

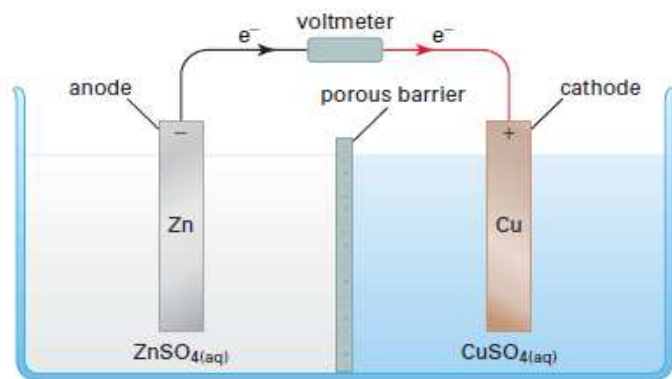
G12 Chemistry

Electrochemistry

Class 16

Galvanic Cells

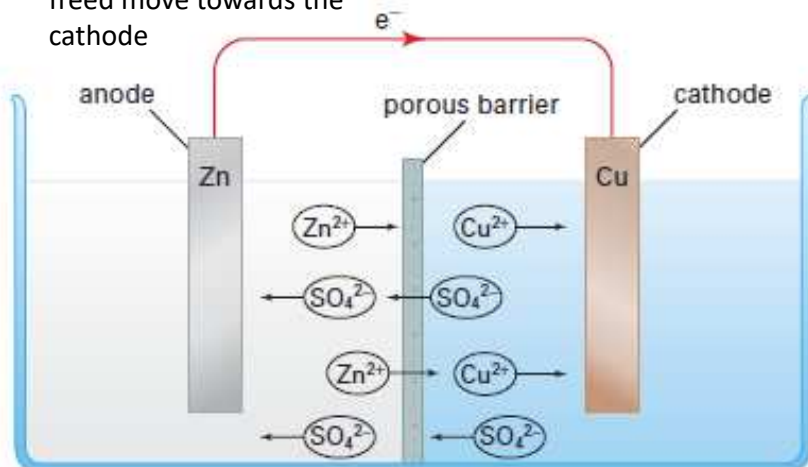
- Converts chemical energy to electrical energy by preventing the reactants from coming into contact with each other
- Electrons flow through an external circuit



Electrodes – the Zn and Cu metal

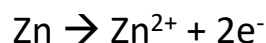
Electrolyte – the $\text{ZnSO}_4(\text{aq})$ and $\text{CuSO}_4(\text{aq})$

1. Electrons that are freed move towards the cathode



2. The Cu^{2+} in solution picks up the electrons and get reduced to copper metal, which accumulates on the copper cathode

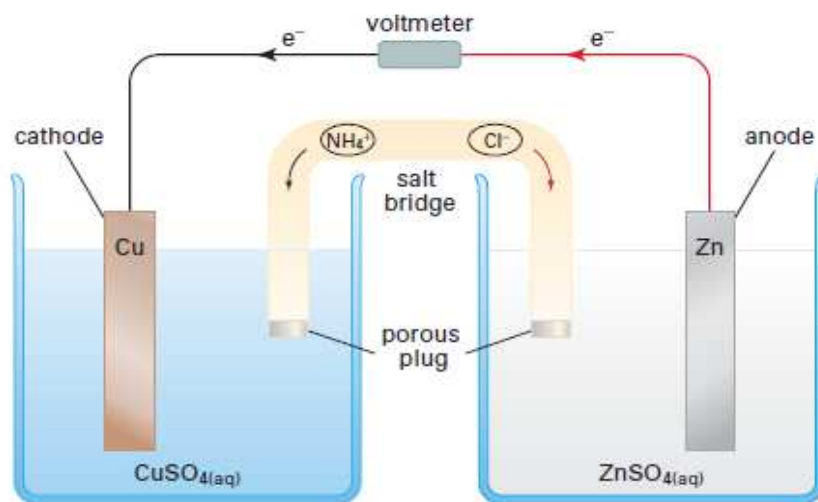
Anode – Site of Oxidation



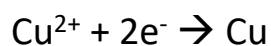
Cathode – Site of Reduction



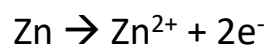
3. The Zn^{2+} that remain in the solution attract SO_4^{2-} through the porous barrier to maintain neutrality



Cathode – Site of Reduction



Anode – Site of Oxidation



2. As the Cu^{2+} from the solution and electrons get reduced to copper metal, the NH_4^{+} migrate towards the CuSO_4 solution to maintain neutrality.

1. When the electrons leave the anode, Zn^{2+} is left in the solution, which causes the Cl^{-} in the salt bridge to migrate towards the ZnSO_4 solution

Cell Diagrams

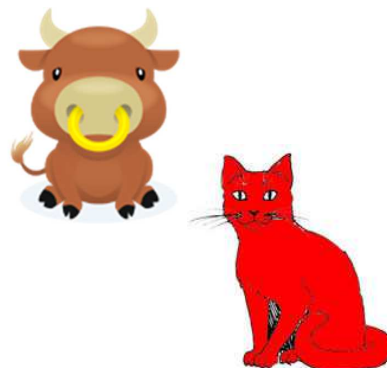
- Use a shorthand notation:

Anode | Anodic solution || Cathodic solution | Cathode



- Remember:

