

Electrochemistry

Chapter 20

Chemical vs Electro-chemical Reactions

- What is the difference between an “ordinary” Chemical Reaction and an Electro-chemical Reaction ?

“Ordinary” Reactions produce Heat

Electrochemical ones produce Voltage

Electrochemistry

20.1 Oxidation-Reduction (Redox) Reactions

20.1 Balancing Redox Reactions

20.3 Voltaic Cells (Batteries)

20.4 EMF

20.5 Spontaneity of Redox Reactions

20.9 Electrolysis

Two Parts to Electrochemistry

A CHEMICAL REACTION EITHER

1. GENERATES Voltage

Therefore A BATTERY

or

2. USES Voltage

WHICH IS ELECTROLYSIS

Two Parts to Electrochemistry

1. The Energy **Released** By A
SPONTANEOUS Chemical Reaction

Is Converted to Electricity

Or In Which

2. Electrical Energy is **USED**
TO CAUSE A NONSPONTANEOUS
Chemical Reaction To Occur

Electrochemical Cells

- **Electrodes:** are where **Oxidation** **Reduction** reactions occur.
- **Anode:** is the electrode where oxidation takes place.
- **Cathode:** is the electrode where reduction takes place.

Review

Chapter 4

Page 128 - 129

Oxidation & Reduction Reactions

Oxidation Numbers

OXIDATION – REDUCTION
(redox) REACTIONS

*electron-***TRANSFER REACTIONS**

TWO STEP PROCESS

OR

TWO HALF-REACTIONS INVOLVED

1. **OXIDATION** – **LOSS** of electrons

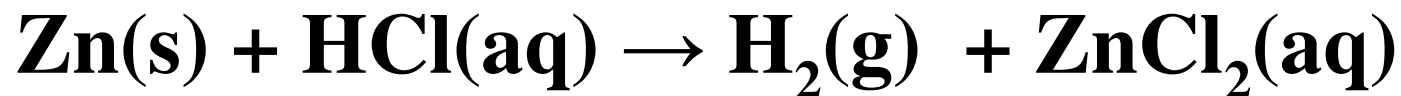
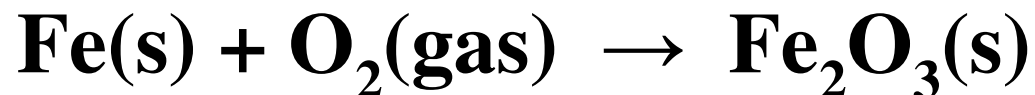
2. **REDUCTION** – **GAIN** of electrons

- ***AN OXIDIZING AGENT “CAUSES”
OXIDATION***

- ***A REDUCING AGENT “CAUSES”
REDUCTION***

OXIDATION REDUCTION *(Redox)* REACTIONS

Examples



Rules for Assigning Oxidation Numbers

MUST KNOW OXIDATION
“RULES”

See Page 128 – 129 Text

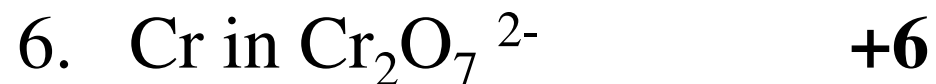
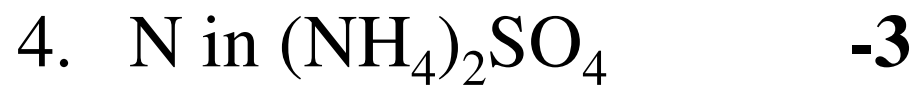
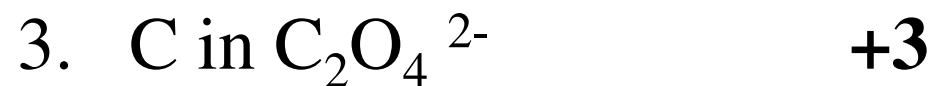
OXIDATION NUMBERS

1. EACH ATOM in a PURE ELEMENT Has An OXIDATION NUMBER OF ZERO
2. For IONS Consisting of a SINGLE ATOM, the Ox Num IS EQUAL TO THE CHARGE ON THE ION
3. F ALWAYS Has an Ox Num of -1 IN ALL OF ITS COMPOUNDS

OXIDATION NUMBERS

4. Cl, Br, and I are -1 EXCEPT when combined with O or F
5. H is $+1$ and O is -2 EXCEPT in
6. Hydrides (CaH_2) & Peroxides (H_2O_2)
7. The ALGEBRAIC SUM of the Oxidation Numbers in a NEUTRAL Compound MUST be ZERO

Prob 4.40 Determine the oxidation number for



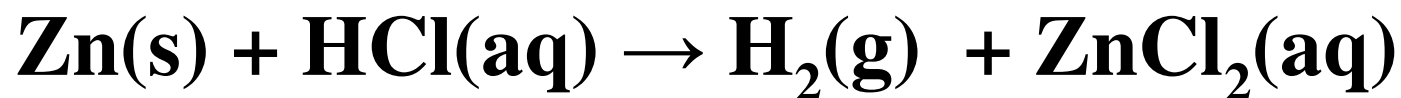
Give OXIDATION NUMBER of
Underlined Atom



Redox Reactions

- Redox reactions are those involving the oxidation and reduction of species.
 - **OIL** – **O**xidation **I**s **L**oss of electrons.
 - **RIG** – **R**eduction **I**s **G**ain of electrons.
- Oxidation and reduction *must* occur together.

OXIDATION – REDUCTION **(redox) REACTIONS**



- 1. How do you know that this is an Oxidation Reduction (Redox) Reaction?**
- 2. Does this reaction occur spontaneously?**

Oxidation Reduction

- **What is The OXIDATION NUMBER For EACH Element Present ?**
- **What is OXIDIZED ?**
- **What is REDUCED ?**
- **What is The OXIDIZING AGENT ?**
- **What is The REDUCING AGENT ?**

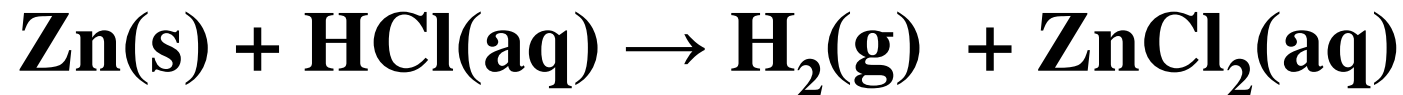
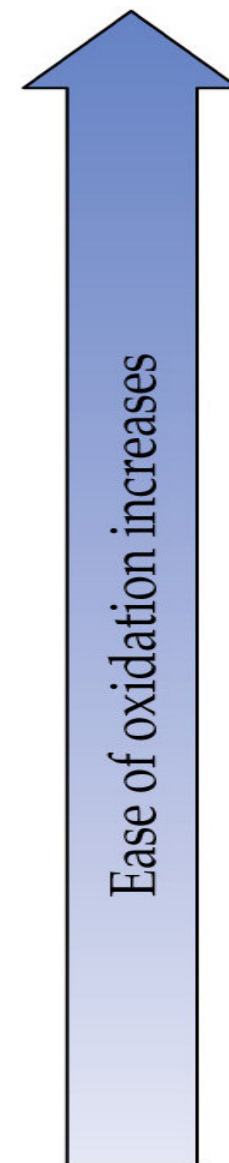


TABLE 4.5 Activity Series of Metals in Aqueous Solution

Metal	Oxidation Reaction				
Lithium	Li(s)	→	Li ⁺ (aq)	+	e ⁻
Potassium	K(s)	→	K ⁺ (aq)	+	e ⁻
Barium	Ba(s)	→	Ba ²⁺ (aq)	+	2e ⁻
Calcium	Ca(s)	→	Ca ²⁺ (aq)	+	2e ⁻
Sodium	Na(s)	→	Na ⁺ (aq)	+	e ⁻
Magnesium	Mg(s)	→	Mg ²⁺ (aq)	+	2e ⁻
Aluminum	Al(s)	→	Al ³⁺ (aq)	+	3e ⁻
Manganese	Mn(s)	→	Mn ²⁺ (aq)	+	2e ⁻
Zinc	Zn(s)	→	Zn ²⁺ (aq)	+	2e ⁻
Chromium	Cr(s)	→	Cr ³⁺ (aq)	+	3e ⁻
Iron	Fe(s)	→	Fe ²⁺ (aq)	+	2e ⁻
Cobalt	Co(s)	→	Co ²⁺ (aq)	+	2e ⁻
Nickel	Ni(s)	→	Ni ²⁺ (aq)	+	2e ⁻
Tin	Sn(s)	→	Sn ²⁺ (aq)	+	2e ⁻
Lead	Pb(s)	→	Pb ²⁺ (aq)	+	2e ⁻
Hydrogen	H ₂ (g)	→	2H ⁺ (aq)	+	2e ⁻
Copper	Cu(s)	→	Cu ²⁺ (aq)	+	2e ⁻
Silver	Ag(s)	→	Ag ⁺ (aq)	+	e ⁻
Mercury	Hg(l)	→	Hg ²⁺ (aq)	+	2e ⁻
Platinum	Pt(s)	→	Pt ²⁺ (aq)	+	2e ⁻
Gold	Au(s)	→	Au ³⁺ (aq)	+	3e ⁻

