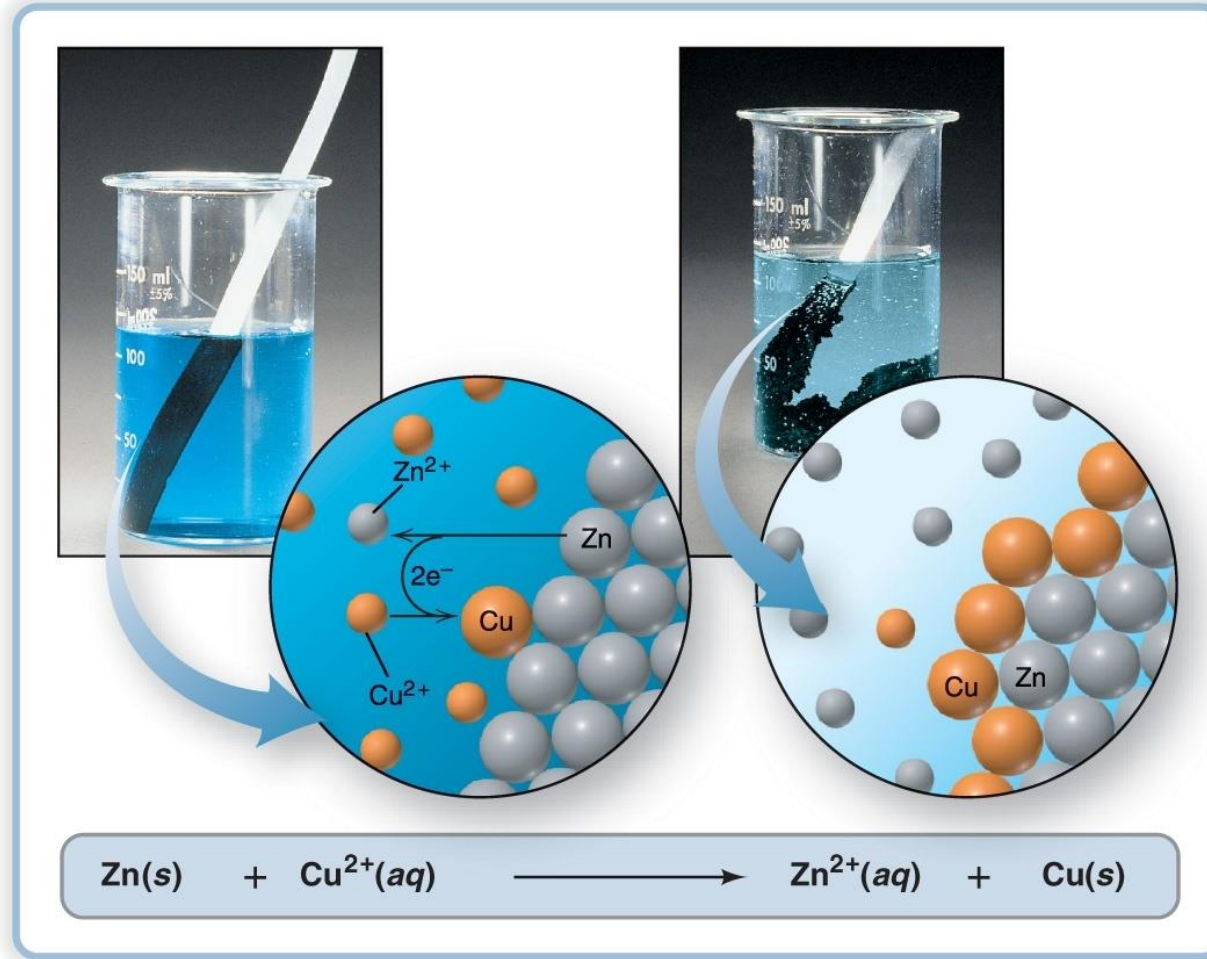


# Electrochemistry & Redox Reactions

“How FAR Does A Reaction Go”? – Chapter 19

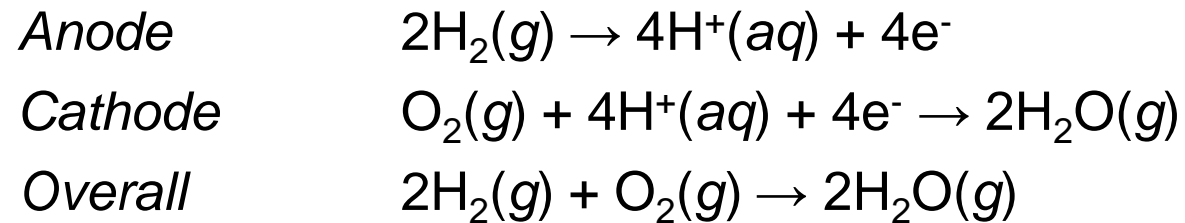
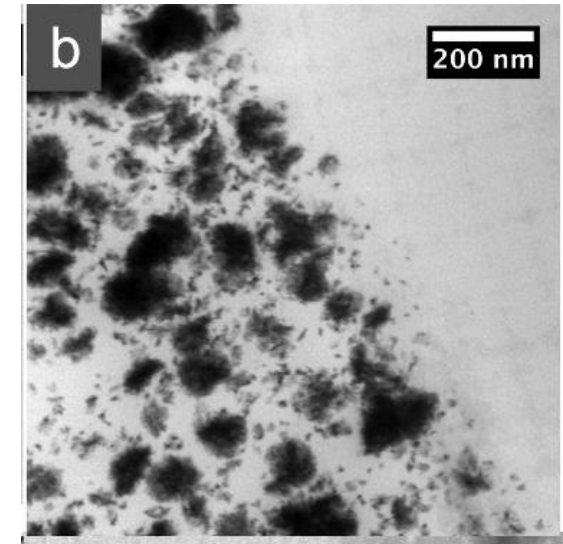
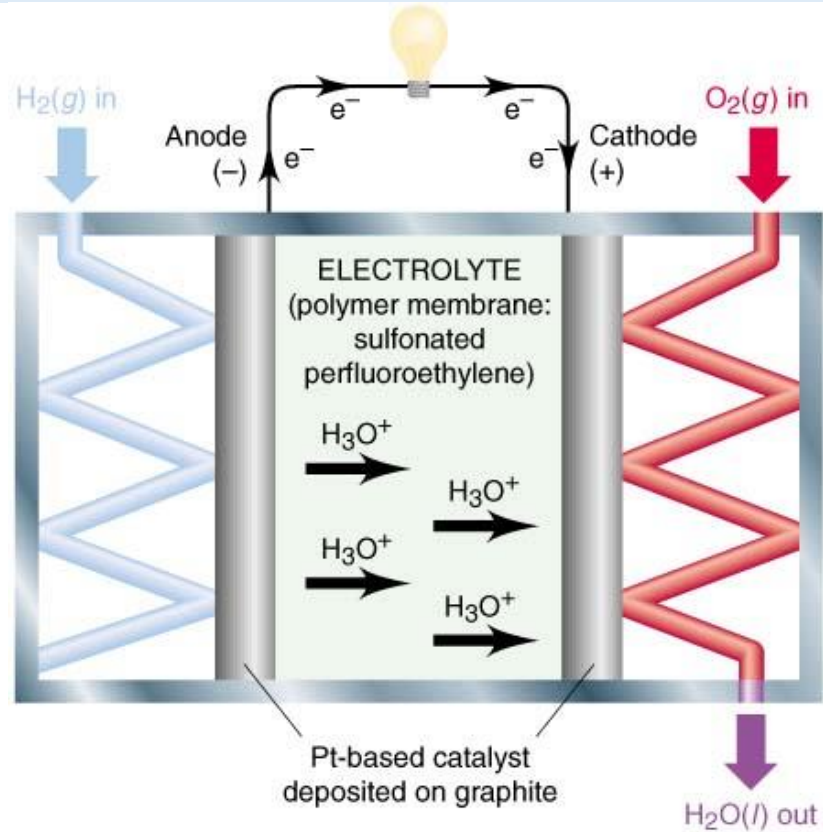
# Harnessing Redox Reactions

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# Fuel Cells (Hydrogen/PEM)



$$E_{\text{cell}} = 1.2 \text{ V}$$

✓ Explain how batteries and fuel cells use redox reactions to store electrical energy.