- AN OX – anode, oxidation
- RED CAT – cathode, reduction



Checkpoint

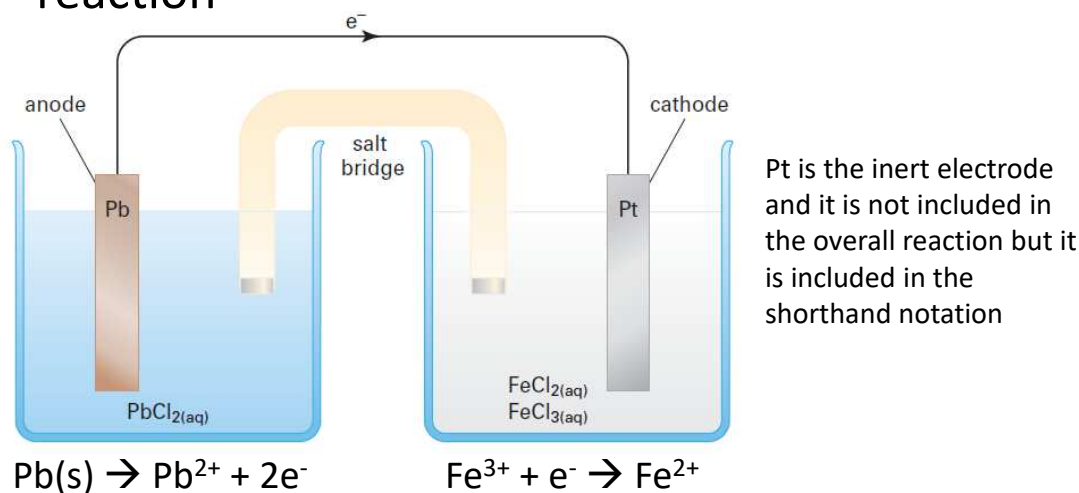


Write the shorthand notation for a galvanic cell that uses the reaction:



Inert Electrodes

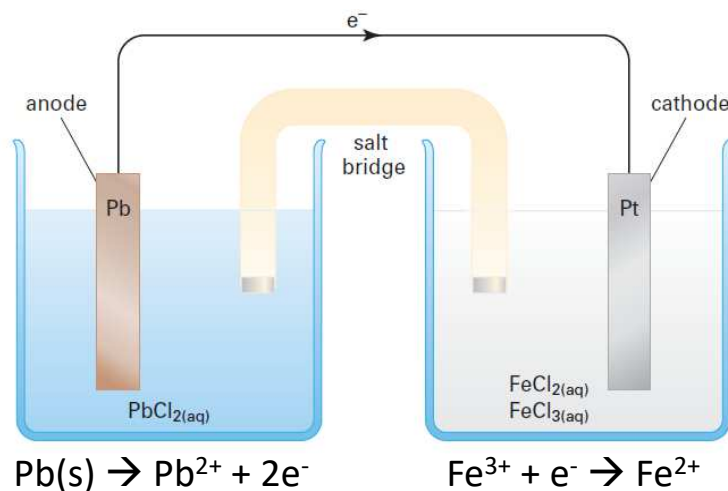
- An electrode that is made from a material that is neither a reactant nor a product of the reaction



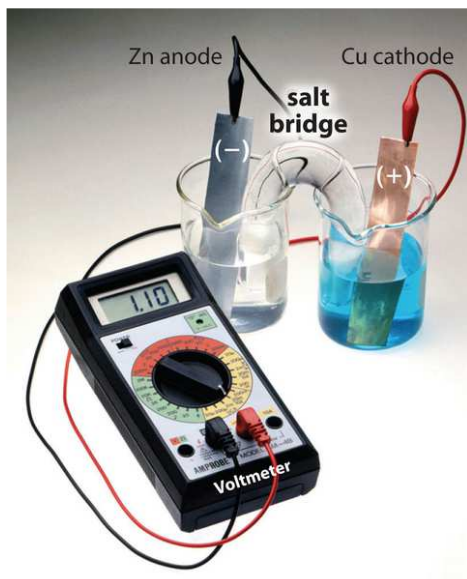
Checkpoint



Write the shorthand notation for the following galvanic cell:



Cell Potentials



- Cell Potential (E) – the difference between the potential energy at the anode and the cathode
– Unit: V or J/C – measured with a voltmeter

$$\text{Cell Potential (E)} = \frac{W}{Q}$$

Standard Reduction Potentials

- Uses hydrogen (E°) as a standard of 0 V

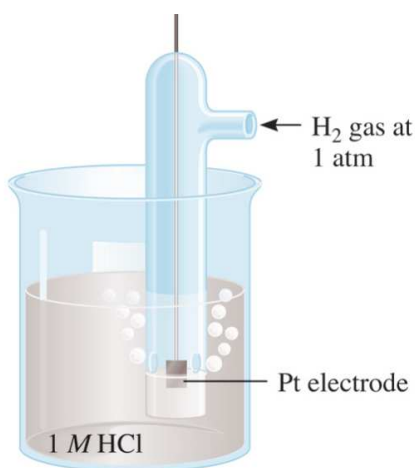
Table 11.1 Standard Half-Cell Potentials (298 K)

Half-reaction	E° (V)
$\text{F}_{2(\text{g})} + 2\text{e}^- \rightleftharpoons 2\text{F}^-_{(\text{aq})}$	2.866
$\text{Br}_{2(\text{l})} + 2\text{e}^- \rightleftharpoons 2\text{Br}^-_{(\text{aq})}$	1.066
$\text{I}_{2(\text{s})} + 2\text{e}^- \rightleftharpoons 2\text{I}^-_{(\text{aq})}$	0.536
$\text{Cu}^{2+}_{(\text{aq})} + 2\text{e}^- \rightleftharpoons \text{Cu}_{(\text{s})}$	0.342
$2\text{H}^+_{(\text{aq})} + 2\text{e}^- \rightleftharpoons \text{H}_{2(\text{g})}$	0.000
$\text{Fe}^{2+}_{(\text{aq})} + 2\text{e}^- \rightleftharpoons \text{Fe}_{(\text{s})}$	-0.447
$\text{Zn}^{2+}_{(\text{aq})} + 2\text{e}^- \rightleftharpoons \text{Zn}_{(\text{s})}$	-0.762
$\text{Al}^{3+}_{(\text{aq})} + 3\text{e}^- \rightleftharpoons \text{Al}_{(\text{s})}$	-1.662
$\text{Na}^+_{(\text{aq})} + \text{e}^- \rightleftharpoons \text{Na}_{(\text{s})}$	-2.711