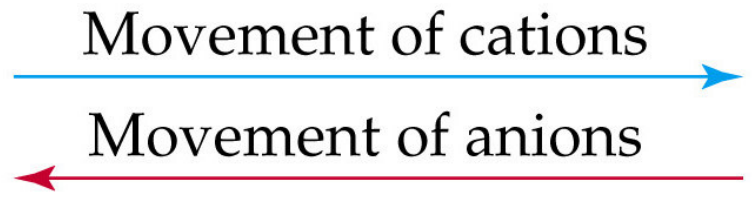
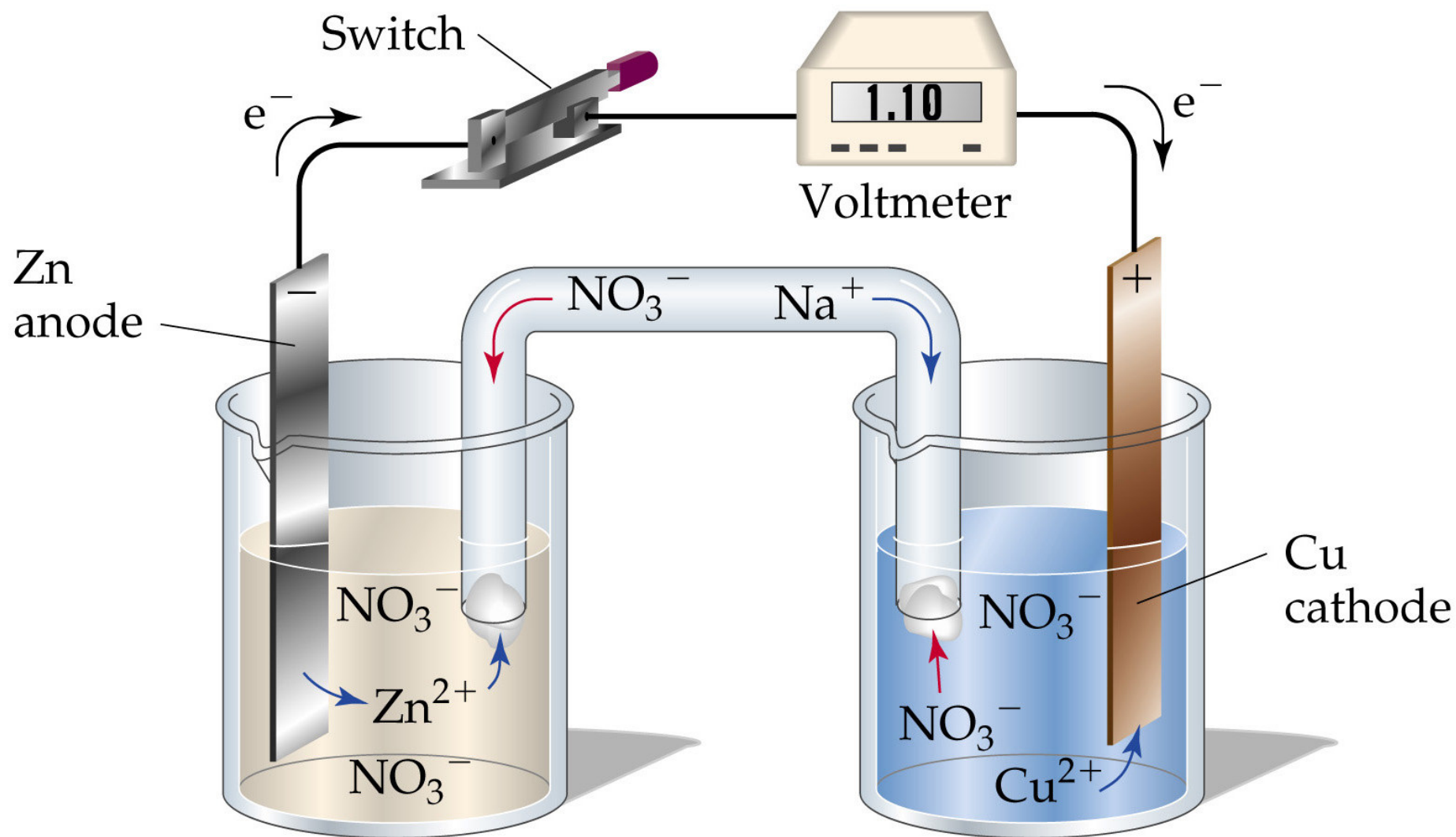


Back to Electrochemistry

Electrochemical Cells

Construct An Electrochemical Cell

1. Two Beakers
2. One containing a solution of Zinc Nitrate with a strip of Zinc Metal in it
3. The other beaker containing a solution of Copper II Nitrate with a strip of Cu Metal
4. A liquid connection between beakers



Electrochemical Cells

Electrodes: are usually metals strips/wires

Salt Bridge: is a U-shaped tube that contains a salt. Used to connect solutions

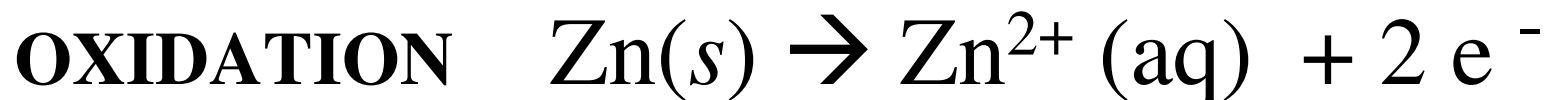
Anode: electrode where oxidation takes place

Cathode: electrode where reduction takes place

Electrochemical Cells

Electrode

OXIDATION REDUCTION REACTIONS



Net Cell Reaction



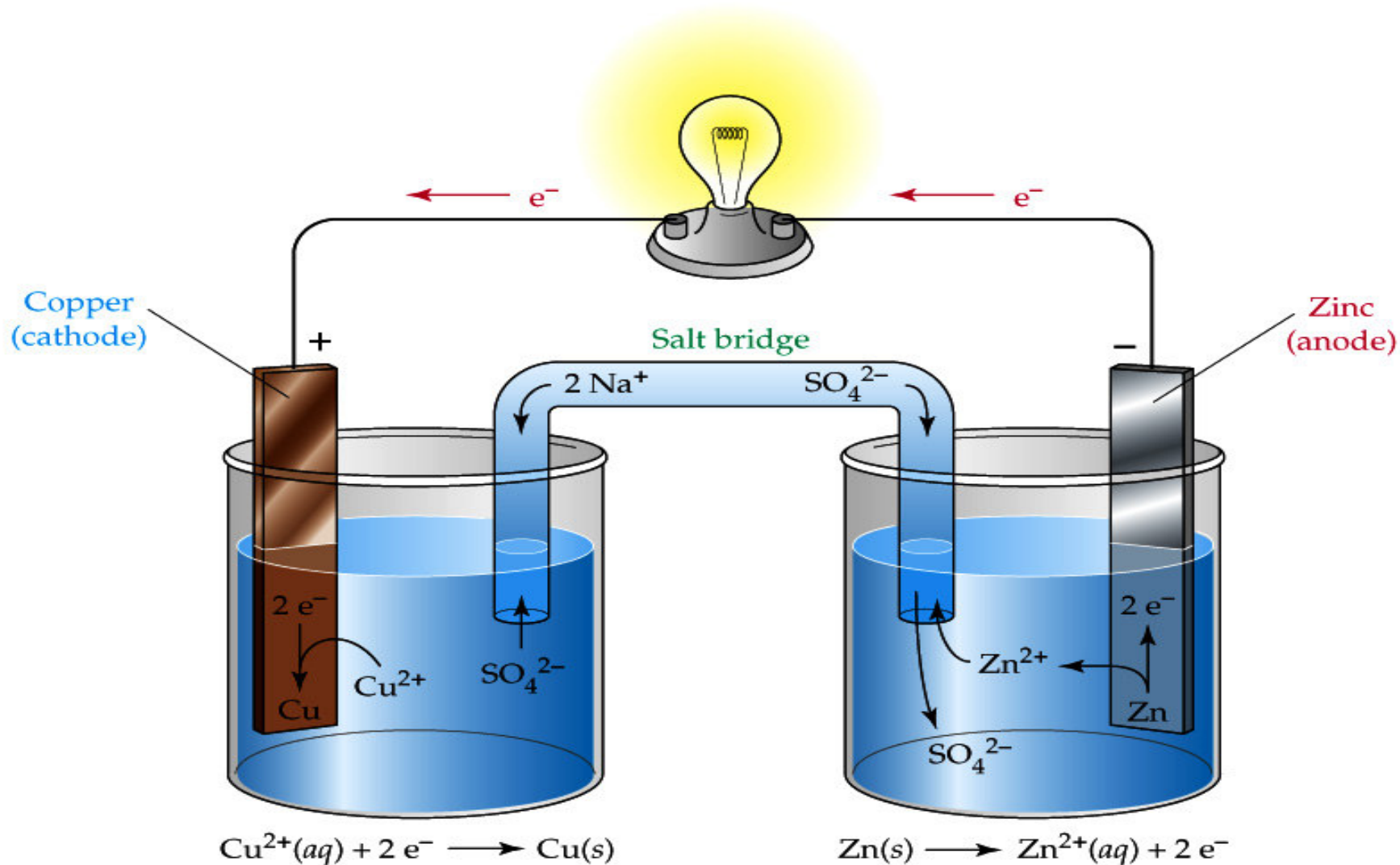
Electrochemical cell Convention



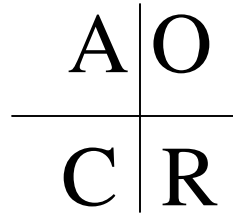
Anode is placed on **left** by convention