# Oxidation and Reduction

**Oxidation**  $\text{Mg} \rightarrow \text{Mg}^{2+} + 2\text{e}^-$  ( Mg is oxidized )

**Reduction**  $\frac{1}{2}\text{O}_2 + 2\text{e}^- \rightarrow \text{O}^{2-}$  (  $\text{O}_2$  is reduced )

The ***oxidizing agent***( $\text{O}_2$ , here) takes electrons from the substance being oxidized.  
The oxidizing agent is therefore reduced.

The ***reducing agent*** (Mg, here) takes electrons from the substance being oxidized.  
The reducing agent is therefore oxidized.



The (unbalanced) reaction below is carried out in acidic solution. Identify which species is the reducing agent.



- A)  $\text{NO}_3^-$
- B) Sb
- C)  $\text{H}_2\text{O}$
- D) NO
- E)  $\text{Sb}_4\text{O}_6$

Table 19.1: Oxidization Numbers

### General Rules

---

1. For an atom in its elemental form (such as Na, O<sub>2</sub>, and Cl<sub>2</sub>): Oxidation number = 0
2. For a monatomic ion: Oxidation number = ion charge (with the sign *before* the numeral)
3. The sum of the oxidation number values for the atoms in a molecule or formula unit of a compound equals zero. The sum of the oxidation number values for the atoms in a polyatomic ion equals the charge of the ion.

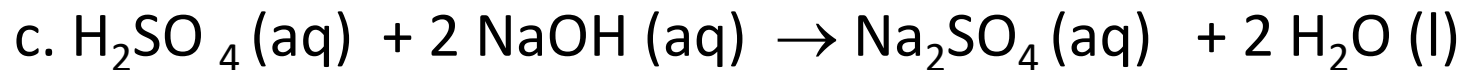
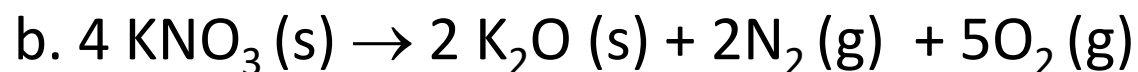
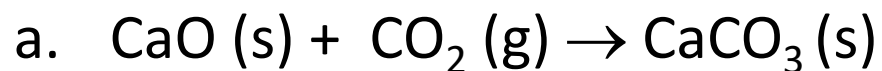
### Rules for Specific Atoms or Periodic Table Groups

1. For Group 1: Oxidation number = +1 in all compounds
2. For Group 2: Oxidation number = +2 in all compounds
3. For hydrogen: Oxidation number = +1 in combination with nonmetals  
Oxidation number = -1 in combination with metals and boron
4. For fluorine: Oxidation number = -1 in all compounds
5. For oxygen: Oxidation number = -2 in most cases, unless coupled to a more electronegative centre (such as F) or a Group 1 or Group 2 metal (in which case, it might be +2 or -1)
6. For Group 17: Oxidation number = -1 in combination with metals, nonmetals (except O), and other halogens lower in the group

What is the oxidization number of Cr and O in  $\text{Cr}_2\text{O}_7^{2-}$ ?



Which of the reactions below is a redox reaction (i.e. one where an oxidation and reduction takes place)?

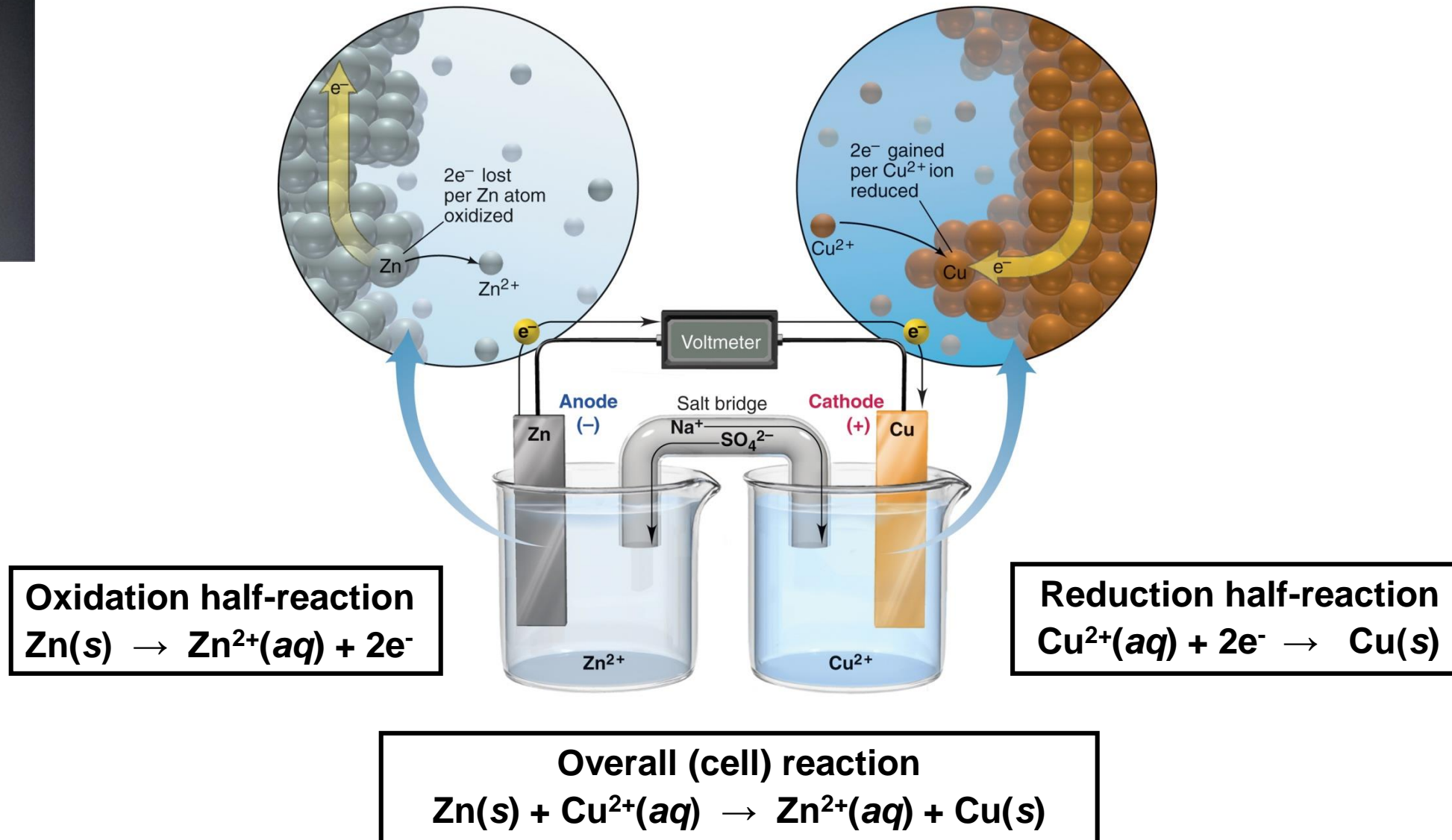




# Voltaic Cells



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✓ Describe voltaic and electrolytic cells, graphically or using cell notation.