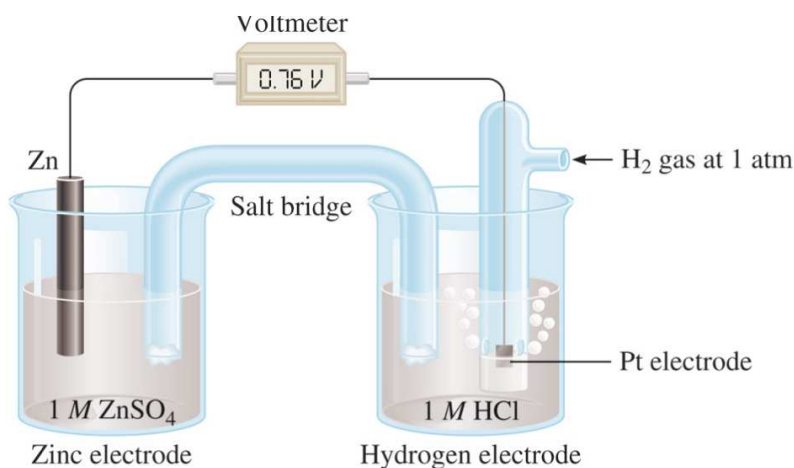
- Tables of half-reaction potentials are given for reductions only
- To get the potential of the oxidation reaction, reverse the sign of the tabulated value

Standard Hydrogen Electrode (SHE)

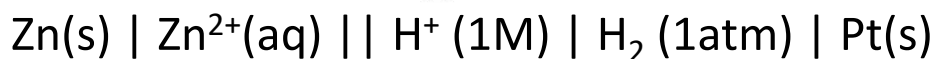
- The hydrogen electrode is used as a reference for all other standard reduction potentials



- Hydrogen gas is bubbled into the [1.0M] HCl solution at 25°C and 1atm
 - The platinum electrode provides a surface for the dissociation of hydrogen molecules and serves as an electrical conductor
- $$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \quad E^\circ = 0\text{V}$$



(a)

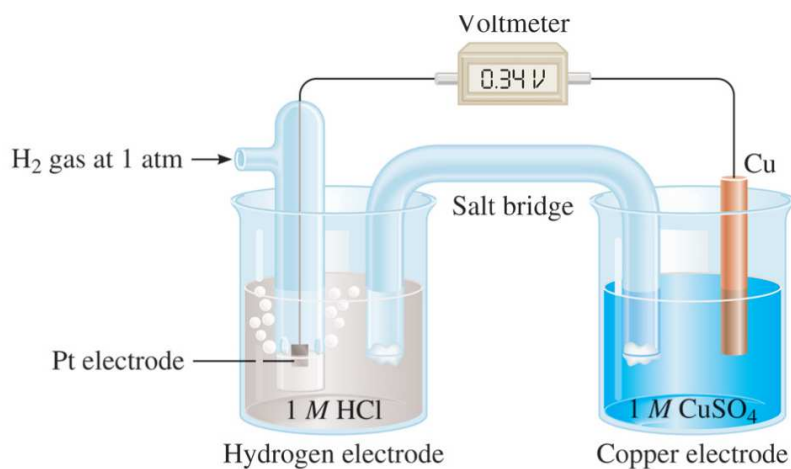


$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

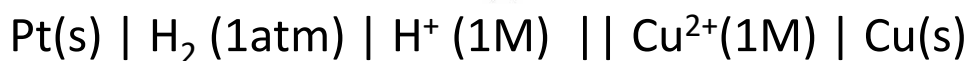
$$E^\circ_{\text{cell}} = E^\circ_{\text{Hydrogen}} - E^\circ_{\text{Zinc}}$$

$$0.76\text{V} = 0 - E^\circ_{\text{Zinc}}$$

$$E^\circ_{\text{Zinc}} = -0.76\text{V}$$



(b)



$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

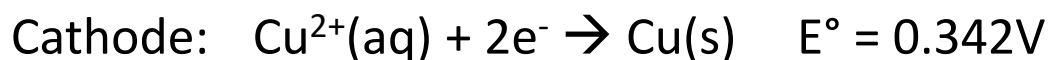
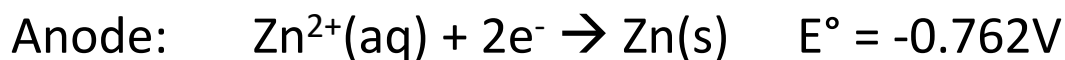
$$E^\circ_{\text{cell}} = E^\circ_{\text{Copper}} - E^\circ_{\text{Hydrogen}}$$