| Used to indicate a change of phase

|| Used to indicate a salt bridge



Electrochemical cell



Electrons “flow” from anode to cathode

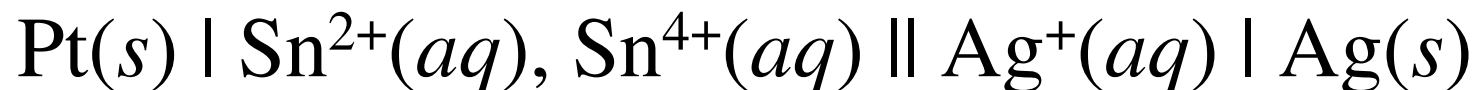
Therefore Anode is Negative Electrode

Anions “flow” from cathode to anode

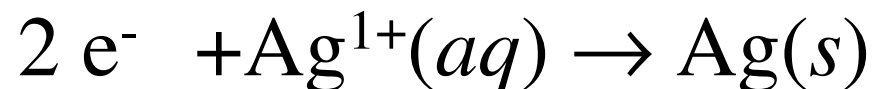
Cations “flow” from anode to cathode

Electrochemical Cells

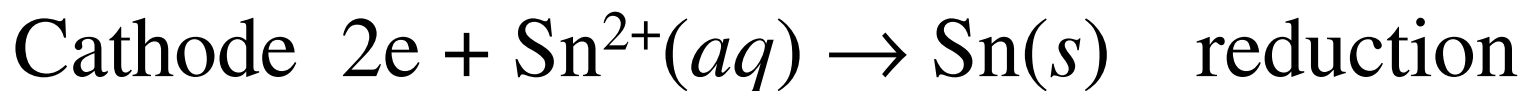
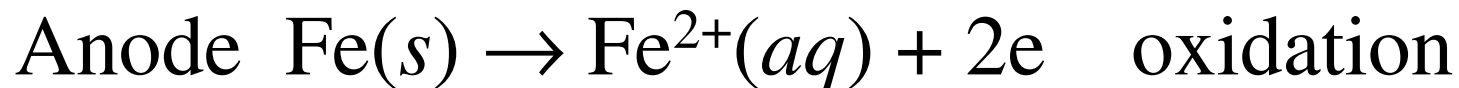
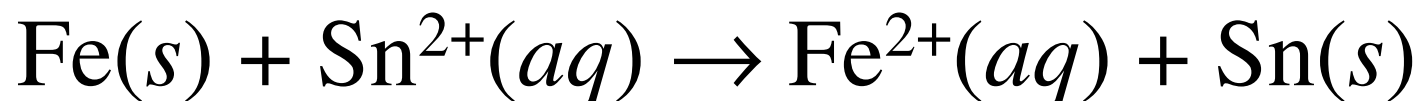
Given the following cell notation,



write the anode and cathode reactions



Write oxidation reduction reactions for



Write the cell shorthand notation



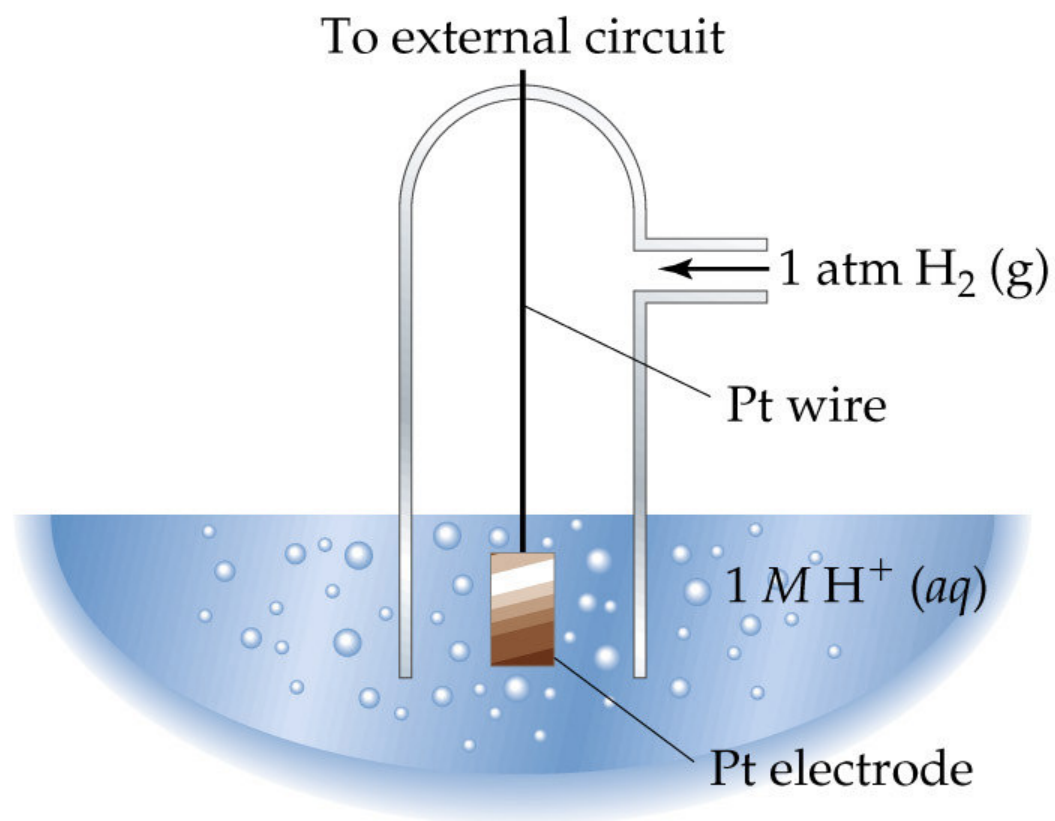
Anode **saltbridge** Cathode

$$E^{\circ}_{\text{Cell}} = E^{\circ}_{\text{oxidation}} + E^{\circ}_{\text{reduction}}$$

The standard potential of any galvanic cell is the **sum** of the standard half-cell potentials for the oxidation and reduction half-cells.

Standard half-cell potentials are always quoted as a reduction process. **The sign must be changed for the oxidation process.**

Standard Hydrogen Electrode (SHE)



standard half-cell potentials

- The reference point is called the *standard hydrogen electrode (S.H.E.)* and consists of a platinum electrode in contact with H₂ gas (1 atm) and aqueous H⁺ ions (1M).
- The *standard hydrogen electrode* is assigned an arbitrary value of exactly 0.00V.

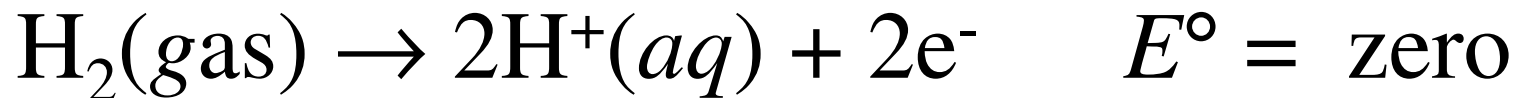
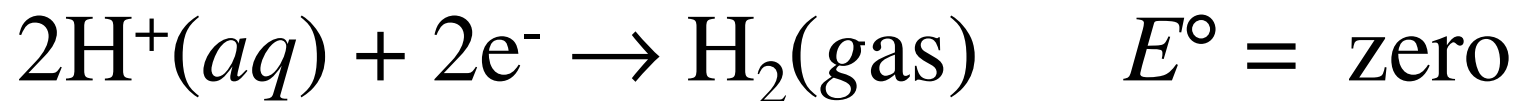
TABLE 20.1 Standard Reduction Potentials in Water at 25°C

Potential (V)	Reduction Half-Reaction
+2.87	$\text{F}_2(\text{g}) + 2\text{e}^- \longrightarrow 2\text{F}^-(\text{aq})$
+1.51	$\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- \longrightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$
+1.36	$\text{Cl}_2(\text{g}) + 2\text{e}^- \longrightarrow 2\text{Cl}^-(\text{aq})$
+1.33	$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6\text{e}^- \longrightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$
+1.23	$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \longrightarrow 2\text{H}_2\text{O}(\text{l})$
+1.06	$\text{Br}_2(\text{l}) + 2\text{e}^- \longrightarrow 2\text{Br}^-(\text{aq})$
+0.96	$\text{NO}_3^-(\text{aq}) + 4\text{H}^+(\text{aq}) + 3\text{e}^- \longrightarrow \text{NO}(\text{g}) + 2\text{H}_2\text{O}(\text{l})$
+0.80	$\text{Ag}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Ag}(\text{s})$
+0.77	$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \longrightarrow \text{Fe}^{2+}(\text{aq})$
+0.68	$\text{O}_2(\text{g}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \longrightarrow \text{H}_2\text{O}_2(\text{aq})$
+0.59	$\text{MnO}_4^-(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) + 3\text{e}^- \longrightarrow \text{MnO}_2(\text{s}) + 4\text{OH}^-(\text{aq})$
+0.54	$\text{I}_2(\text{s}) + 2\text{e}^- \longrightarrow 2\text{I}^-(\text{aq})$
+0.40	$\text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4\text{e}^- \longrightarrow 4\text{OH}^-(\text{aq})$
+0.34	$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Cu}(\text{s})$
0	$2\text{H}^+(\text{aq}) + 2\text{e}^- \longrightarrow \text{H}_2(\text{g})$
-0.28	$\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Ni}(\text{s})$
-0.44	$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Fe}(\text{s})$
-0.76	$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Zn}(\text{s})$
-0.83	$2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \longrightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$
-1.66	$\text{Al}^{3+}(\text{aq}) + 3\text{e}^- \longrightarrow \text{Al}(\text{s})$
-2.71	$\text{Na}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Na}(\text{s})$
-3.05	$\text{Li}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Li}(\text{s})$

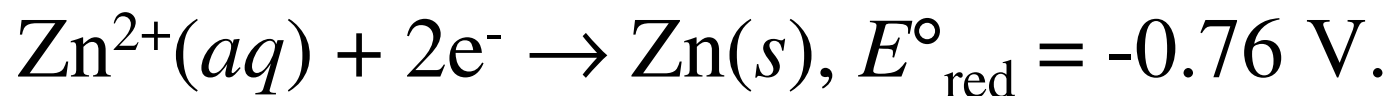
Standard Hydrogen Electrode (SHE)

The SHE consists of a Pt electrode in a tube placed in $\text{H}^+(\text{aq})$. H_2 is bubbled over electrode

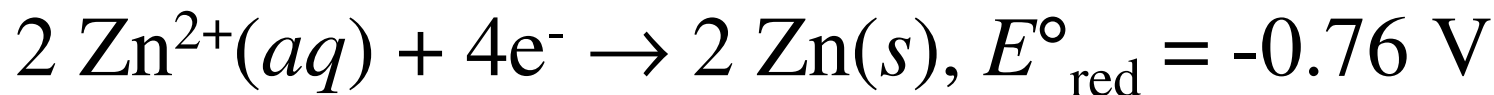
$E^\circ = \text{zero}$ by definition



reduction potentials



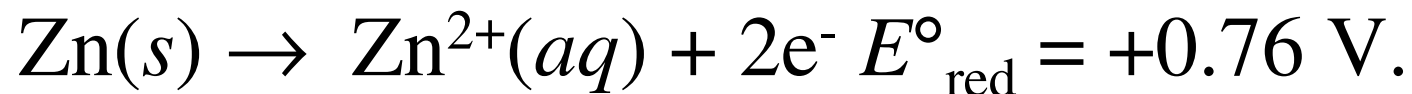
Changing the stoichiometric coefficient does
not affect E°



Reactions with $E < 0$ are nonspontaneous

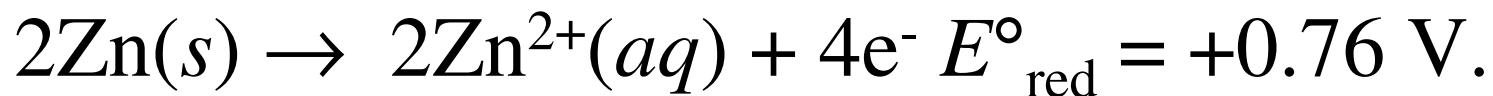
oxidation potentials

Only the sign is changed !