# Definitions & Conventions

**Electrode**

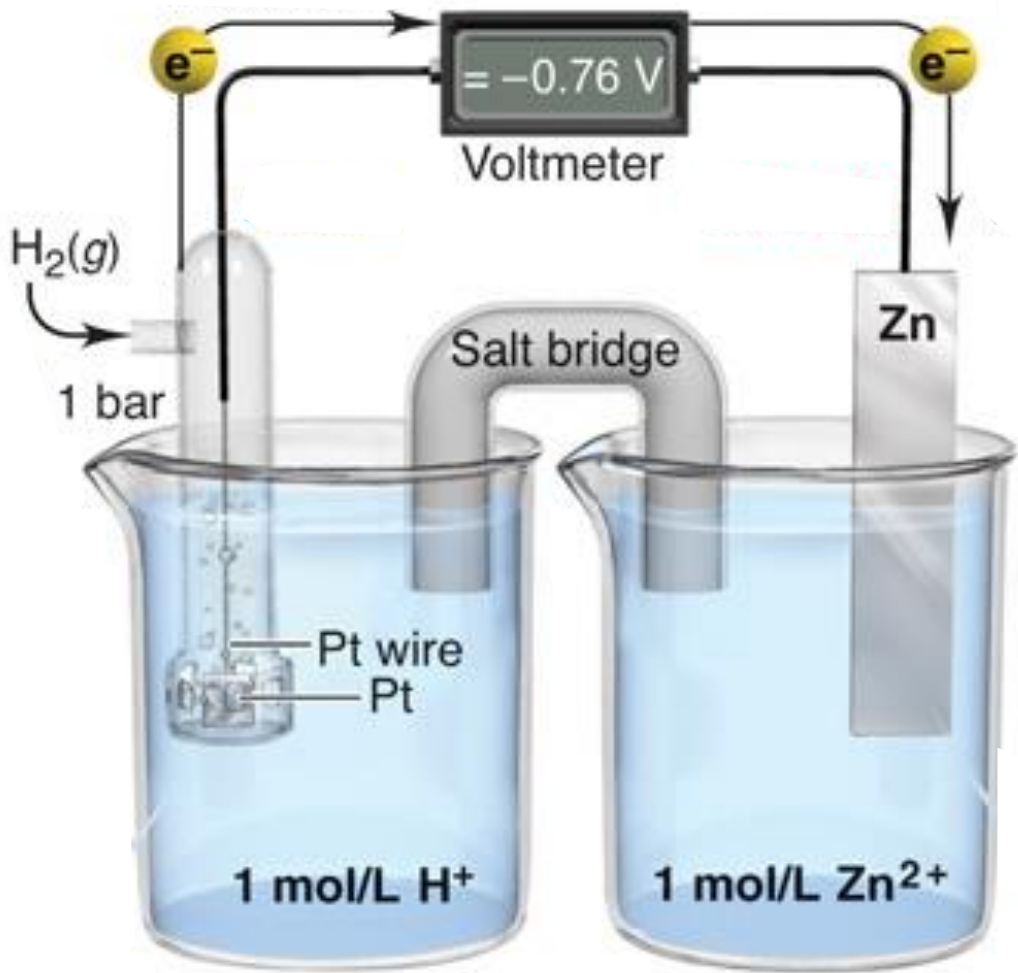
**Anode**

**Cathode**

Using the diagram below, identify the cell components:



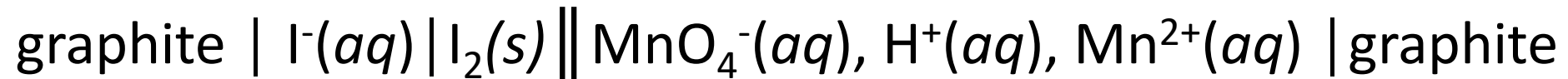
	Cathode	Anode	Species Being Reduced	Species Being Oxidized
a	H <sub>2</sub>	Zn	H <sup>+</sup>	Zn
b	Pt	Zn	Pt	H <sup>+</sup>
c	Zn	Pt	Zn <sup>2+</sup>	H <sub>2</sub>
d	Zn	H <sub>2</sub>	H <sup>+</sup>	Pt



# Line Notation for Cells

The anode components are written on the *left*.

The cathode components are written on the *right*.



# Cell Potential

The **cell potential** ( $E^0$ ) – also called the *voltage* of the cell or the *electromotive force (emf)* – describes the **equilibrium condition** of the reaction combination.

$$E^{\circ} = \frac{RT}{nF} \ln K$$

A **positive** value for the cell potential means that the reaction (as written) has an equilibrium that favors the products ( **$K > 1$** ) – it is *spontaneous in the forward direction*.

A **negative** value for the cell potential means that the reaction (as written) will favor the reactants at equilibrium ( **$K < 1$** ) – it is *nonspontaneous in the forward direction*.

✓ Describe, qualitatively and quantitatively, the relationship between the equilibrium constant and cell potential.

# Standard Conditions: Standard State

The ° in  $E^\circ$  informs us that this value represents the reaction when measured at **standard state**.

For electrochemistry, this means:

- All gases at 100 kPa (1 bar)
- Aqueous solutions at 1 M
- Pure substances are in their most stable form at the temperature of interest
- $E^\circ$  is measured using near-0 current flow.

Note that temperature is **not** part of standard state! You can measure  $E^\circ$  equally well at 298K or 398K: the temperature must be specified.

Most work in this course is done at 298K, unless stated otherwise.

✓ Calculate  $E^\circ_{\text{cell}}$  for a given reaction using tabulated half-cell data, and use it to predict reaction spontaneity.

A reaction has  $E^\circ = +0.092 \text{ V}$  at 298 K. If the reaction involves the transfer of 2 mol electrons per mol reaction, what is the equilibrium constant?

✓ *Describe, qualitatively and quantitatively, the relationship between the equilibrium constant and cell potential.*

The reaction from the previous example ( $E^\circ = +0.092 \text{ V}$ ,  $K_{\text{eq}} = 1.3 \times 10^3$ ) is allowed to come to equilibrium, and the cell potential at equilibrium is measured. What voltage will be observed?



- a.  $E > E^\circ$
- b.  $E = E^\circ$
- c.  $E < E^\circ$
- d.  $E \neq E^\circ$ , but we cannot determine in which direction
- e.  $E = 0$



# Reactions *not* at standard state

Most chemistry isn't done at standard state. To predict the potential of a reaction that is not at standard state, we can use the **Nernst Equation**:

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

When  $Q > 1$ :

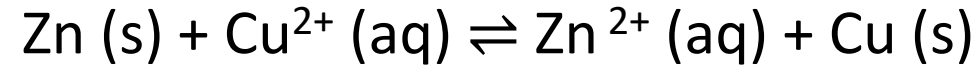
When  $Q = 1$ :

When  $Q < 1$ :

When  $Q = K$ :

✓ Calculate  $E_{\text{cell}}$  using the Nernst equation.

The reaction between Zn and Cu (as in the Voltaic Piles) has  $E^\circ = 1.10 \text{ V}$ . If  $[\text{Zn}^{2+}] = 0.050 \text{ M}$  and  $[\text{Cu}^{2+}] = 0.0025 \text{ M}$  in the electrolyte between discs, what potential will be measured across one element of the pile?