$$0.34\text{V} = E^\circ_{\text{Copper}} - 0$$

$$E^\circ_{\text{Copper}} = 0.34\text{V}$$

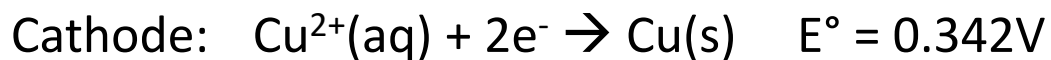
Calculating Standard Cell Potentials

$$\text{Method 1: } E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

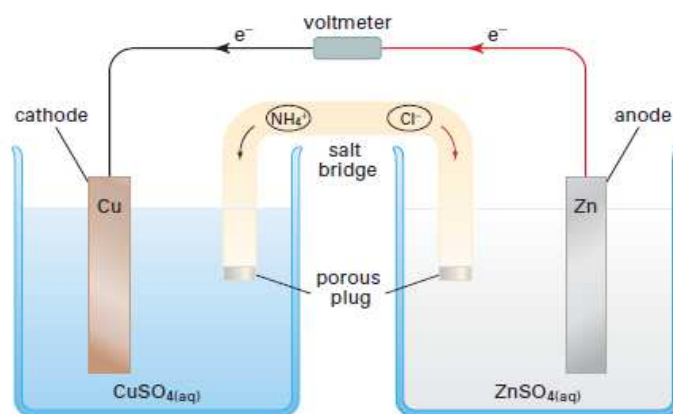


$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \\ &= 0.342\text{V} - (-0.762\text{V}) \\ &= 1.104\text{V} \end{aligned}$$

$$\text{Method 2: } E^{\circ}_{\text{cell}} = E^{\circ}_{\text{red}} + E^{\circ}_{\text{ox}}$$



$$\begin{aligned} E^{\circ}_{\text{cell}} &= E^{\circ}_{\text{red}} + E^{\circ}_{\text{oxid}} \\ &= 0.342\text{V} + 0.762\text{V} \\ &= 1.104\text{V} \end{aligned}$$



$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$$

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{Copper}} - E^{\circ}_{\text{Zinc}}$$

$$E^{\circ}_{\text{cell}} = 0.34\text{V} - (-0.76\text{V})$$

$$E^{\circ}_{\text{cell}} = 1.10\text{V}$$

REDUCTION
(Stronger OA)
More Positive

OXIDATION
(Stronger RA)
More Negative

TABLE 10.1 Standard Reduction Potentials at 25°C

Reduction Half-Reaction	E° (V)
$\text{F}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{F}^-(\text{aq})$	2.87
$\text{H}_2\text{O}_2(\text{aq}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}(\text{l})$	1.78
$\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$	1.51
$\text{Cl}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{Cl}^-(\text{aq})$	1.36
$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6\text{e}^- \rightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$	1.33
$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}(\text{l})$	1.23
$\text{Br}_2(\text{l}) + 2\text{e}^- \rightarrow 2\text{Br}^-(\text{aq})$	1.09
$\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$	0.80
$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{Fe}^{2+}(\text{aq})$	0.77
$\text{O}_2(\text{g}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2(\text{aq})$	0.70
$\text{I}_2(\text{s}) + 2\text{e}^- \rightarrow 2\text{I}^-(\text{aq})$	0.54
$\text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4\text{e}^- \rightarrow 4\text{OH}^-(\text{aq})$	0.40
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$	0.34
$\text{Sn}^{4+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Sn}^{2+}(\text{aq})$	0.15
$2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$	0
$\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Pb}(\text{s})$	-0.13
$\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Ni}(\text{s})$	-0.26
$\text{Cd}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cd}(\text{s})$	-0.40
$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Fe}(\text{s})$	-0.45
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Zn}(\text{s})$	-0.76
$2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$	-0.83
$\text{Al}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Al}(\text{s})$	-1.66
$\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Mg}(\text{s})$	-2.37
$\text{Na}^+(\text{aq}) + \text{e}^- \rightarrow \text{Na}(\text{s})$	-2.71
$\text{Li}^+(\text{aq}) + \text{e}^- \rightarrow \text{Li}(\text{s})$	-3.04



Checkpoint



Calculate the standard cell potential for the galvanic cell in which the following reaction occurs.

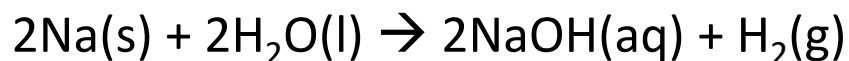




Checkpoint



Calculate the standard cell potential for the galvanic cell in which the following reaction occurs.



Thermodynamics of Redox Reactions

- How are standard cell potentials (E°) and free-energy changes (ΔG) related?

$$\Delta G^\circ = -nFE^\circ$$

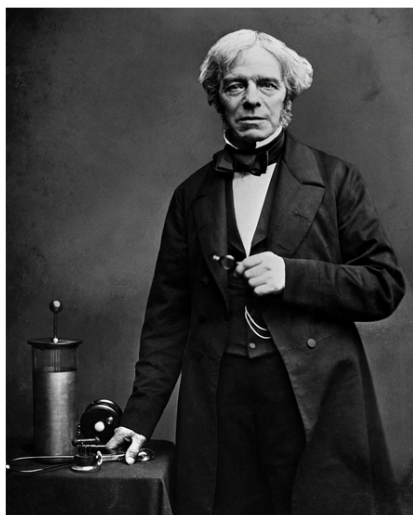
ΔG° = free energy change under standard conditions

n = moles of electrons transferred in the reaction

F = Faraday constant (96 500 C/mol e^-)

Faraday constant (F) – charge of 1 mol of e⁻

$$\begin{aligned}\text{Charge on one mole of electrons} &= \frac{1.602 \times 10^{-19} \text{ C}}{1e^-} \times \frac{6.022 \times 10^{23} e^-}{1 \text{ mol}} \\ &= 9.647 \times 10^4 \text{ C/mol}\end{aligned}$$



$$F = \frac{q_e}{n_e}$$

$$q_e = n_e F$$

Where:

n_e = number of moles of electrons exchanged in the redox reaction



Checkpoint



Calculate the standard free-energy change at 25°C for the following reaction. The standard cell potential is 1.10V.



