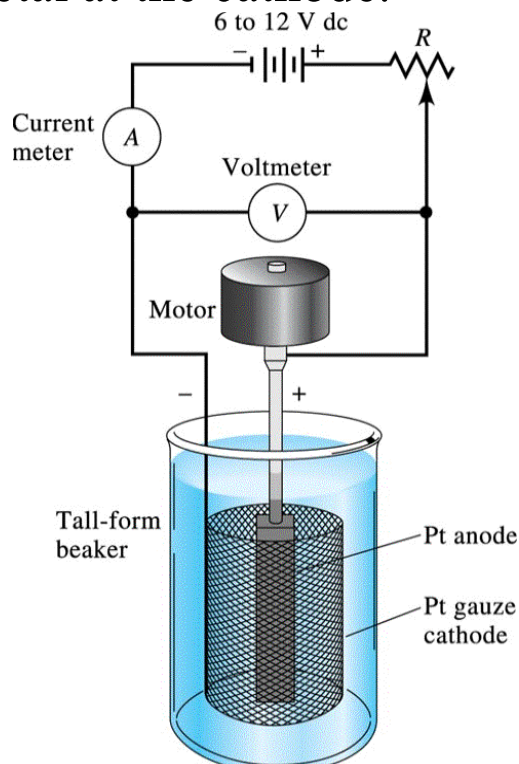
$$E_{applied} = E_{cell} - IR - \Pi$$

$$E_{cell} = E_{applied} + IR + \Pi$$

$E_{cell} \rightarrow E_{applied}$ as $IR \rightarrow 0$ (until Π becomes significant)


(a)

(b)

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Note that as the cathode potential becomes more negative, metals that are reduced at points A and D will co-deposit with the analyte. At point B, reduction of H^+ begins to contribute. Therefore, metals that are reduced at point C will not co-deposit due to reduction of H^+.

A more sophisticated approach to bulk electrogravimetry (than use of a constant applied potential) is needed for the selective deposition of species that differ in reduction potential by few tenths of volts…

$$E_{cell} = E_{applied} + IR + \Pi$$

To avoid co-deposition of metals with higher reduction potentials, E_{cell} should be held constant by varying $E_{applied}$ as IR and Π change. This is done with a three-electrode arrangement in which the working electrode potential (cathode) is continuously monitored and this signal is used via a feedback circuit to maintain constant E_{cell}.

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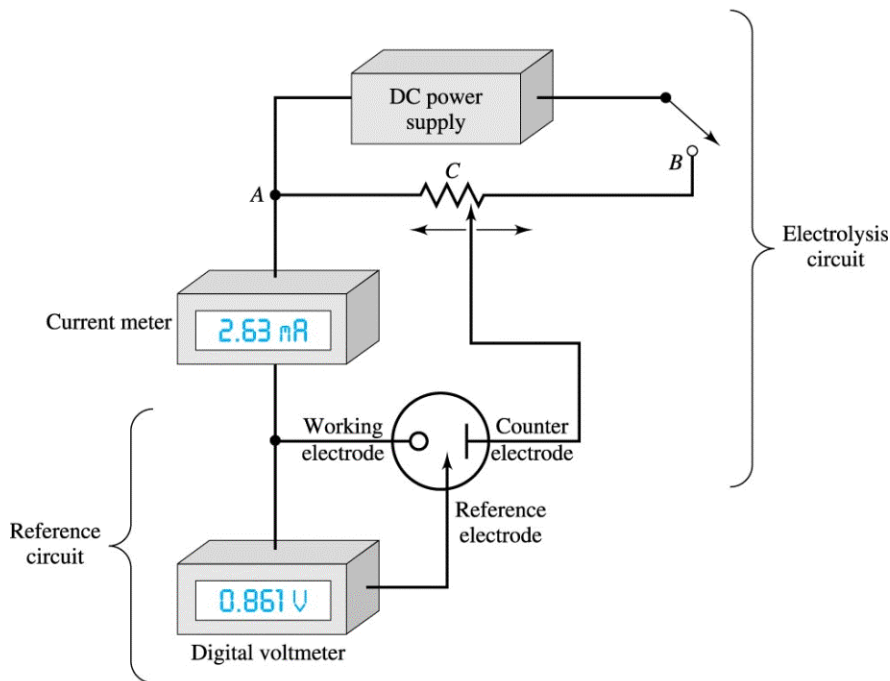
A high impedance reference circuit (very little current flow) monitors E_{cell} while current flows between working electrode and counter electrode. Feedback circuitry varies $E_{applied}$ to maintain constant $E_{cathode}$.
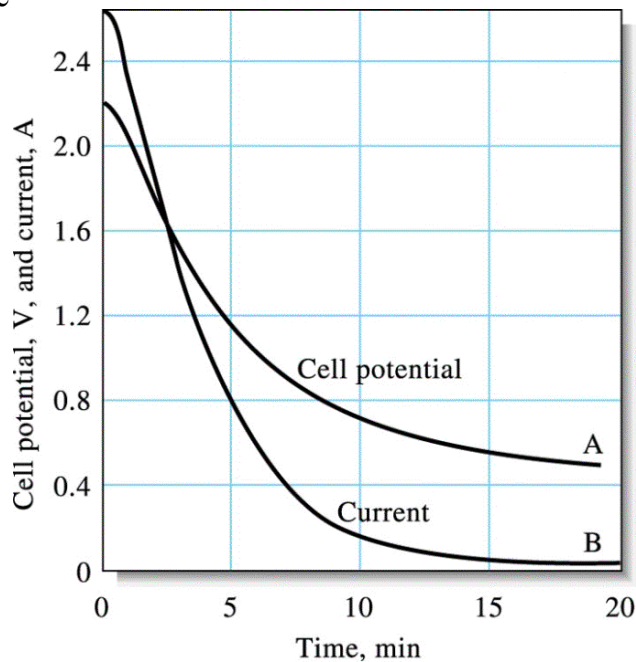
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TABLE 22-2