# $E_{\text{cell}}$ during operation

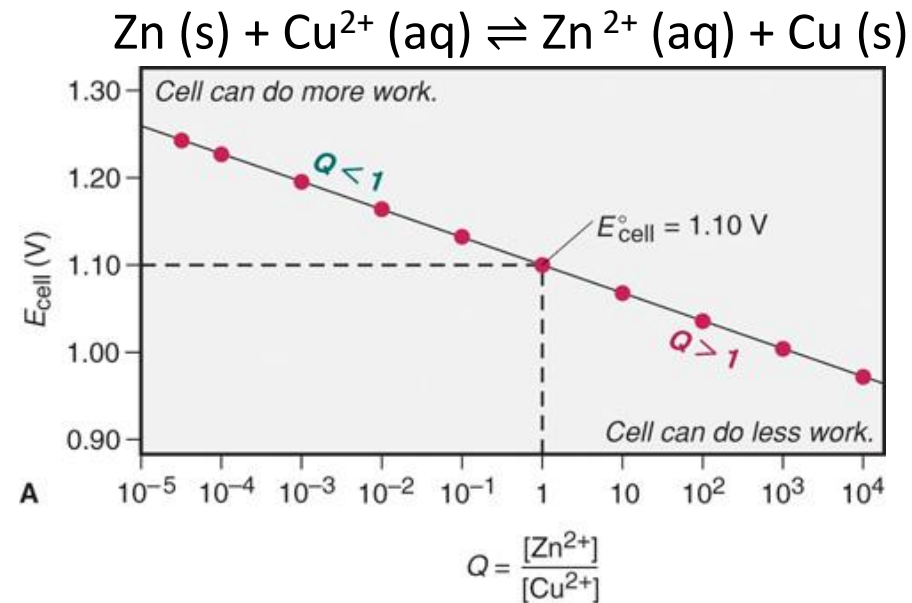


Figure 19.14

As the cell runs, more reactants are consumed (and products created), so  $Q$  increases.

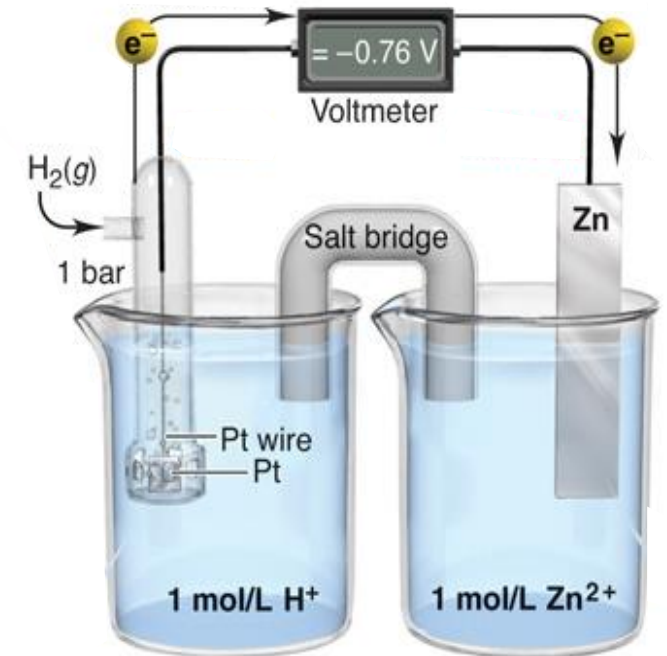
Cell voltage is thus reduced over time, until equilibrium is reached.

✓ Calculate  $E_{\text{cell}}$  using the Nernst equation.

# Predicting $E^\circ_{\text{cell}}$

Besides calculating it from  $K$  (or measuring it directly), how can we find the cell potential for a reaction?

**Standard Reduction Potentials** are tabulated for common reactions. These are the potentials measured *against the standard hydrogen electrode (SHE)*, and at standard state.

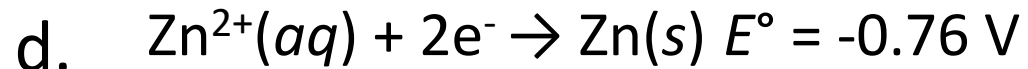
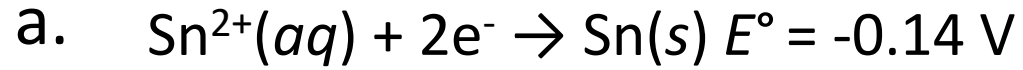


The same rules apply for  $E^\circ$  in half-reactions; a positive  $E^\circ$  is 'spontaneous' and will have an equilibrium that favours the products.

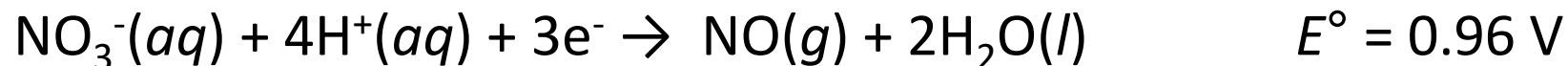
The larger the  $E^\circ$  value is, the more products will be formed at equilibrium, and the more favourable the reaction is.

✓ Calculate  $E^\circ_{\text{cell}}$  for a given reaction using tabulated half-cell data, and use it to predict reaction spontaneity.

Which reaction below is the most favourable **reduction**?  
(i.e. which one will move most strongly towards the products)




Based on the information below, which species will have the most favourable **oxidation** reaction?



- a. Sn
- b. Ag
- c. NO (+ H<sub>2</sub>O)
- d. Zn

TABLE 19.3

Selected Standard Electrode Potentials (298 K)

	Half-Reaction	$E^\circ_{\text{half-cell}}$ (V)
	$\text{F}_2(g) + 2e^- \rightleftharpoons 2\text{F}^-(aq)$	+2.87
	$\text{Cl}_2(g) + 2e^- \rightleftharpoons 2\text{Cl}^-(aq)$	+1.36
	$\text{MnO}_2(s) + 4\text{H}^+(aq) + 2e^- \rightleftharpoons \text{Mn}^{2+}(aq) + 2\text{H}_2\text{O}(l)$	+1.23
	$\text{NO}_3^-(aq) + 4\text{H}^+(aq) + 3e^- \rightleftharpoons \text{NO}(g) + 2\text{H}_2\text{O}(l)$	+0.96
	$\text{Ag}^+(aq) + e^- \rightleftharpoons \text{Ag}(s)$	+0.80
	$\text{Fe}^{3+}(aq) + e^- \rightleftharpoons \text{Fe}^{2+}(aq)$	+0.77
	$\text{O}_2(g) + 2\text{H}_2\text{O}(l) + 4e^- \rightleftharpoons 4\text{OH}^-(aq)$	+0.40
	$\text{Cu}^{2+}(aq) + 2e^- \rightleftharpoons \text{Cu}(s)$	+0.34
	$2\text{H}^+(aq) + 2e^- \rightleftharpoons \text{H}_2(g)$	0.00
	$\text{N}_2(g) + 5\text{H}^+(aq) + 4e^- \rightleftharpoons \text{N}_2\text{H}_5^+(aq)$	-0.23
	$\text{Fe}^{2+}(aq) + 2e^- \rightleftharpoons \text{Fe}(s)$	-0.44
	$\text{Zn}^{2+}(aq) + 2e^- \rightleftharpoons \text{Zn}(s)$	-0.76
	$2\text{H}_2\text{O}(l) + 2e^- \rightleftharpoons \text{H}_2(g) + 2\text{OH}^-(aq)$	-0.83
	$\text{Na}^+(aq) + e^- \rightleftharpoons \text{Na}(s)$	-2.71
	$\text{Li}^+(aq) + e^- \rightleftharpoons \text{Li}(s)$	-3.05


 Strength of reducing agent

# Combining Half-Cell Reactions

To find the potential for an overall redox reaction, we combine the two reduction half-cell reaction values:

$$E_{cell}^{\circ} = E_{red,cathode}^{\circ} - E_{red,anode}^{\circ}$$

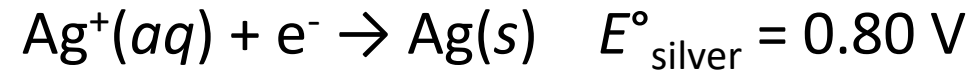
$$E_{cell}^{\circ} = E_{cathode}^{\circ} - E_{anode}^{\circ}$$

When calculating cell potential this way, **do not** reverse the sign of either potential or multiply by any coefficients.