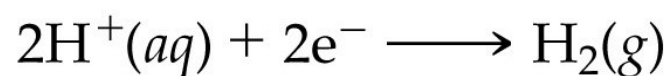
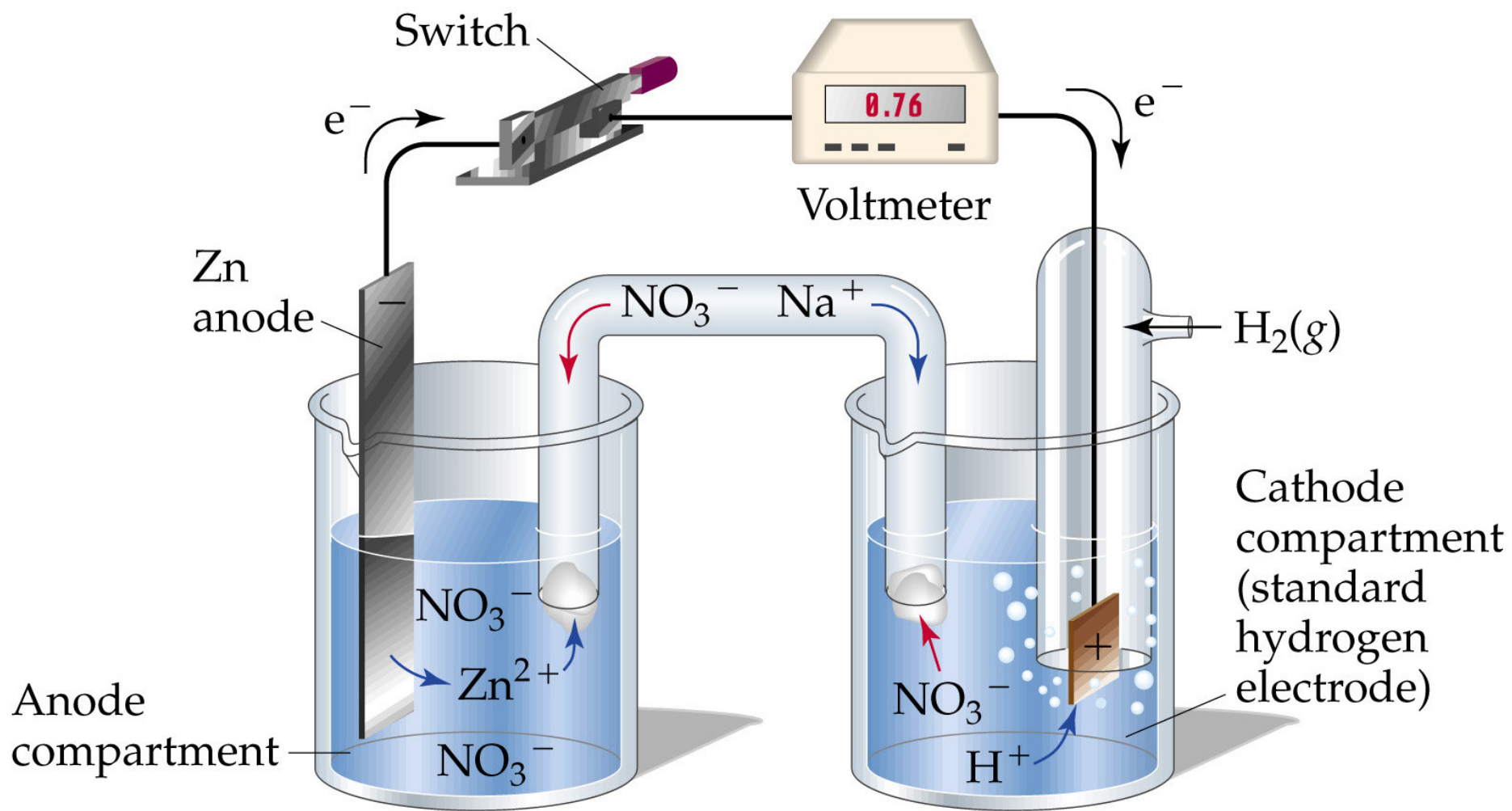


Changing the stoichiometric coefficient

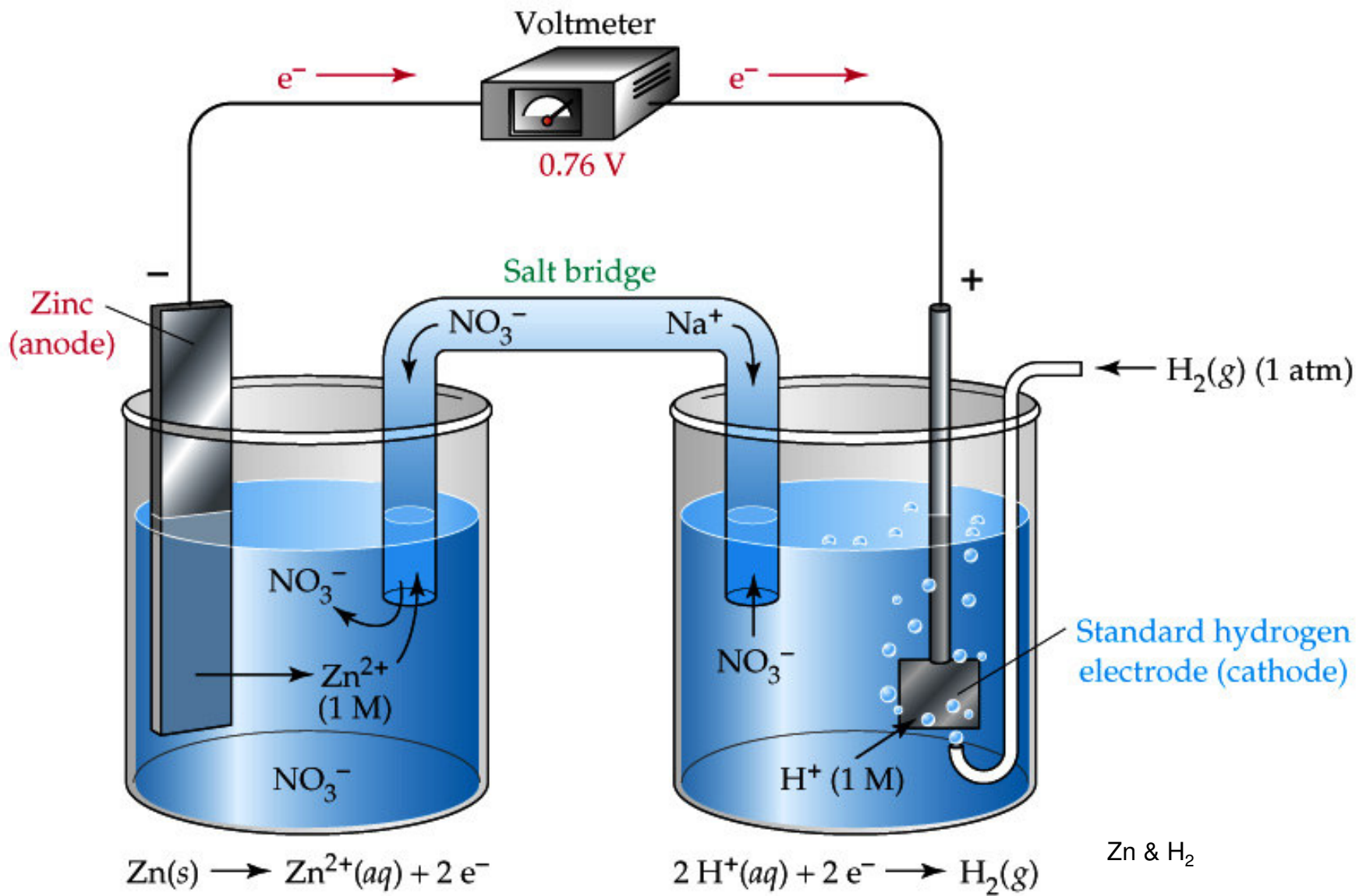
does not affect E°



Reactions with $E > 0$ are spontaneous



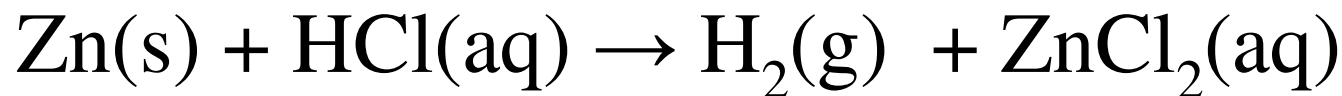
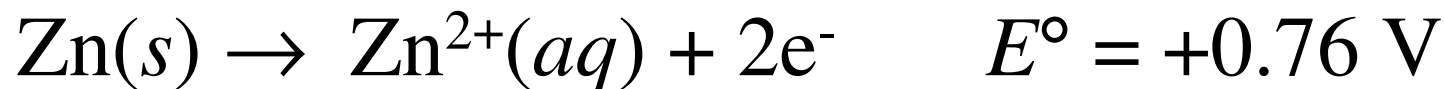
Cell Voltage