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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Coulometric methods

Based on the stoichiometry associated with the conversion of species from one oxidation state to another:

$$Cu^{2+} + 2e^- \rightarrow Cu^0$$

2 moles e^- needed to convert 1 mole of Cu^{2+} to Cu^0. (2 mole e^-/mole Cu)

a unit charge (electron or proton) has an absolute value of **1.602 x 10^{-19} C**. One mole of e^-, therefore, is

$$(1.6022 \times 10^{-19} C/e^-)(6.022 \times 10^{23}\ e^-) = 96,485\ C$$

96,485 C = 1 faraday (F)
(charge of 1 mole of elementary charges)

a measure of the charge transfer associated with a redox reaction is a measure of the number of electrons transferred.

$$n_A = \frac{Q}{nF}$$ **Faraday's law**, moles of analyte, n_A, is given by charge, Q, divided by moles of electrons in half-reaction, n, times the Faraday constant.
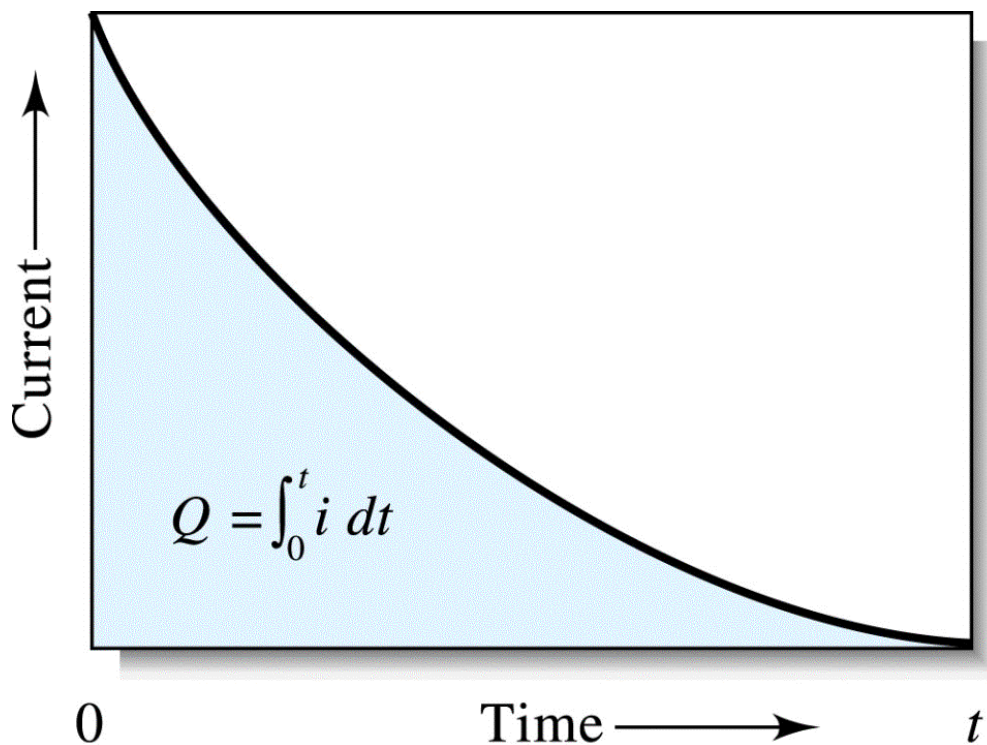
How to determine total charge associated with a redox reaction?