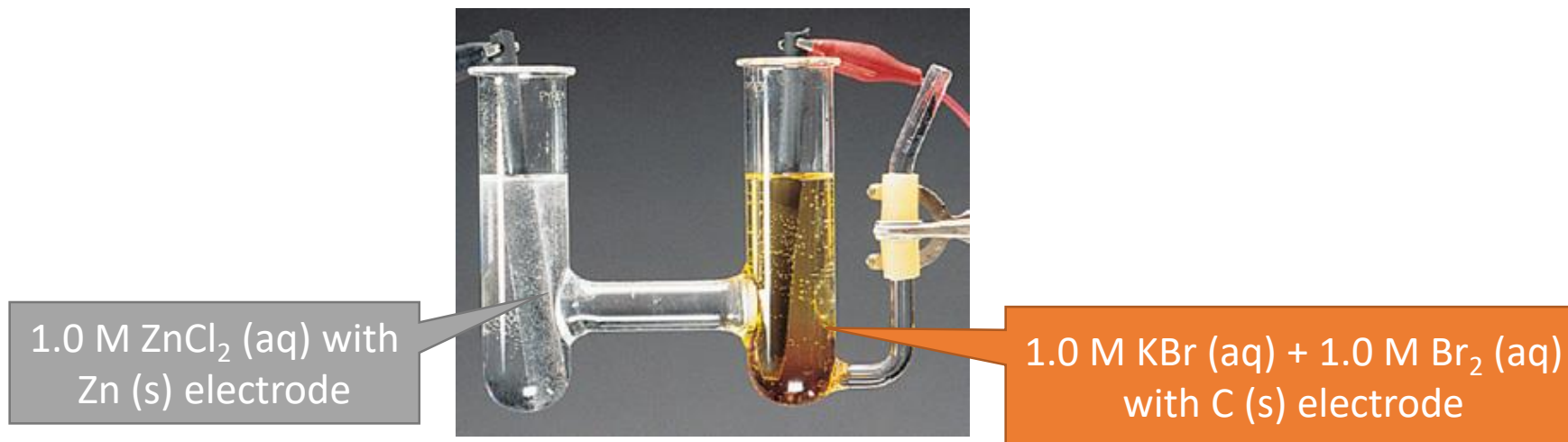
✓ Calculate  $E_{cell}^{\circ}$  for a given reaction using tabulated half-cell data, and use it to predict reaction spontaneity.



Write a spontaneous overall cell reaction using the following half-cell reactions:



The cell below was assembled as labelled, and the voltage across the leads was measured as +1.83 V.



The overall cell reaction is:

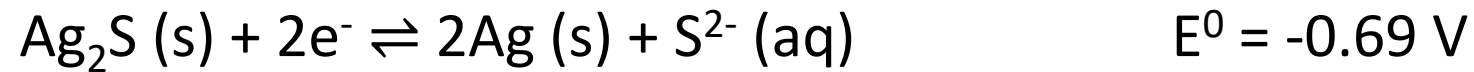


Given that Zn has a standard reduction potential of -0.76 V, predict the standard reduction potential of  $\text{Br}_2$ .

# Demo – Silver Polishing

‘Tarnish’ is mostly silver sulfide ( $\text{Ag}_2\text{S}$ ). It can be removed in a reaction with Al.

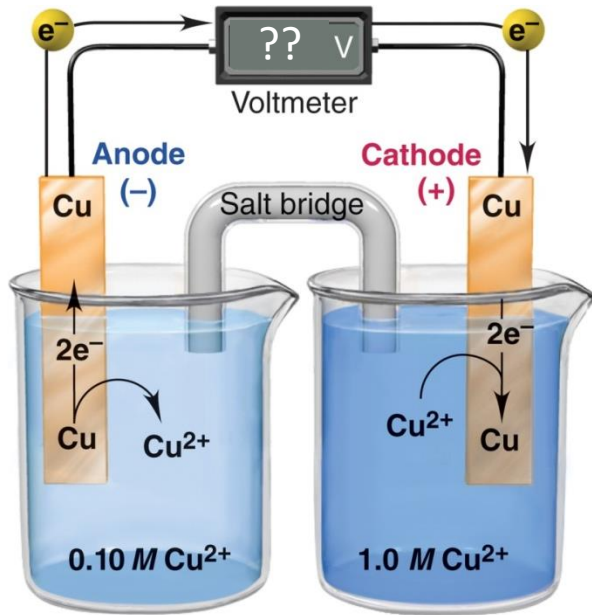
What is the  $E^\circ_{\text{cell}}$  for the reaction between Al (s) and  $\text{Ag}^+$ ?



$\text{Al}^{3+}$  can then react with the  $\text{S}^{2-}$  to form a precipitate of  $\text{Al}_2\text{S}_3$ .

# Concentration Cells

Knowing how half-cells combine, and the effect of concentration on cell potential, we can use cell potential to find the concentration of an analyte in one of the half-cells (the other must be known):



First, let's use concentration to predict the cell voltage:  
(The standard reduction potential for  $\text{Cu}^{2+}$  is +0.34 V.)