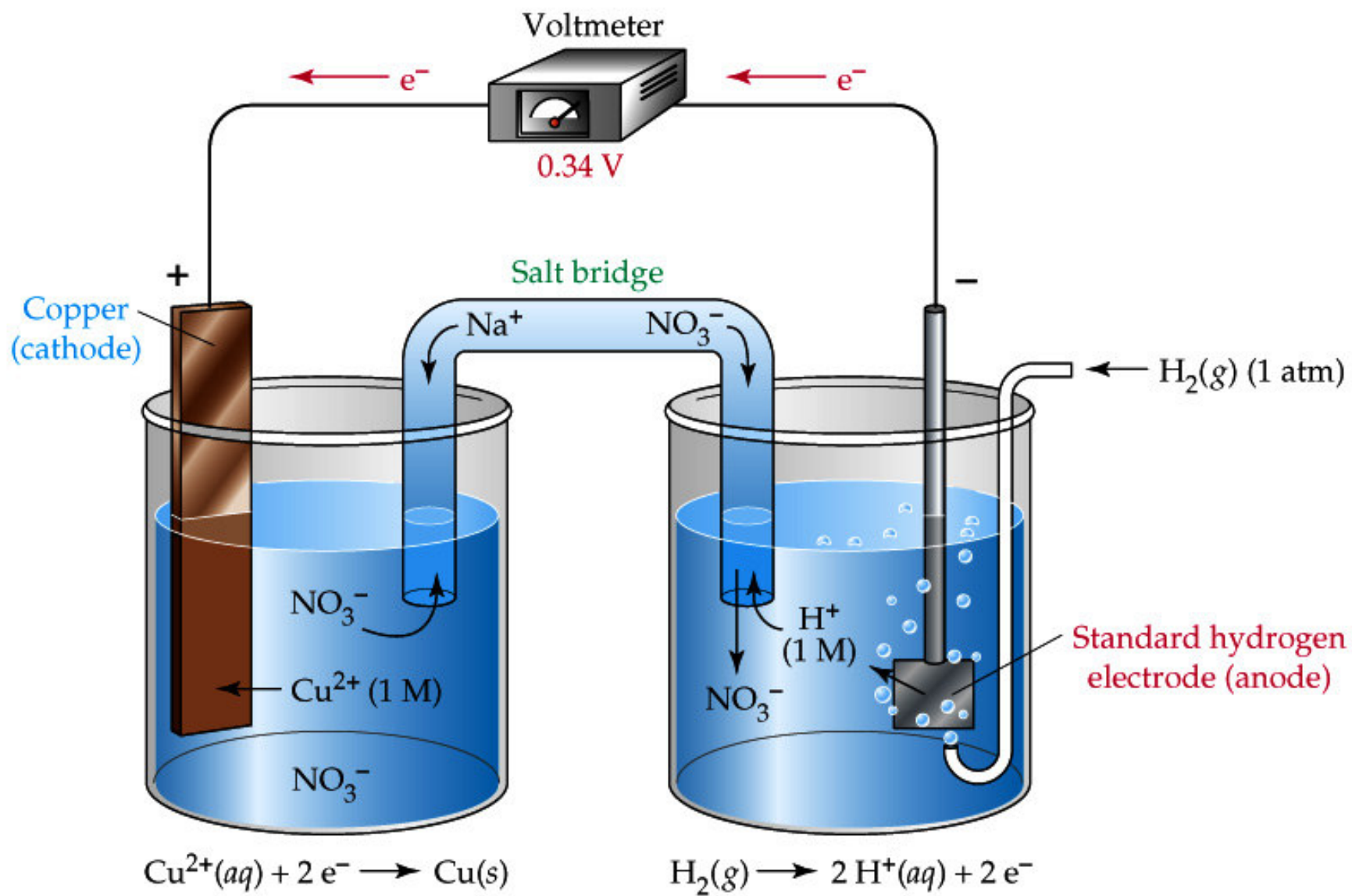


E_{cell} measured relative to the SHE

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{red}}(\text{cathode}) - E^{\circ}_{\text{red}}(\text{anode}) = +0.76$$



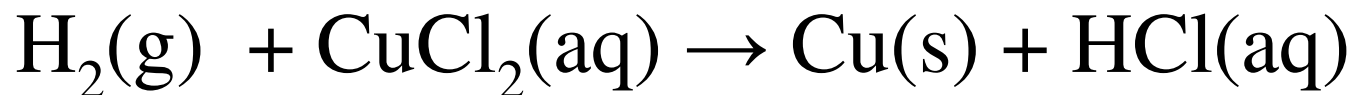
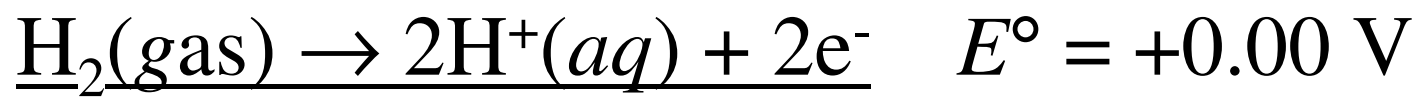
For Copper

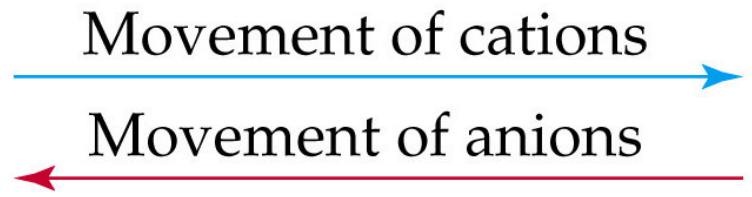
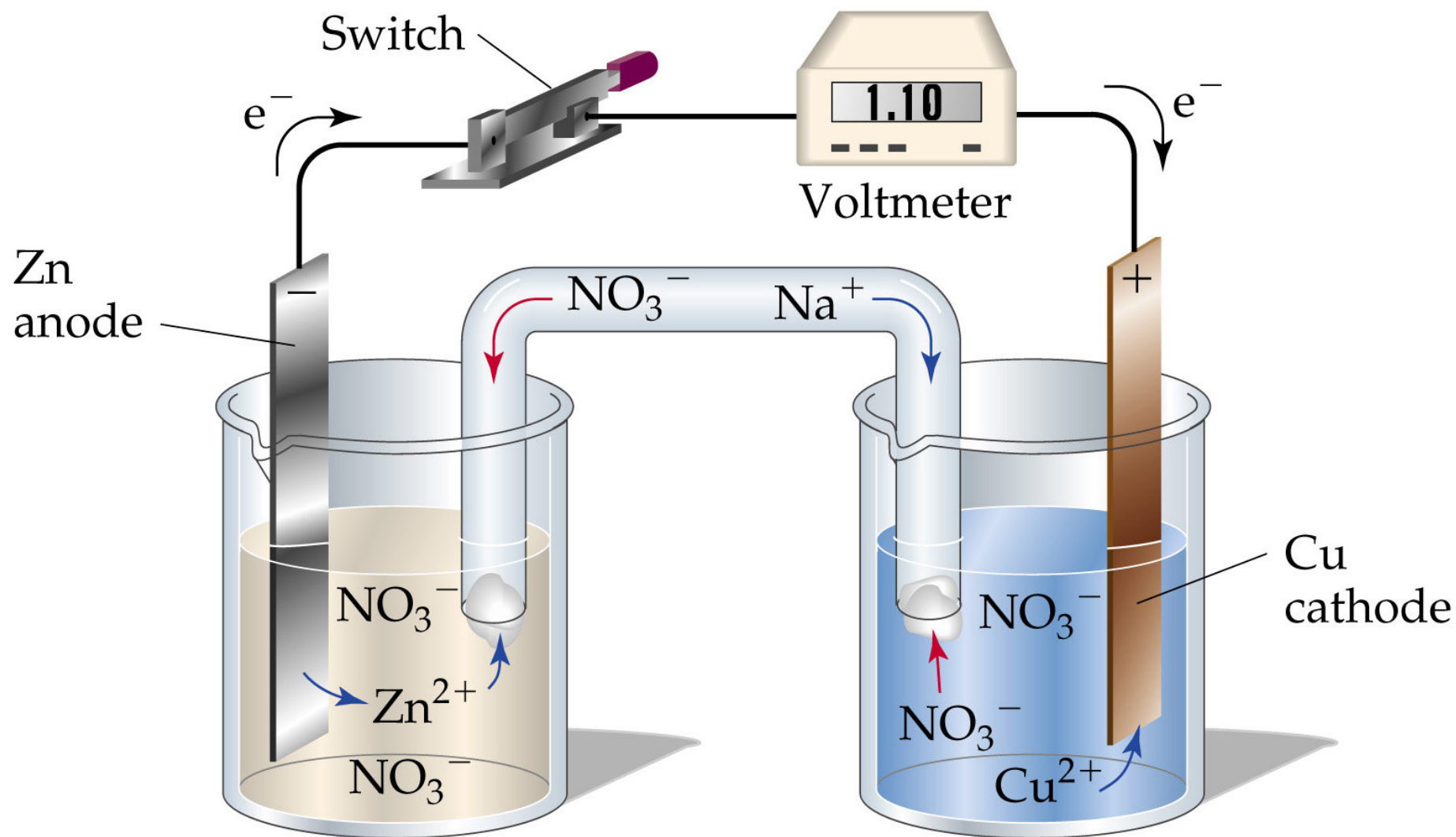




E_{cell} measured relative to the SHE

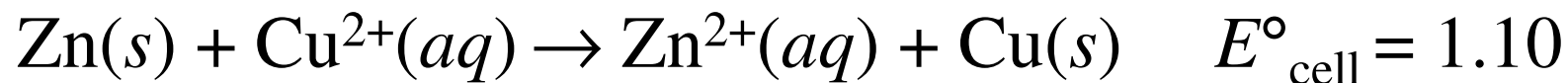
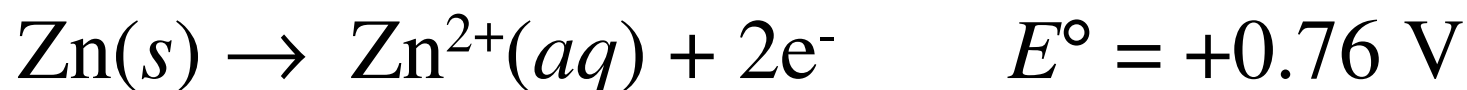
$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{red}}(\text{cathode}) - E^{\circ}_{\text{red}}(\text{anode}) = +0.34$$







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



Reactions with $E > 0$ are spontaneous

Reactions with $E < 0$ are nonspontaneous

When selecting two half cell reactions the more negative value will form the oxidation half-cell.