Concentration and Cell Potentials

To understand the relationship between concentration and cell potential changes, use the Nernst equation:

Nernst equation
$$E = E^{\circ} - \frac{RT}{nF} \ln Q$$

E = cell potential in non-standard state

E° = cell potential at standard state

R = 8.314 J/molK

F = 96 500 C/mol of e^{-}

n = mol of electrons transferred

Q = reaction quotient

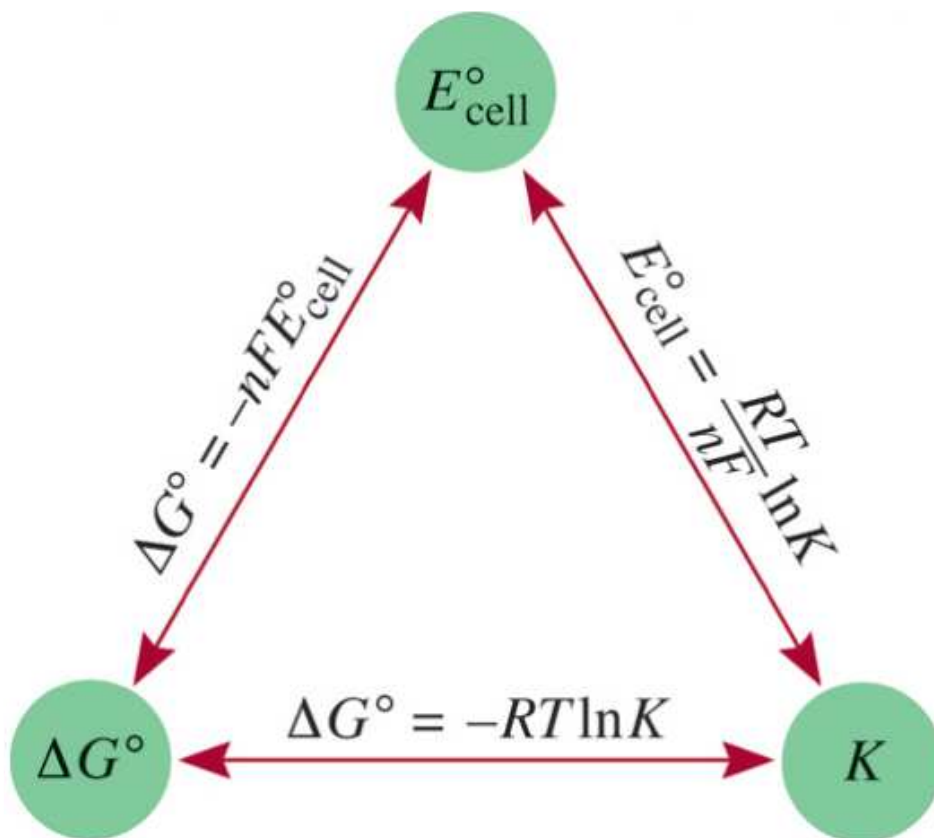


Checkpoint



Predict whether the following reaction would proceed spontaneously as written at 298K given that $[\text{Co}^{2+}] = 0.15\text{M}$ and $[\text{Fe}^{2+}] = 0.68\text{M}$





Checkpoint

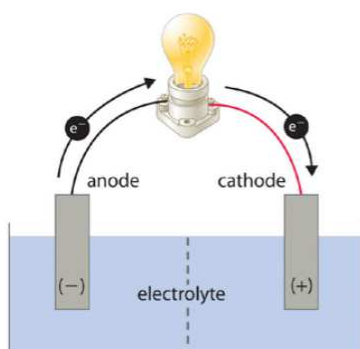


Calculate the equilibrium constant for the following reaction at 25°C:

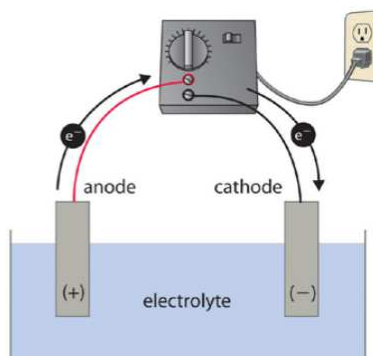


Electrolytic Cells

- The use of electricity to power a nonspontaneous redox reaction
- The external power can be a battery or an electrical outlet which forces the products to turn back into reactants
- Process is called electrolysis
- ΔE° is negative (nonspontaneous)



GALVANIC CELL



ELECTROLYTIC CELL

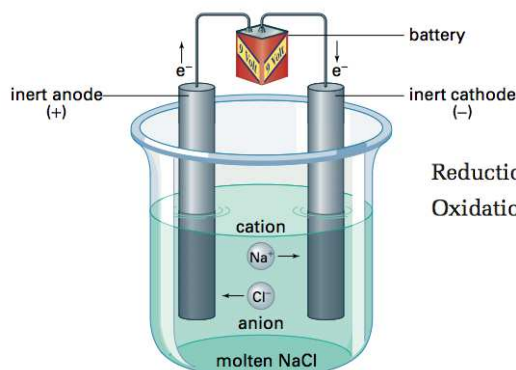
Galvanic	Electrolytic
Spontaneous ($\Delta G < 0$)	Nonspontaneous ($\Delta G > 0$)
Is a battery	Needs a battery
Two half-cells to generate electricity	Occurs in a single container
Anode (Oxidation; Negative)	Anode (Oxidation; Positive)
Cathode (Reduction; Positive)	Cathode (Reduction; Negative)

Predicting the Products of Electrolysis

- If there is no water present and you have a pure molten ionic compound, then:
 - The cation will be reduced
 - The anion will be oxidized
- If water is present and you have an aqueous solution of the ionic compound, then:
 - Deduce whether the ions are reacting or the water is reacting:
 - No Group 1 or 2 metals will be reduced, water will be reduced instead
 - No Polyatomic ions will be oxidized, water will be oxidized instead