Current (amperes) = charge (Coulombs)/unit time (s)

I = Q/t   where I is constant current, Q is charge, t is time

Q = It

$$Q = \int_{t=0}^{t} i\, dt$$ where i is variable current

$$Q = \int_{0}^{t} i\, dt$$

0   Time ⟶   t

Basic types of coulometric methods:

1. Controlled potential coulometry
2. Controlled current coulometry

Controlled potential coulometry: Highly analogous to controlled potential electrogravimetry (see above)

Advantages of coulometry over electrogravimetry:

requires no weighing (requires current measurement) reaction need not give rise to formation of a solid product.
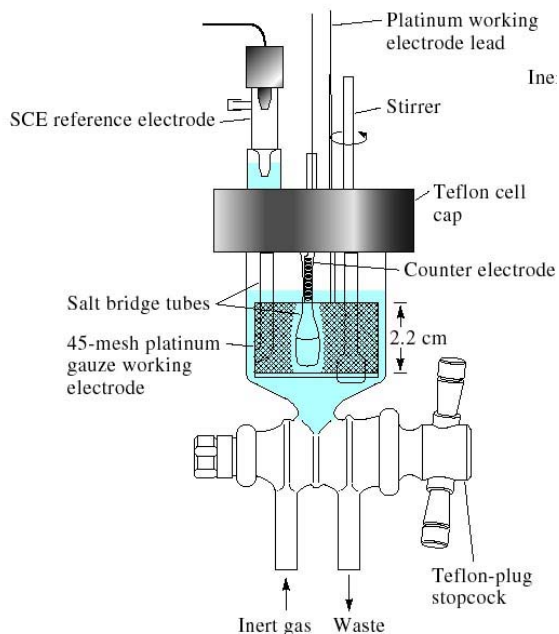
(a)

Counter electrode is isolated from the analyte solution to prevent products formed at the counter electrode from reacting with products formed at the working electrode.

## Controlled current coulometry (coulometric titration):

Volumetric titration: The volume of a standard solution required to reach an equivalence point is measured.

Coulometric titration: The charge required to reach an equivalence point is measured.

Supply of constant current over a fixed time period is analogous to adding a fixed volume of a standard solution. "titrating with electrons"