Consider the reaction between zinc and silver:



- Therefore zinc forms the oxidation half-cell:

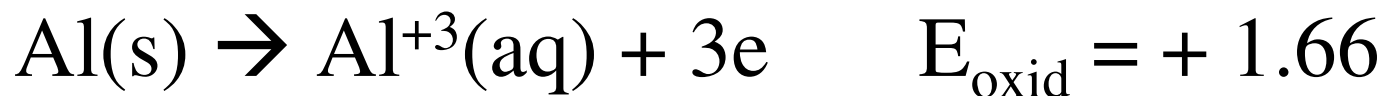


Electrochemical Cells

Can $\text{Fe}^{2+}(\text{aq})$ oxidize $\text{Al}(\text{s})$?

(a) yes (b) no (c) I do not know

Write Reaction



$$E_{\text{cell}} = E_{\text{oxid}} + E_{\text{red}} = + \text{ therefore YES!}$$

Electrochemical Cells

- Can $\text{Pb}^{2+}(\text{aq})$ oxidize $\text{Cu}(\text{s})$?
- Calculate E°_{cell} formed with lead and copper

Batteries

They produce POSITIVE voltage

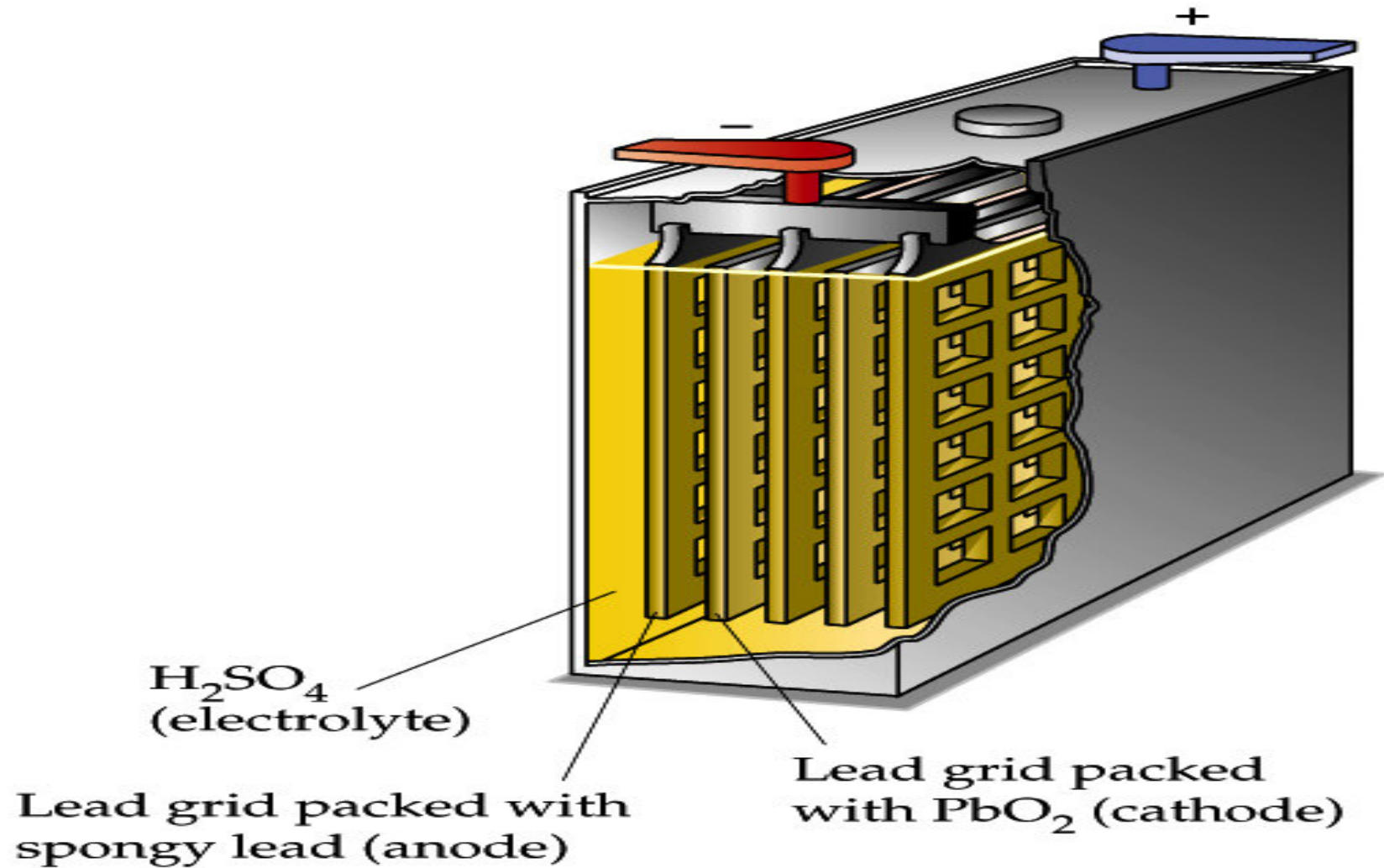
Batteries 101

Batteries are the most important practical application of galvanic cells.

Single cell batteries consist of one galvanic cell.

Multicell batteries consist of several galvanic cells linked in series to obtain the desired voltage

Lead Storage Battery:



Lead-Acid Battery

The overall electrochemical reaction is



for which

$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{red}}(\text{cathode}) - E^\circ_{\text{red}}(\text{anode}) \\ &= (+1.685 \text{ V}) - (-0.356 \text{ V}) \\ &= +2.041 \text{ V}. \end{aligned}$$

Wood or glass-fiber spacers are used to prevent the electrodes from touching

Lead Storage Battery:

A typical “12 volt” battery consists of six individual cells connected in series.

Cell Potential: 1.924V {each cell

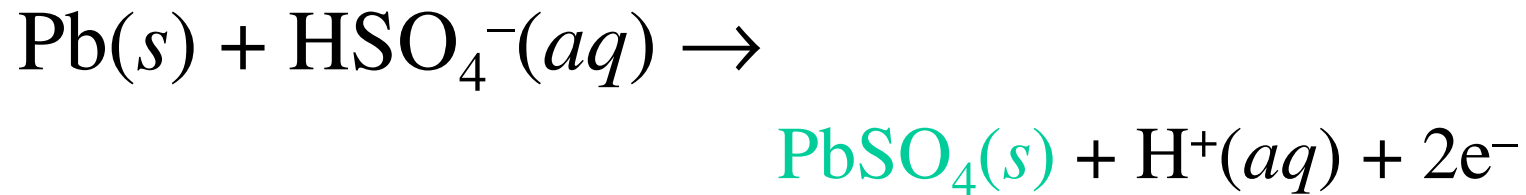
Electrolyte: 38% by mass Sulfuric Acid.

Anode: Lead grid packed with spongy lead.

Cathode: Lead grid packed with lead IV oxide.

Lead Storage Battery:

Anode: lead



Cathode: lead IV oxide



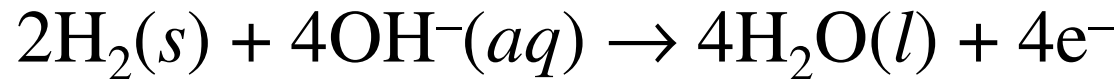
Lead Storage Battery:

- Pb is **oxidized** to PbSO_4 at the anode, and
- PbO_2 is **reduced** to PbSO_4 at the cathode
- PbSO_4 adheres to the electrodes causing the battery to “run–down.”
- Recharging the battery reverses this reaction to reform Pb and PbO_2 .

Fuel Cell:

Uses externally fed CH_4 or H_2 , which react to form water. Most common is H_2 .