Applications of Electrolytic Cells

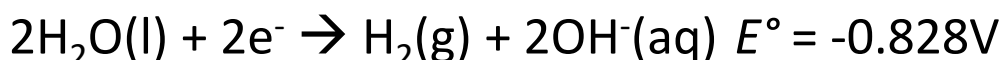
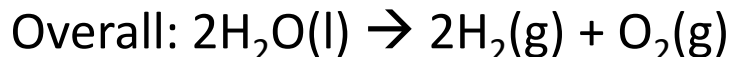
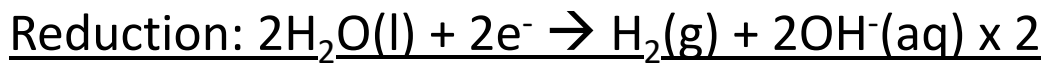
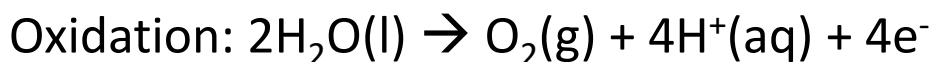
- In **molten-salt electrolysis**, metal cations are reduced to metal atoms at the cathode and nonmetal anions are oxidized at the anode
 - Ex: Manufacture of Na metal



Reduction half-reaction (occurs at the cathode): $\text{Na}^+_{(\ell)} + \text{e}^- \rightarrow \text{Na}_{(\ell)}$

Oxidation half-reaction (occurs at the anode): $2\text{Cl}^-_{(\ell)} \rightarrow \text{Cl}_{2(\text{g})} + 2\text{e}^-$

Electrolysis of Water



$$\begin{aligned} E^\circ &= E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \\ &= -0.828\text{V} - 1.229\text{V} \\ &= -2.057\text{V (nonspontaneous)} \end{aligned}$$

Procedure for Analyzing Electrolytic Cells

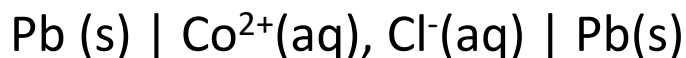
- 1) Use the redox table to identify the SOA (strongest oxidizing agent) and SRA (strongest reducing agent)
 - Don't forget to consider water for aqueous electrolytes
- 2) Write equations for the reduction and oxidation. Include all the reduction potentials if required.
- 3) Balance the electrons and write the net cell reaction and cell potential.
- 4) State the minimum electric potential to force the reaction to occur. The minimum voltage is the absolute value of E°_{cell}



Checkpoint



An electrolytic cell containing cobalt(II) chloride solution and lead electrodes is assembled.



- Predict the reactions at the cathode and anode and in the overall cell
- Draw and label a cell diagram for this electrolytic cells, including the power supply
- What minimum voltage must be applied to make this cell work?

Stoichiometry of Cell Reactions

- Using stoichiometry, we can predict the mass of the reactant used or product made at the electrodes
- Look at the mole ratio of electrons

$$q_e = It$$

$$n_e F = It$$

Where:

q_e = charge of e^- (C)

I = current (A)

t = time (s)

n_e = moles of e^-

F = 96500 C/mol



Checkpoint



Calculate the mass of aluminum produced by the electrolysis of molten AlCl_3 , if a current of 500mA passes for 1.50h.



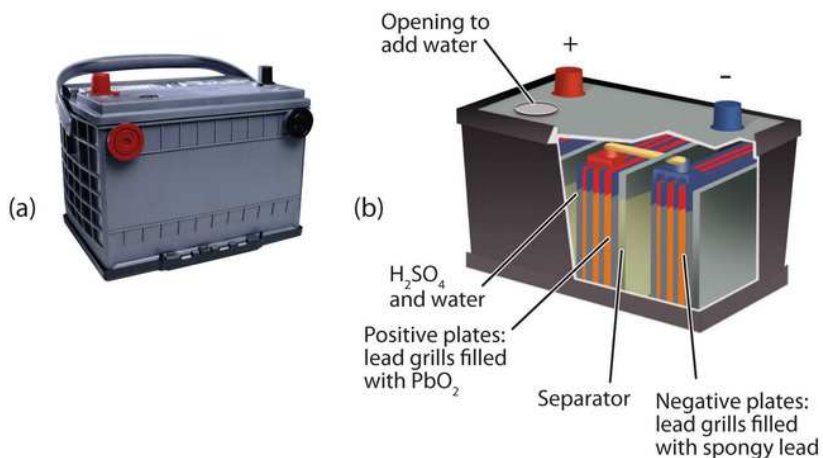
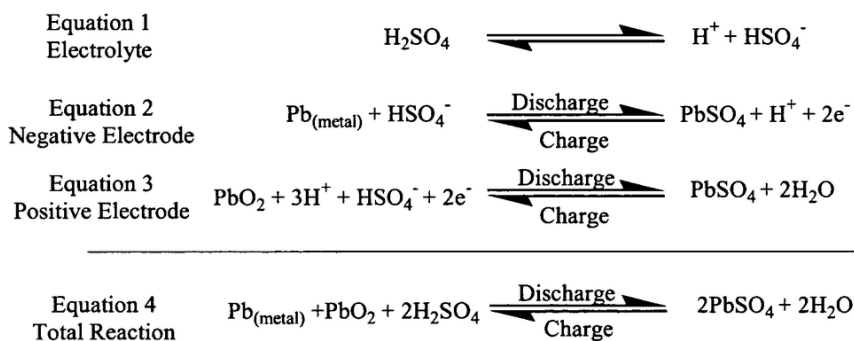
Checkpoint