The cell is typically used to produce electrochemically a reagent that will react immediately with the analyte.
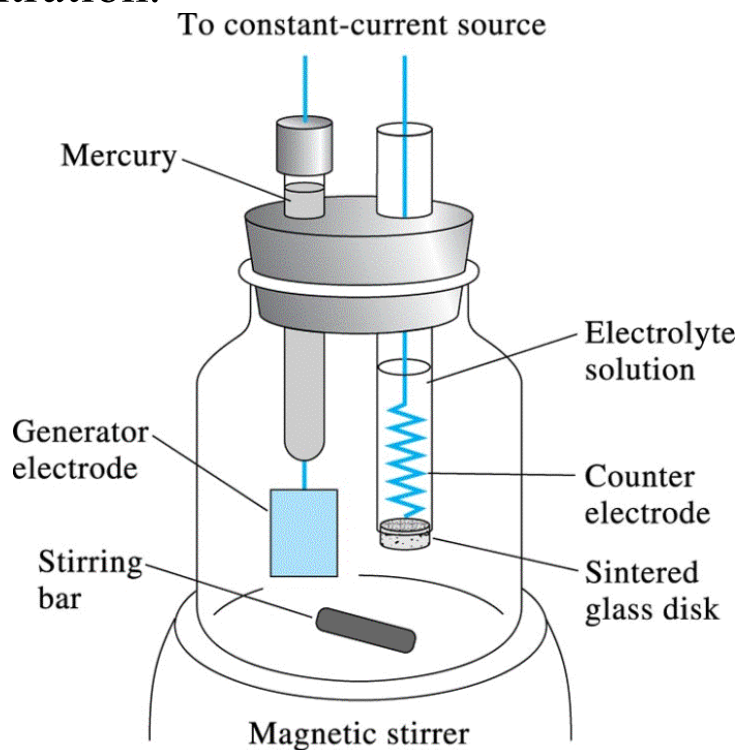
e.g., the determination of Fe^{2+}. Generate Ce^{4+} from an excess of Ce^{3+} electrochemically in solution to give rise to:
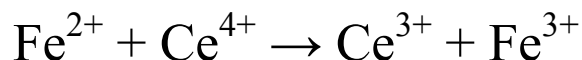
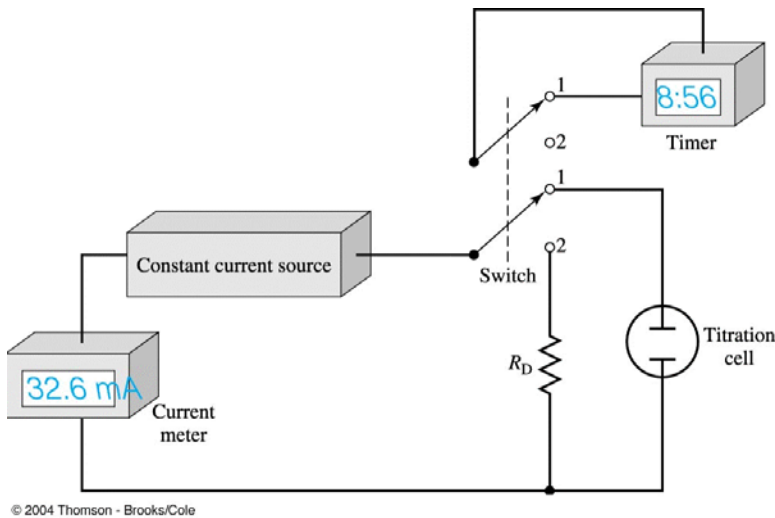$$Fe^{2+} + Ce^{4+} \rightarrow Ce^{3+} + Fe^{3+}$$
(detect equivalence point with a redox indicator)
The quantity of Ce^{4+} is known based on current x time to reach the equivalence point. The quantity of Fe^{2+} is determined via reaction stoichiometry.

Completely analogous to titrating a solution of Fe^{2+} with a standard solution of Ce^{4+} with known Ce^{4+} concentration.

To constant-current source

Mercury

Generator electrode

Stirring bar

Magnetic stirrer

Electrolyte solution

Counter electrode
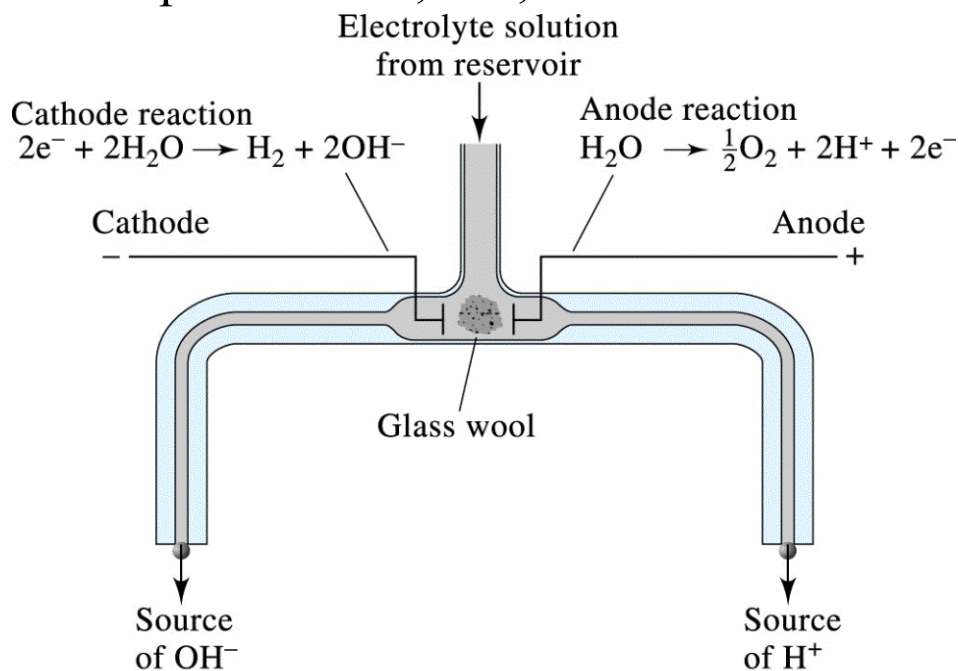
Sintered glass disk

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I.   Current x time = moles of reagent
(analogous to volume x molarity of reagent = moles of reagent)
II.   Switch used to gate moles of reagent
(analogous to stopcock in buret)
III.   Timer
(analogous to buret)
IV. Variety of means for equivalence point determination