Anode: Porous carbon containing metallic catalysts



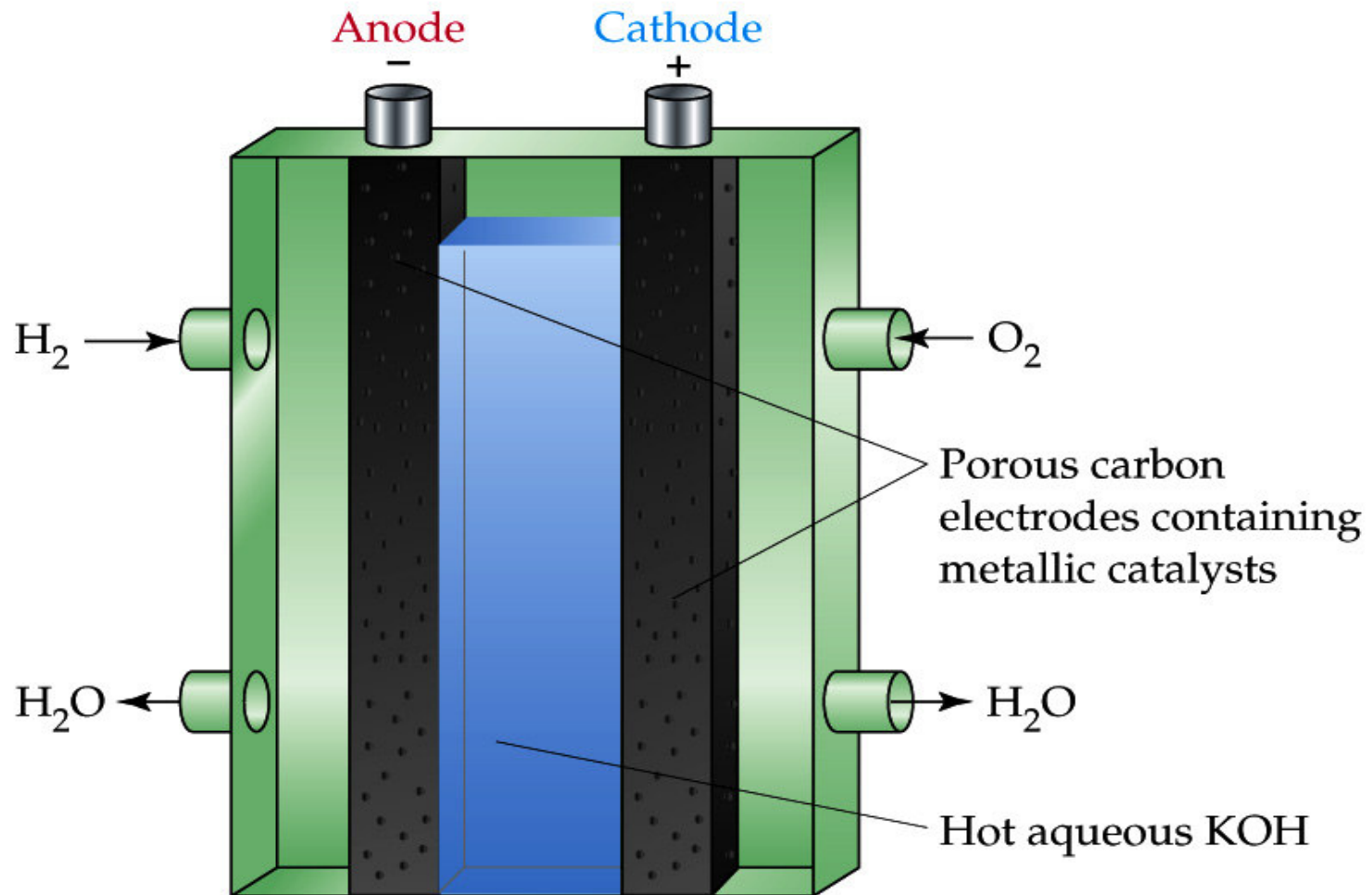
Cathode: Porous carbon containing metallic



Electrolyte: Hot aqueous KOH solution.

Cell Potential: 1.23V

Fuel Cell:



Fuel Cell:

- Fuel cells are **not batteries** because they are not self contained.
- Fuel cells are typically have about 40% conversion to electricity, the remainder is lost as heat.
- Excess heat can be used to drive turbine generators.

Electrolysis

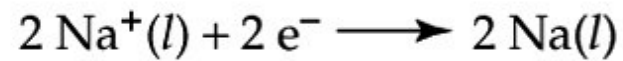
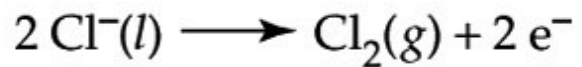
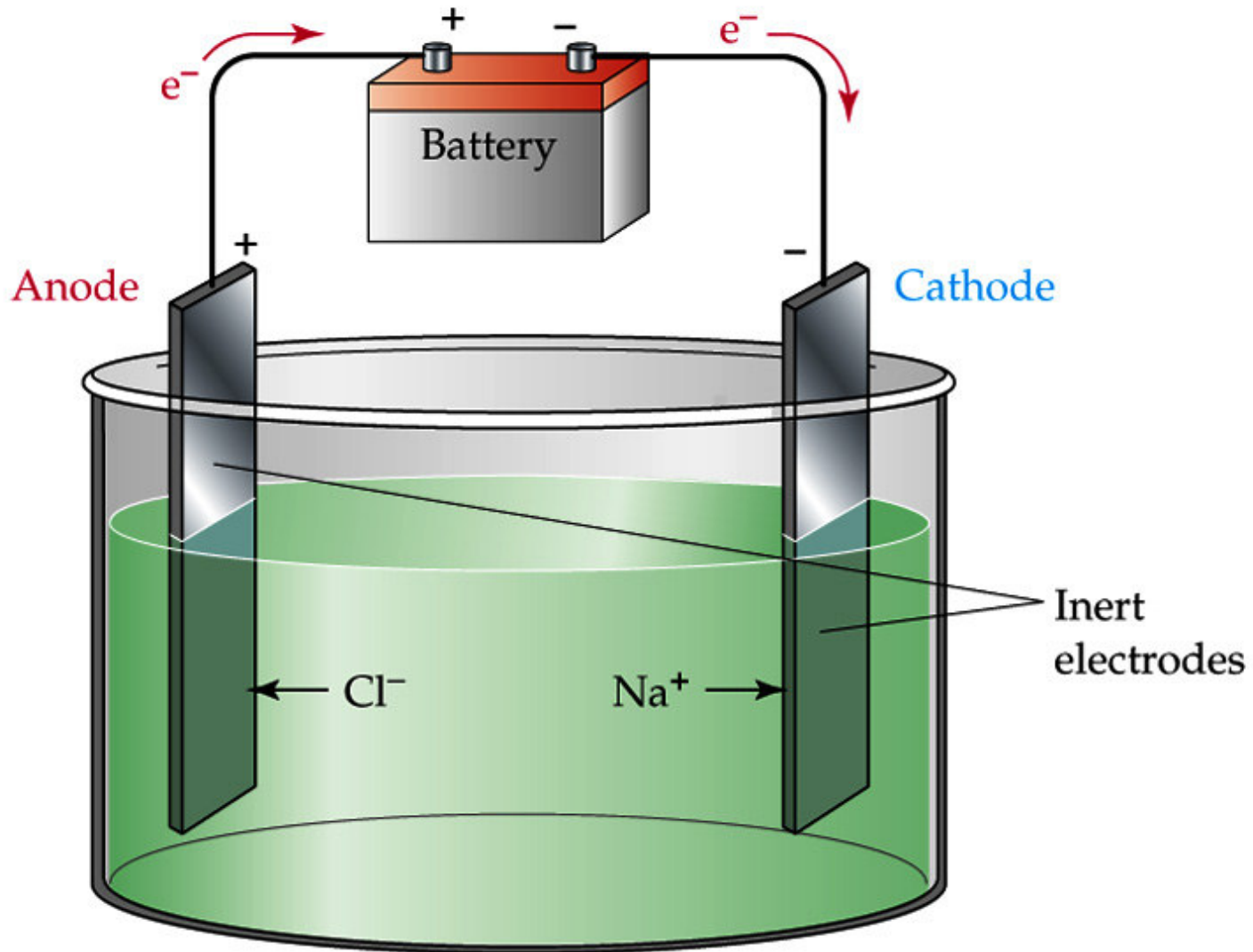
It is the OPPOSITE of batteries

It does not occur UNLESS
you **make it happen**

Electrolysis 101

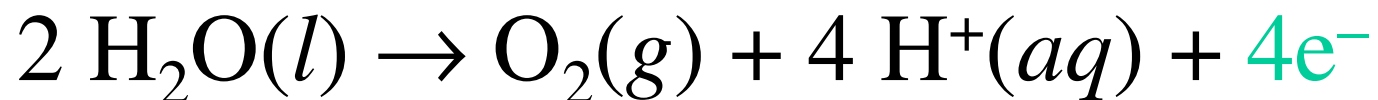
- **Electrolysis:** is the process in which electrical energy is used to drive a *nonspontaneous* chemical reaction.
- Processes in an electrolytic cell are the *reverse* of those in a galvanic cell.

Electrolysis of Molten Sodium Chloride:



Electrolysis of Water

- **Anode**: Water is oxidized to oxygen gas.



- **Cathode**: Water is reduced to hydrogen gas.



Quantitative Electrolysis:

The amount of substance produced at an electrode by electrolysis depends on the quantity of charge passed through the cell.

Reduction of **1 mol of sodium ions** requires **1 mol of electrons** to pass through the system.

The charge on 1 mol of electrons is 96,500 Coulombs.

To determine the moles of electrons passed measure current and time

$$\text{Charge (C)} = \text{Current (A)} \times \text{Time (s)}$$

- Because the charge on 1 mol of e^- is 96,500C, the number of moles of e^- passed through the cell is:

$$\text{Moles of } e^- = \text{Charge (C)} \times \frac{1 \text{ mole } e^-}{96,500 \text{ C}}$$