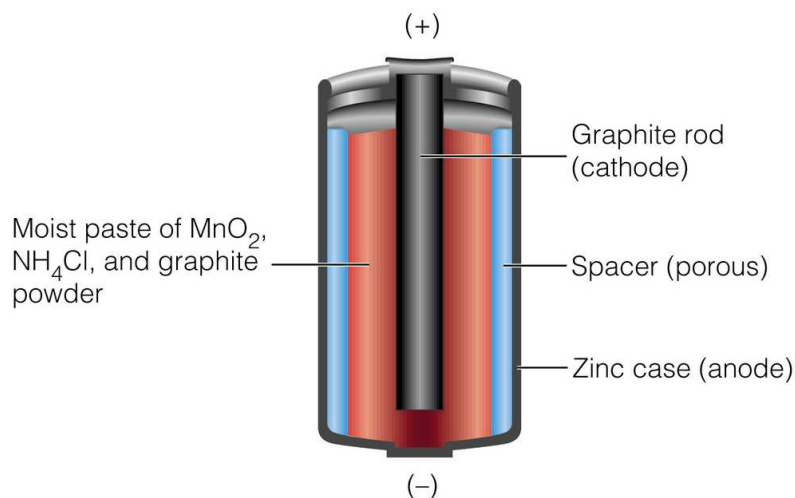
How many minutes does it take to plate 0.925g of silver onto the cathode of an electrolytic cell using a current of 1.55A?

Batteries

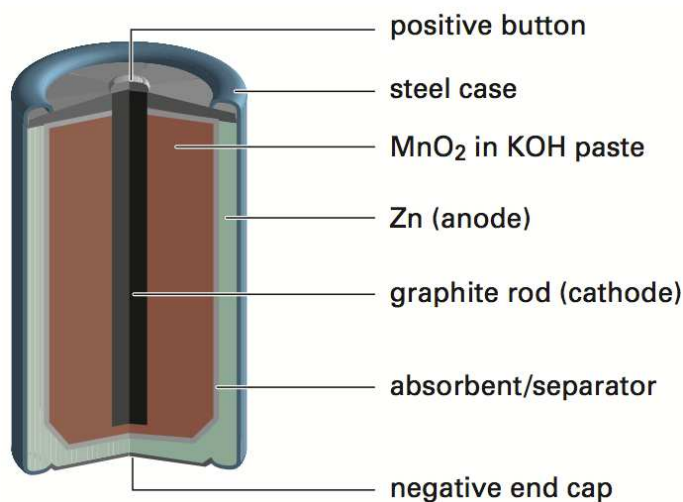
- Batteries are the most practical application of galvanic cells and electrolytic cells
 - Lead-Storage Battery** – used for automobiles; the product that forms is solid PbSO_4 sticks to the surface of the electrodes so it can be recharged with an external current to drive the cell in its reverse, nonspontaneous direction
 - If PbSO_4 dislodges from the electrodes due to driving on bumpy roads, the battery cannot be jumped



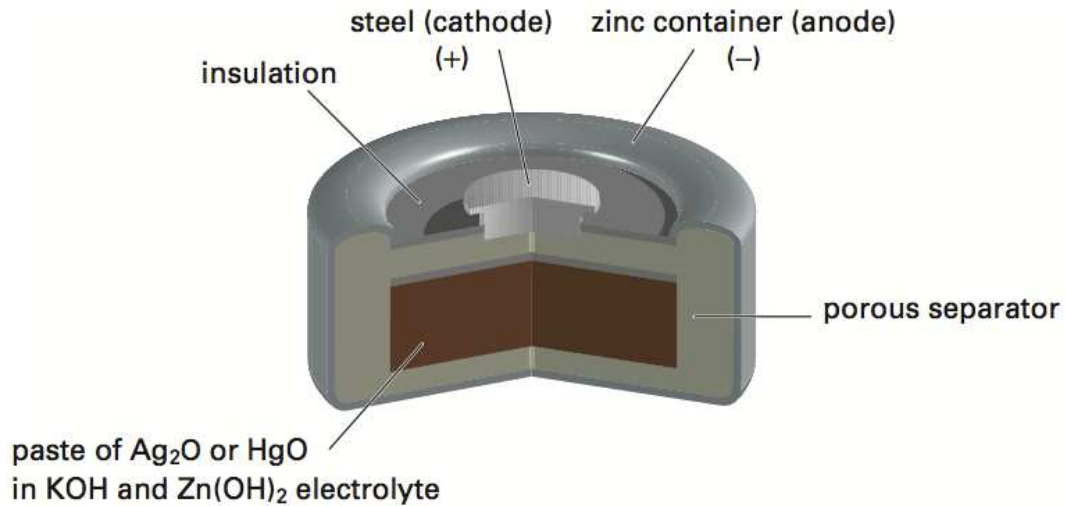
- **Dry-Cell Battery** – zinc metal can (anode) with an inert graphite rod surrounded by a solid manganese dioxide paste (cathode). Surrounding this paste is the electrolyte



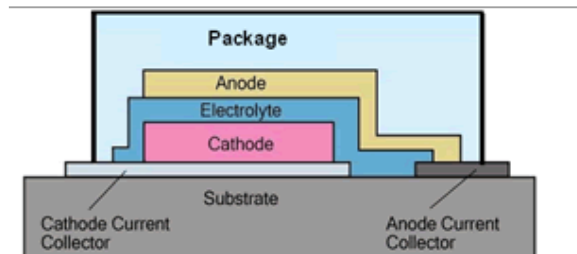
- **Alkaline Cell Battery** – longer lasting version of the dry cell
 - Alkaline (basic) solution such as KOH replaces the NH₄Cl and ZnCl₂ in dry cells