# Measuring pH with a pH probe

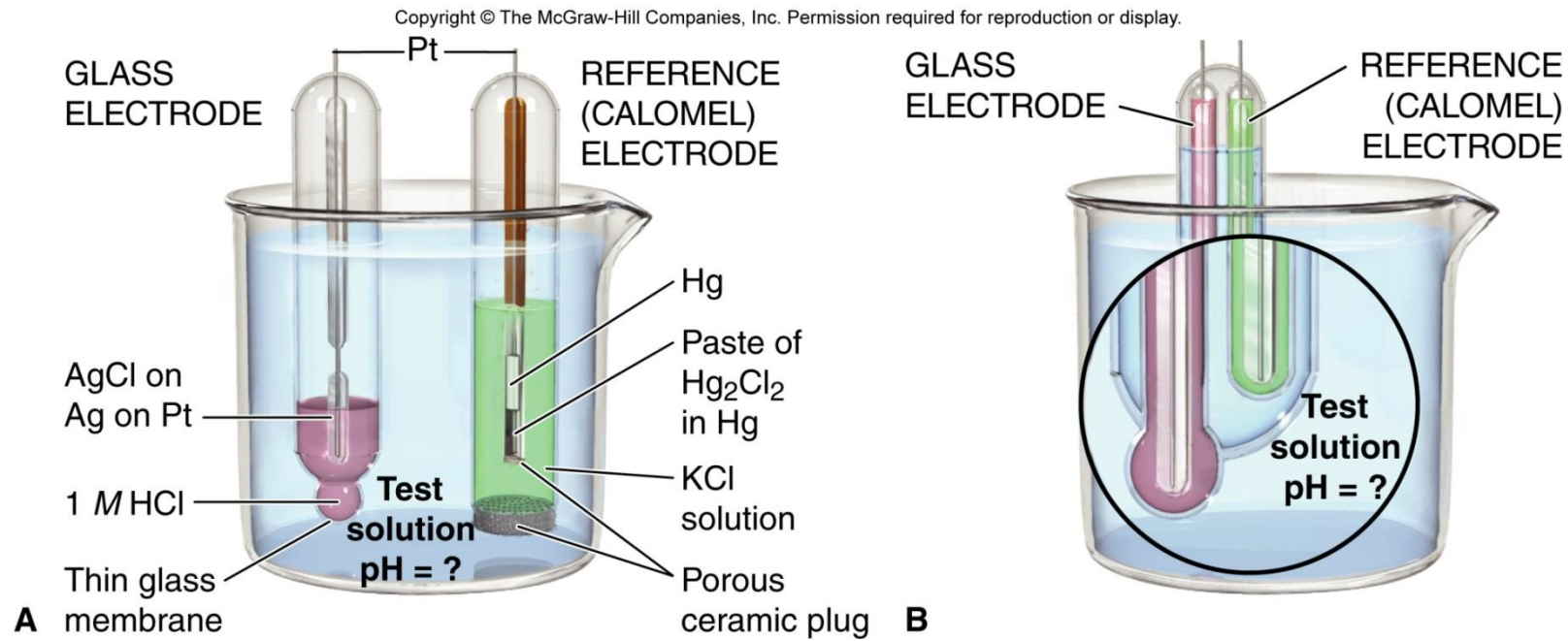


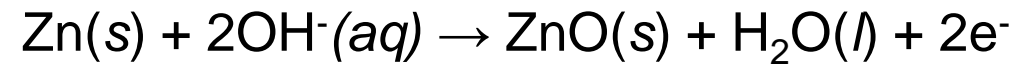
Figure 19.16

# Alkaline Batteries

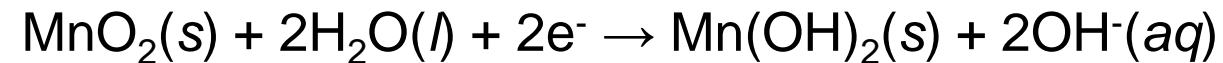
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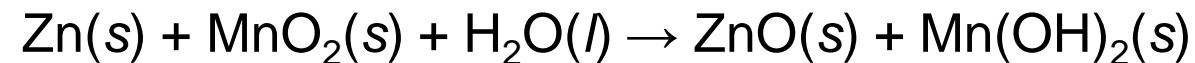
*Anode*



*Cathode*

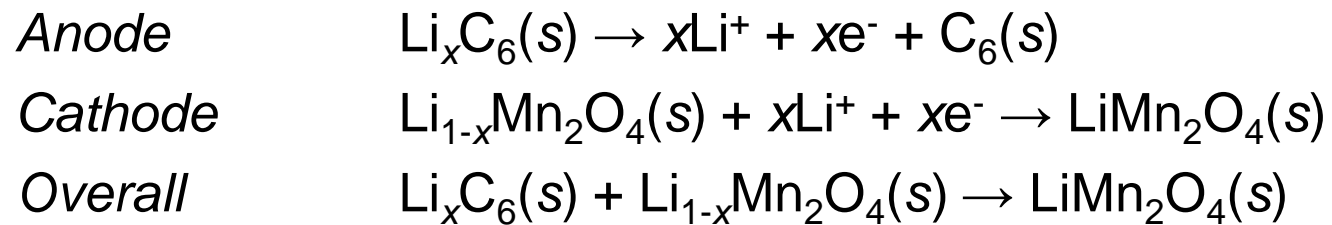
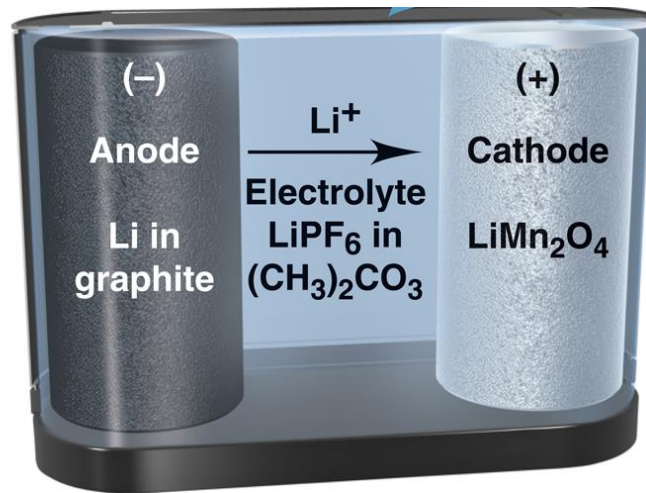


*Overall*



$$E_{\text{cell}} = 1.5 \text{ V}$$

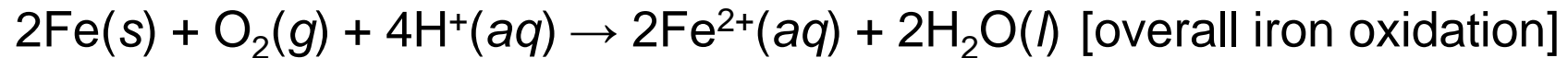
# Lithium-Ion Batteries



$$E_{\text{cell}} = 3.7 \text{ V}$$

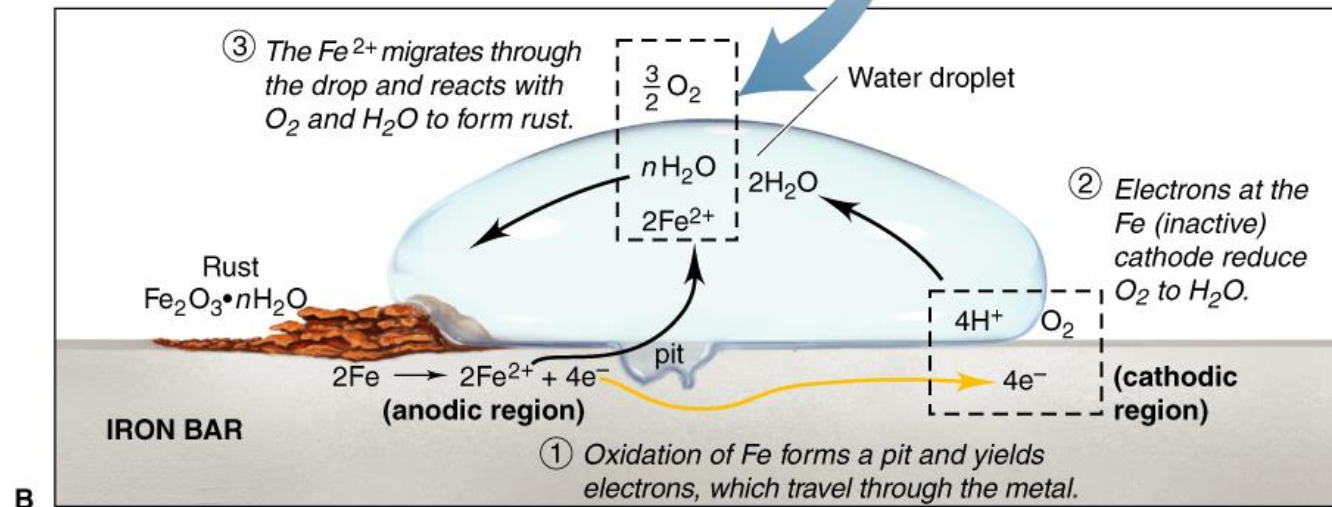
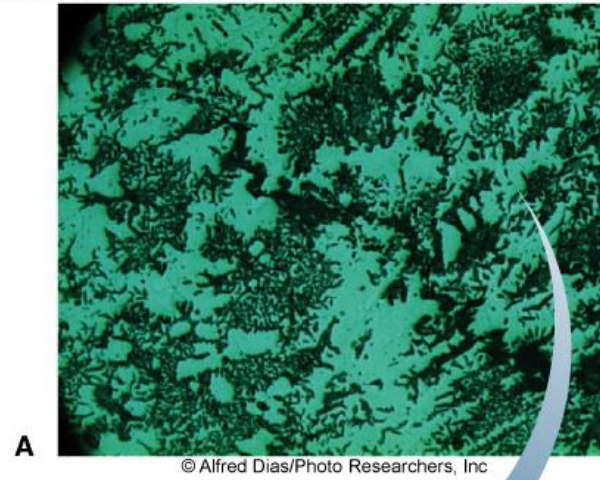
# Corrosion

*Corrosion* is the process where metals are oxidized to their oxides and sulfides.