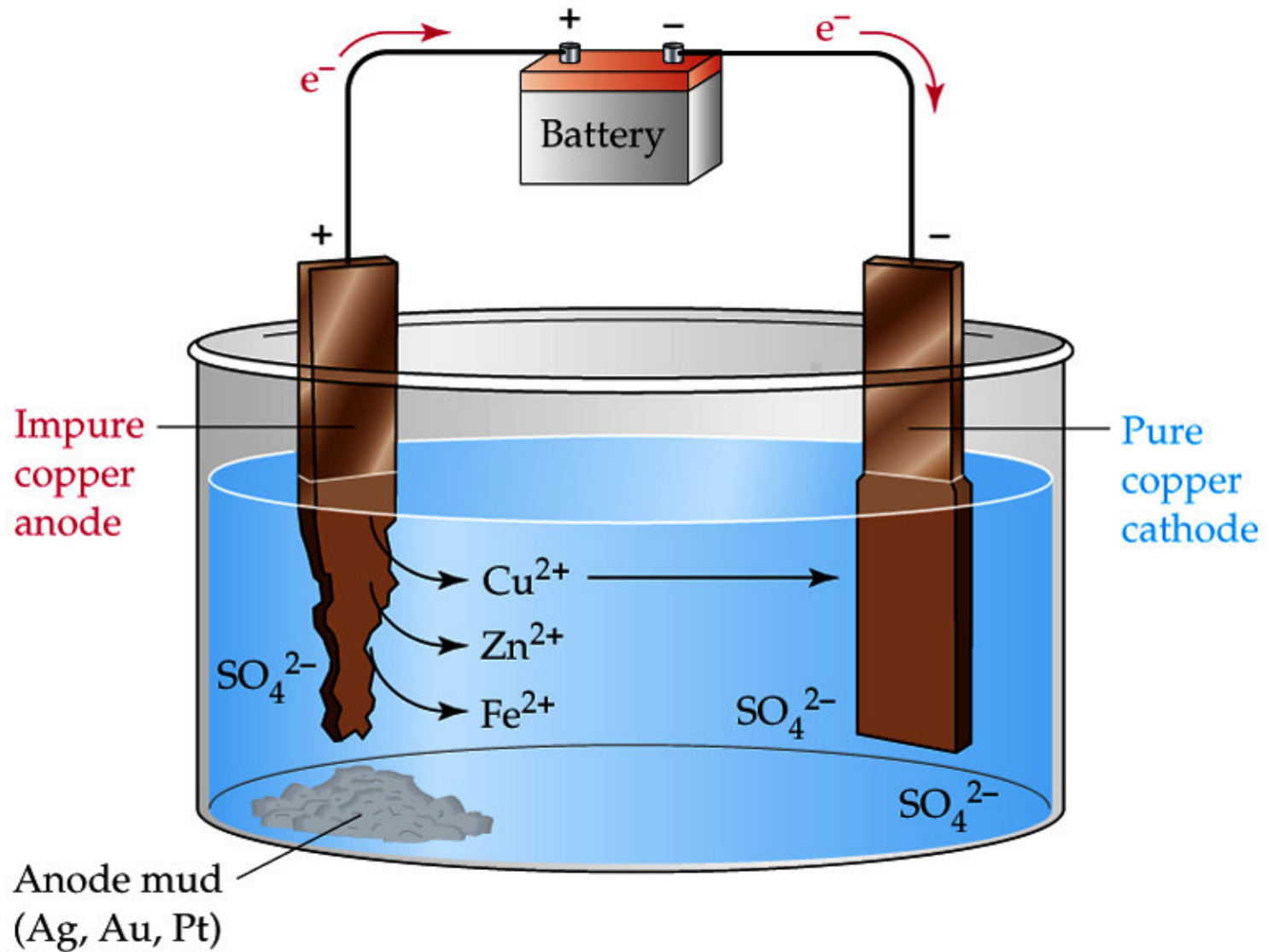
Electrolysis

A constant current of 30.0A is passed through an aqueous solution of NaCl for a time of 1.00 hour. How many grams of NaOH and how many liters of Cl₂ gas at STP are produced?

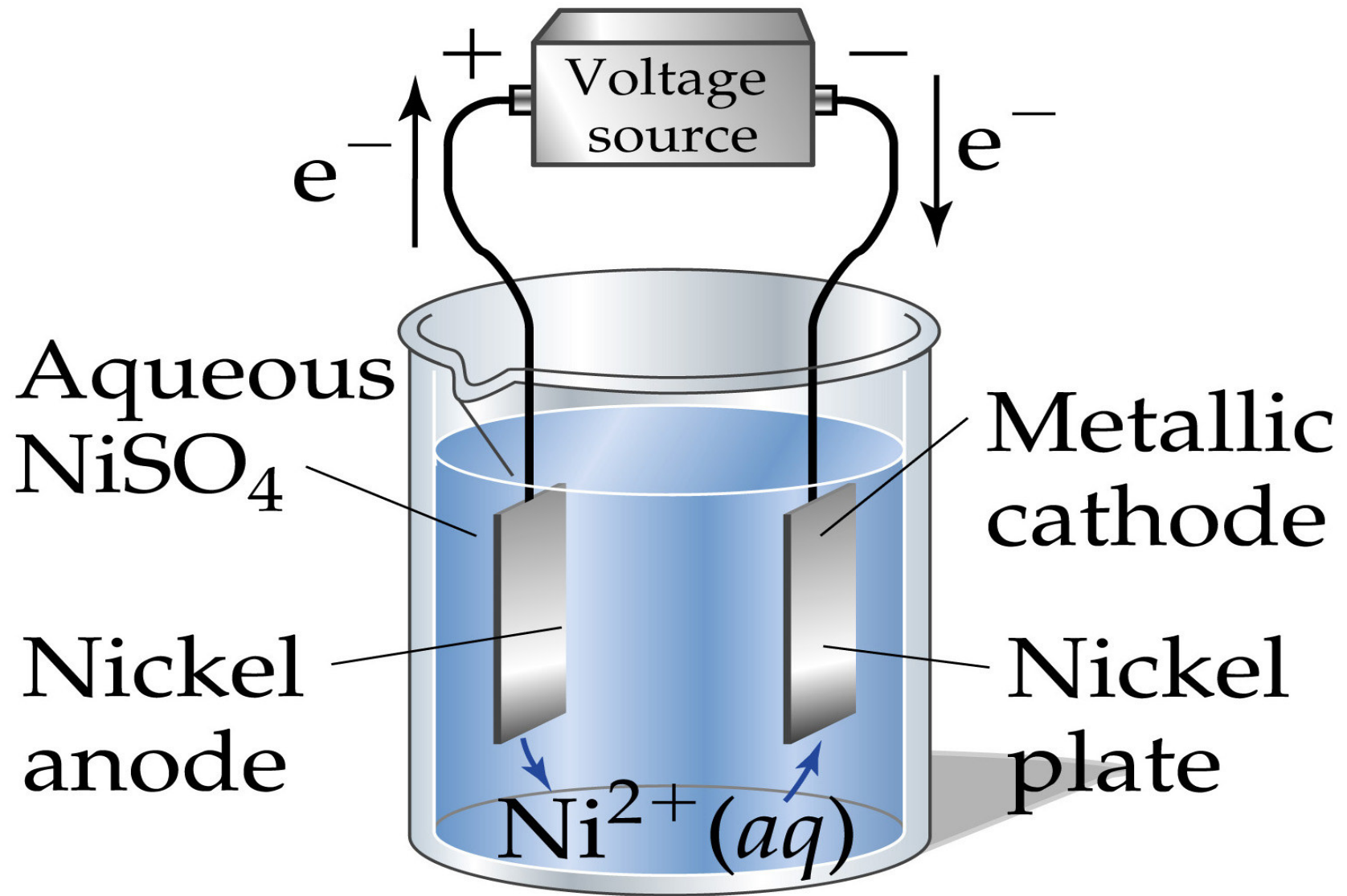
Electrolysis

A constant current is passed through a cell containing molten MgCl_2 for 1 hour. If 71.0 g of Cl_2 is obtained, How many grams of Mg is obtained and what is the current in amperes?

Electrolysis Applications: **Electroplating**



External source to drive reaction



Electrolysis Electroplating

Ni electrode and another metallic electrode in a solution of $\text{Ni}^{2+}(\text{aq})$

- Anode: $\text{Ni}(s) \rightarrow \text{Ni}^{2+}(\text{aq}) + 2e^{-}$
- Cathode: $\text{Ni}^{2+}(\text{aq}) + 2e^{-} \rightarrow \text{Ni}(s)$
- Ni plates on the inert electrode

Balancing Oxidation-Reduction Reactions

**Balancing Equations by the
Method of Half Reactions**

Balancing Oxidation-Reduction Reactions

1. Write down the two half reactions.
2. Balance each half reaction:
 - a. First with elements other than H and O
 - b. Then balance O by adding water.
 - c. Then balance H by adding H^+ .
 - d. Finish by balancing charge by adding electrons

Balancing Oxidation-Reduction Reactions

3. Multiply each half reaction to make the number of electrons equal.
4. Add the reactions and simplify.
5. Check!

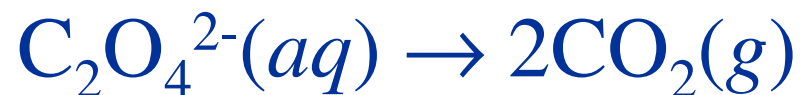
Balancing Oxidation-Reduction Reactions

- Reaction of an acidic solution of $\text{Na}_2\text{C}_2\text{O}_4$ (sodium oxalate, colorless) with KMnO_4 (deep purple).
- MnO_4^- is reduced to Mn^{2+} (pale pink) while the $\text{C}_2\text{O}_4^{2-}$ is oxidized to CO_2 .

Balancing Oxidation-Reduction Reactions

For $\text{KMnO}_4 + \text{Na}_2\text{C}_2\text{O}_4$

1. The two incomplete half reactions are



For $\text{KMnO}_4 + \text{Na}_2\text{C}_2\text{O}_4 \rightarrow$

1. For the MnO_4^- half reaction



2. Adding water and H^+ yields



There is a 7+ charge on the left and 2+ on the right.

So 5 electrons need to be added to the left:



Balancing Reactions

- In the oxalate reaction, there is a 2- charge on the left and a 0 charge on the right, so we need to add two electrons:

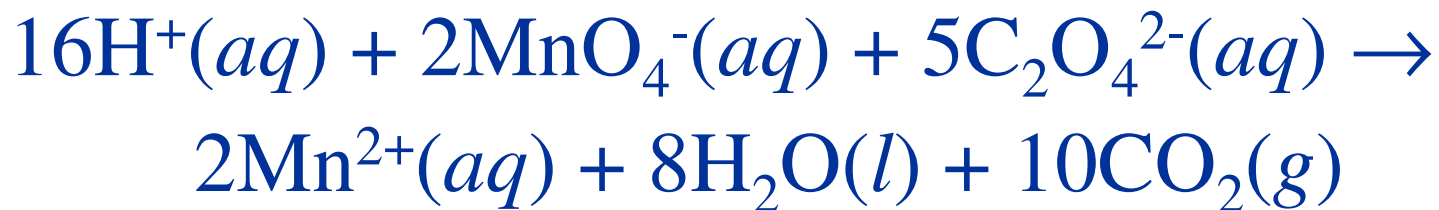


3. To balance the 5 electrons for permanganate and 2 electrons for oxalate, we need 10 electrons for both. Multiplying gives:



Balancing Reactions

4. Adding gives:



5. Which is balanced!

Balancing Oxidation-Reduction Reactions

Balancing Equations for Reactions Occurring in Basic Solution

- We use OH^- and H_2O rather than H^+ and H_2O .
- The same method as above is used, but OH^- is added to “neutralize” the H^+ used.