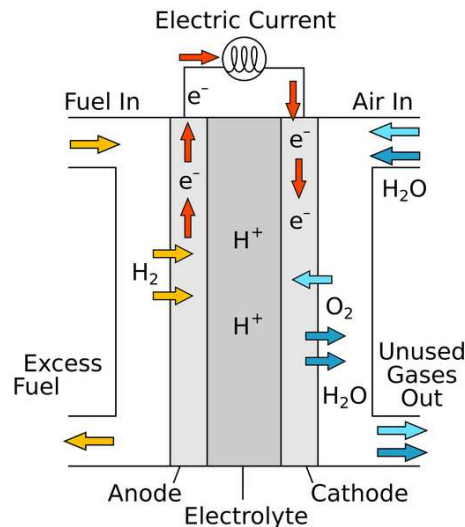
- **Button Cell Battery** – used in watches, pacemakers; anode is zinc and cathode is steel in contact with HgO in an alkaline medium of KOH and Zn(OH)_2



- **Lithium Battery** – used in rechargeable electronics; anode is lithium, cathode is a metal oxide or metal sulfide in an electrolyte of a lithium salt

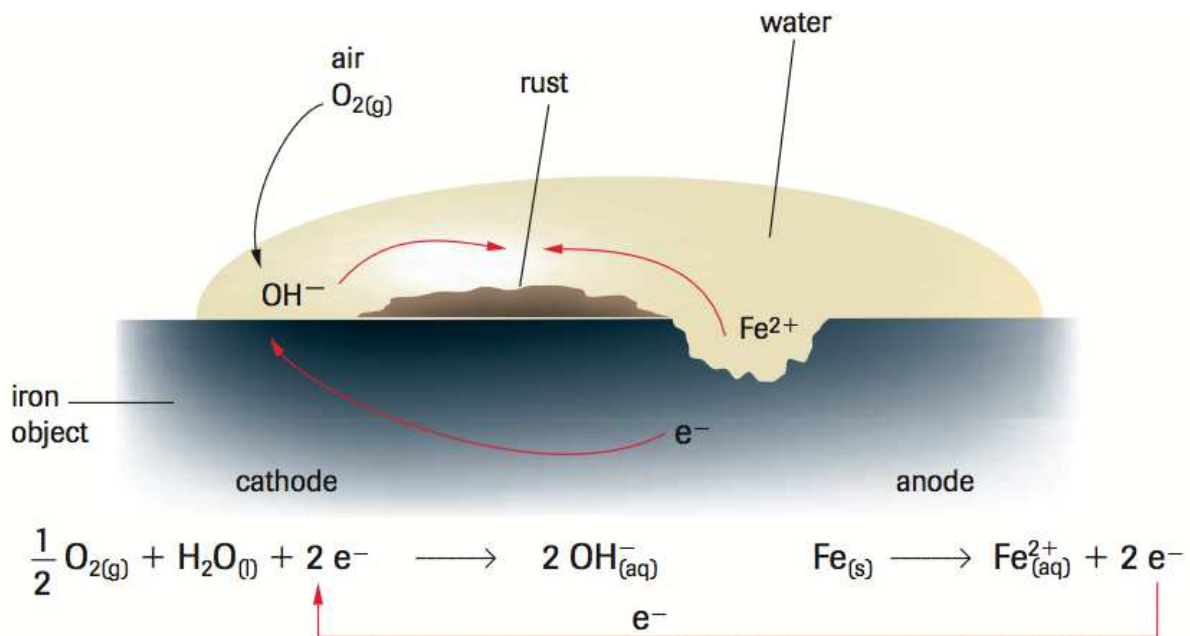


- **Fuel Cells** – used in electric vehicles; reactants are not contained but rather supplied through an external reservoir and one of the reactants is methane or hydrogen



Corrosion

- We live in an oxidizing environment and spontaneous oxidation (corrosion) of metal occurs
- Iron Rusting in Water and Oxygen
 - Anode: $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$
 - Cathode: $\frac{1}{2}O_2(g) + H_2O(l) + 2e^- \rightarrow 2OH^-(aq)$
- Combination of Fe^{2+} and OH^- forms iron (II) hydroxide which is further oxidized to iron (III) hydroxide (yellow-brown solid)



- The red-brown rust is formed by the dehydration of $Fe(OH)_3$ to form a hydrated form Fe_2O_3
- Rusting can be slowed down significantly by removing oxygen or water
- Electrolytes and acids accelerate rusting (i.e. seawater, road salt, acid rain, etc.)
- Corrosion can be prevented through protective coatings (i.e. paint), galvanizing or cathodic protection

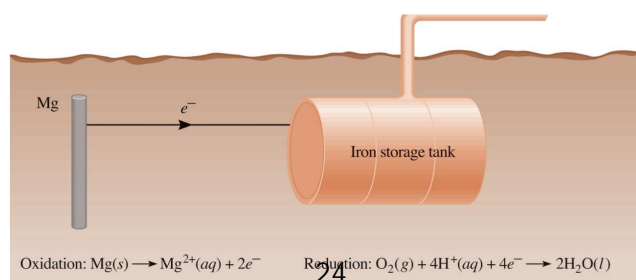
Galvanizing



- Process in which iron is covered with a protective layer of zinc
 - Zinc acts as a protective layer since it is more easily oxidized than iron; Zn becomes the sacrificial anode
 - Iron acts as the cathode
- Used to make metal buckets and chain-link fences

Cathodic Protection

- A more reactive metal is attached to the iron object to act as the sacrificial anode while the iron becomes the cathode
- Unlike galvanizing, the metal used in cathodic protection does not completely cover the iron and must be replaced periodically



Other Applications



- Electrorefining (extraction) is a process used to obtain high-grade metals at the cathode from an impure metal at the anode
- Electroplating is a process in which a metal is deposited on the surface of an object placed at the cathode of an electrolytic cell