[iron forms insoluble iron oxide]

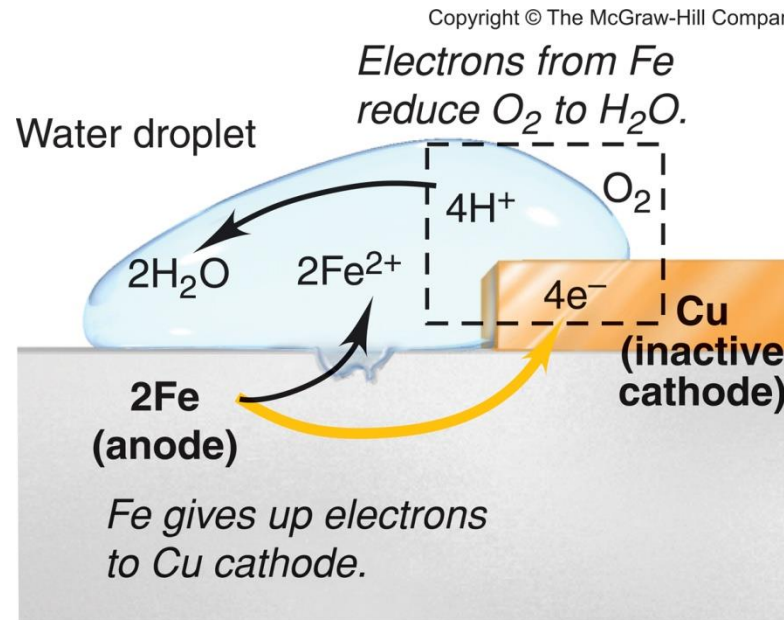




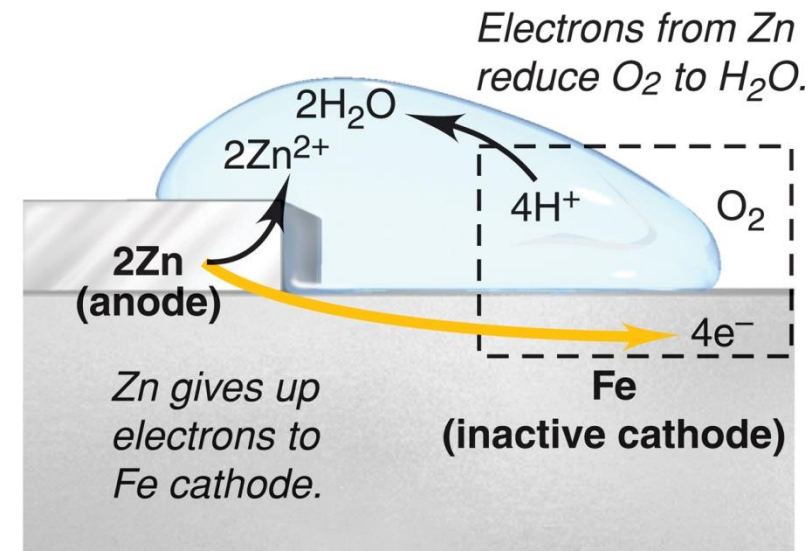
# Corrosion Prevention

Coatings, paints, passivation layers (e.g. galvanization) provide a first defense.

**Cathodic protection** (sacrificial cathodes) prevent corrosion electrochemically:



**A Enhanced corrosion**



**B Cathodic protection**

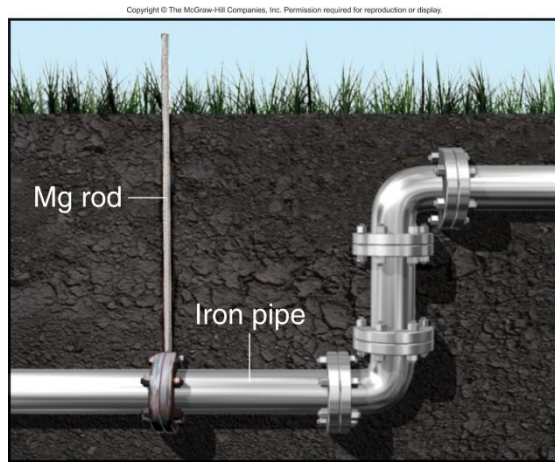


Image: <http://www.anodeoutlet.co.uk/>

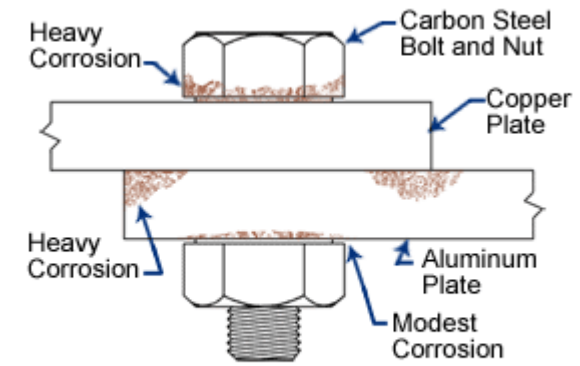


"Electrode protecting a screw" by Rémi Kaupp. CC BY-SA 3.0  
[https://commons.wikimedia.org/wiki/File:Electrode\\_protecting\\_a\\_screw.jpg#/media/File:Electrode\\_protecting\\_a\\_screw.jpg](https://commons.wikimedia.org/wiki/File:Electrode_protecting_a_screw.jpg#/media/File:Electrode_protecting_a_screw.jpg)

In cathodic protection, an active metal, such as zinc, magnesium, or aluminum, acts as the anode and is sacrificed instead of the iron.

Active protection can also be used, when an electrical potential is directly applied to the metal object.

# Galvanic Corrosion



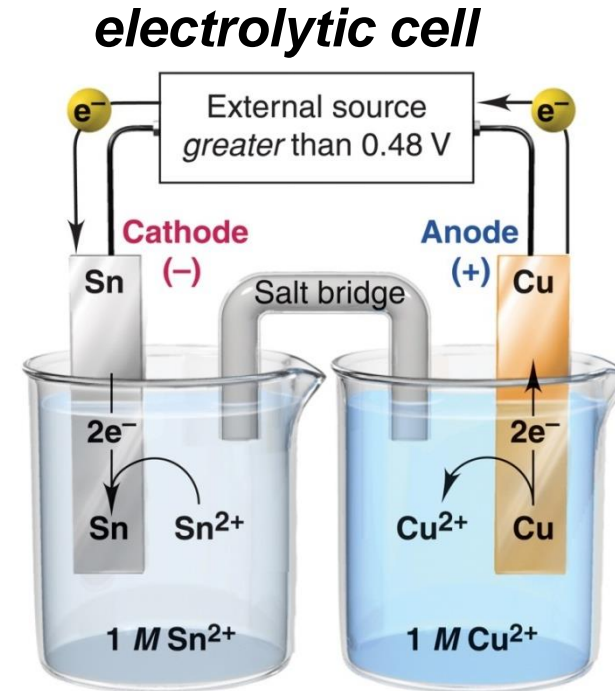
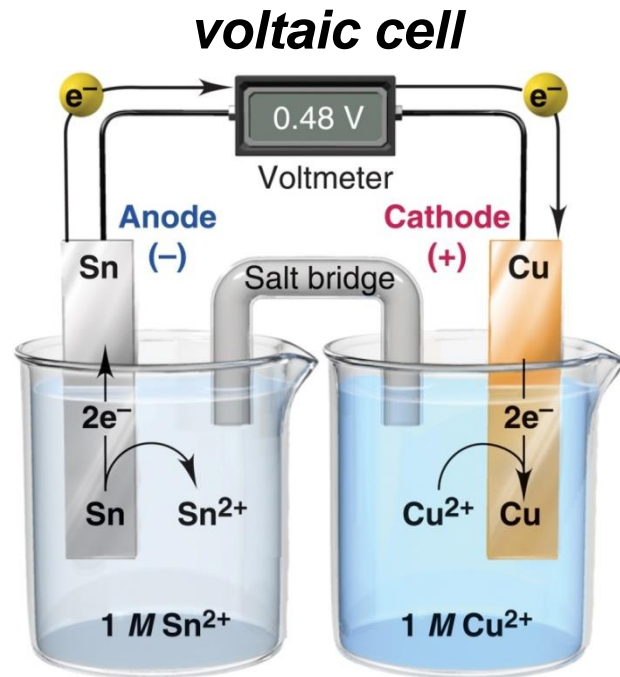
Effects of Galvanic Corrosion