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Advantages of coulometric titration versus volumetric titration:

1. No need to prepare, standardize, store standard sol'n.
2. Can prepare unstable reagents, since they react almost as soon as they are generated – e.g., Cl_2, Br_2
3. Straightforward to generate tiny quantities of reagent with good accuracy since it is easy to control current and time electronically.
4. A single coulometric titration apparatus can be used for redox, acid/base, precipitation, complexometric, etc., titrations

Electrolyte solution from reservoir

Cathode reaction
$2e^- + 2H_2O \rightarrow H_2 + 2OH^-$

Anode reaction
$H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-$

Cathode
$-$

Anode
$+$

Glass wool

Source of OH^-

Source of H^+

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advantage of volumetric titrations - simple

TABLE 22-3

Summary of Coulometric Titrations Involving Neutralization, Precipitation, and Complex-Formation Reactions

Species Determined	Generator Electrode Reaction	Secondary Analytical Reaction
Acids	$2H_2O + 2e^- \rightleftharpoons 2OH^- + H_2$	$OH^- + H^+ \rightleftharpoons H_2O$
Bases	$H_2O \rightleftharpoons 2H^+ + \frac{1}{2}O_2 + 2e^-$	$H^+ + OH^- \rightleftharpoons H_2O$
Cl^-, Br^-, I^-	$Ag \rightleftharpoons Ag^+ + e^-$	$Ag^+ + X^- \rightleftharpoons AgX(s)$
Mercaptans (RSH)	$Ag \rightleftharpoons Ag^+ + e^-$	$Ag^+ + RSH \rightleftharpoons AgSR(s) + H^+$
Cl^-, Br^-, I^-	$2Hg \rightleftharpoons Hg_2^{2+} + 2e^-$	$Hg_2^{2+} + 2X^- \rightleftharpoons Hg_2X_2(s)$
Zn^{2+}	$Fe(CN)_6^{3-} + e^- \rightleftharpoons Fe(CN)_6^{4-}$	$3Zn^{2+} + 2K^+ + 2Fe(CN)_6^{4-} \rightleftharpoons K_2Zn_3[Fe(CN)_6]_2(s)$
$Ca^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}$	See Equation 22-9	$HY^{3-} + Ca^{2+} \rightleftharpoons CaY^{2-} + H^+$, etc.

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TABLE 22-4

Summary of Coulometric Titrations Involving Oxidation/Reduction Reactions

Reagent	Generator Electrode Reaction	Substance Determined
Br_2	$2Br^- \rightleftharpoons Br_2 + 2e^-$	As(III), Sb(III), U(IV), Tl(I), I$^-$, SCN$^-$, NH$_3$, N$_2$H$_4$, NH$_2$OH, phenol, aniline, mustard gas, mercaptans, 8-hydroxyquinoline, olefins
Cl_2	$2Cl^- \rightleftharpoons Cl_2 + 2e^-$	As(III), I$^-$, styrene, fatty acids
I_2	$2I^- \rightleftharpoons I_2 + 2e^-$	As(III), Sb(III), S$_2$O$_3^{2-}$, H$_2$S, ascorbic acid
Ce^{4+}	$Ce^{3+} \rightleftharpoons Ce^{4+} + e^-$	Fe(II), Ti(III), U(IV), As(III), I$^-$, Fe(CN)$_6^{4-}$
Mn^{3+}	$Mn^{2+} \rightleftharpoons Mn^{3+} + e^-$	H$_2$C$_2$O$_4$, Fe(II), As(III)
Ag^{2+}	$Ag^+ \rightleftharpoons Ag^{2+} + e^-$	Ce(III), V(IV), H$_2$C$_2$O$_4$, As(III)
Fe^{2+}	$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	Cr(VI), Mn(VII), V(V), Ce(IV)
Ti^{3+}	$TiO^{2+} + 2H^+ + e^- \rightleftharpoons Ti^{3+} + H_2O$	Fe(III), V(V), Ce(IV), U(VI)
$CuCl_3^{2-}$	$Cu^{2+} + 3Cl^- + e^- \rightleftharpoons CuCl_3^{2-}$	V(V), Cr(VI), IO$_3^-$
U^{4+}	$UO_2^{2+} + 4H^+ + 2e^- \rightleftharpoons U^{4+} + 2H_2O$	Cr(VI), Ce(IV)

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