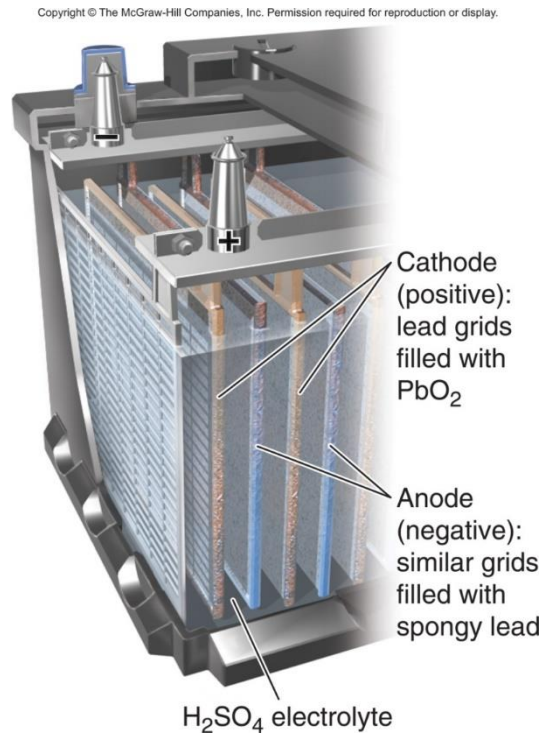
# Electrolysis

Electrolytic cells use an **outside source of energy** to power a **nonspontaneous** redox reaction.

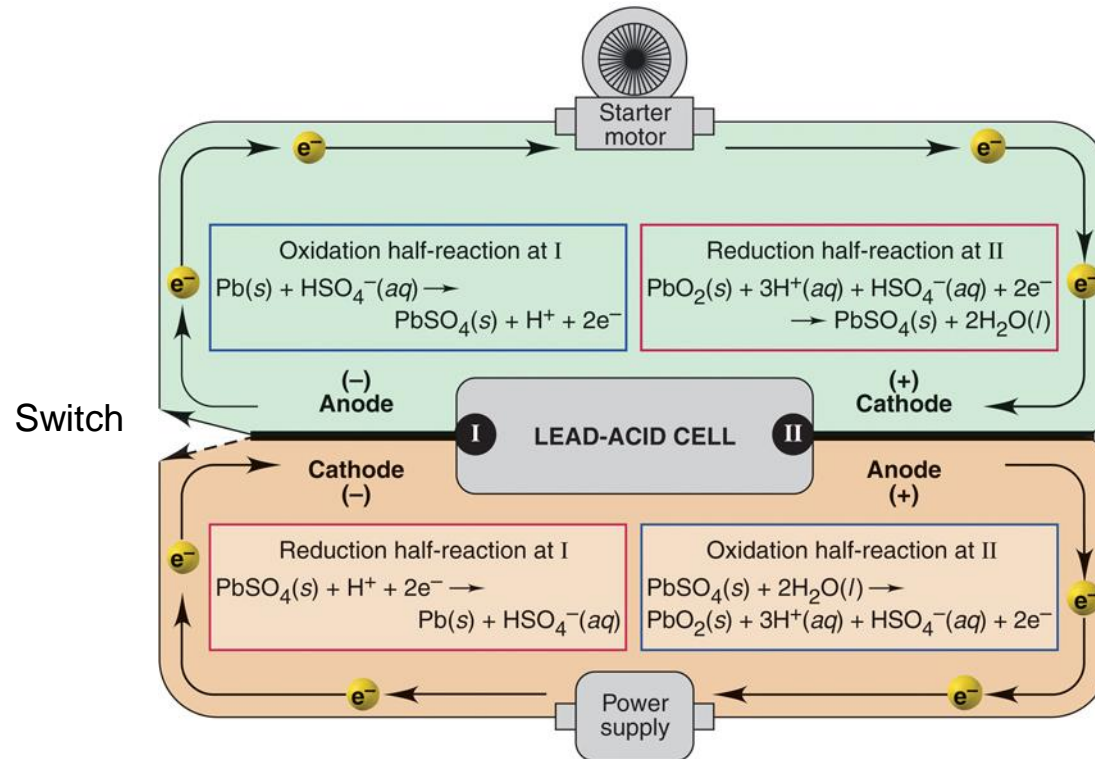


✓ Distinguish between electrolytic and voltaic/galvanic processes, and predict the products of each type of reaction.

# Lead-acid batteries



## VOLTAIC (discharge)



## ELECTROLYTIC (recharge)

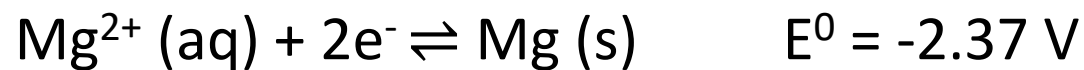
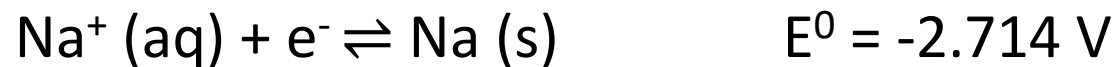
# Electrolysis in Molten Salts

During electrolysis of a pure, molten salt, the *cation* will be *reduced* and the *anion* will be *oxidized*.

During electrolysis of a **mixture** of molten salts:

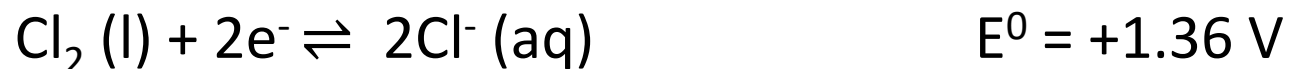
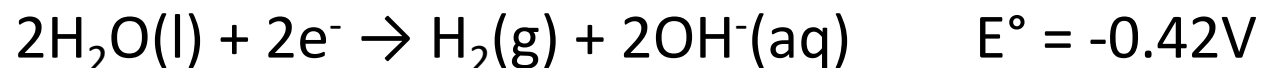
- the more easily oxidized species (*stronger reducing agent*) reacts at the *anode*, and
- the more easily reduced species (*stronger oxidizing agent*) reacts at the *cathode*.

A chemical engineer melts a naturally occurring mixture of NaBr and MgCl<sub>2</sub> and decomposes it in an electrolytic cell. Predict the substance formed at each electrode, and write the overall cell reaction.





# Can we extract sodium metal from brine electrochemically?



In the mixture:  $\text{Na}^+$ ,  $\text{Cl}^-$ , and  $\text{H}_2\text{O}$ .

What will reduce?

What will oxidize?

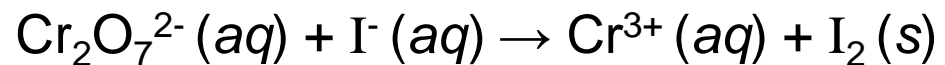
# Balancing Equations: Oxidation Number

Balance the following reaction:



# Balancing Reactions: Half-Reaction (Acidic)

Balance this reaction in acidic solution:



# Balancing Reactions: Half-Reaction (Basic)

Balance this reaction in basic solution:

