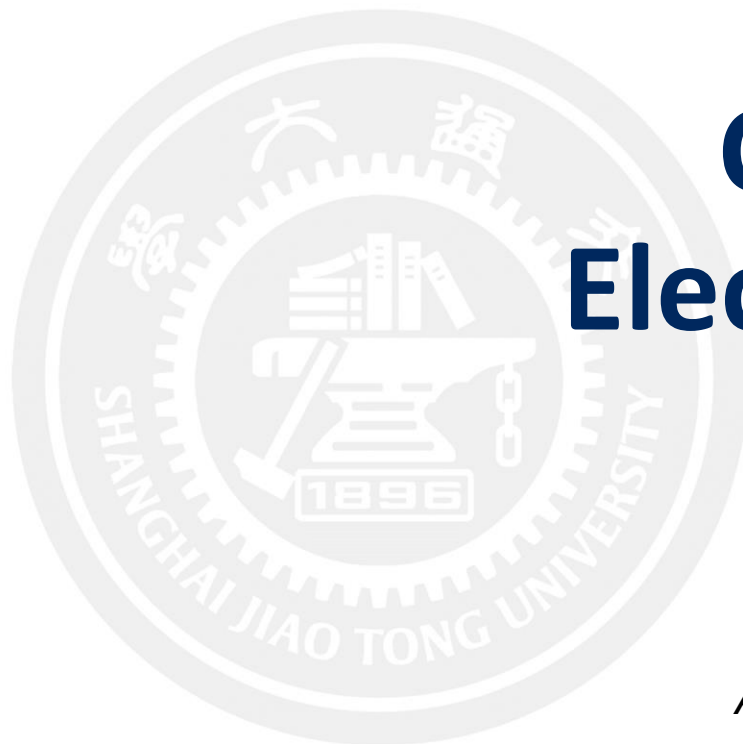




# CHEM2100J Chemistry Autumn 2024

## Chapter 13 Electrochemistry



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# Reduction Oxidation (Redox) Reactions

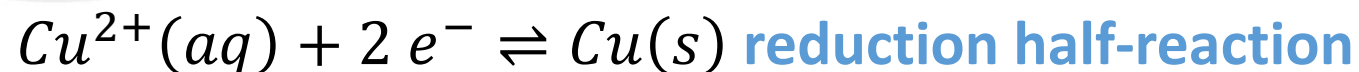
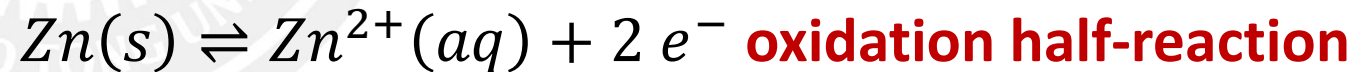
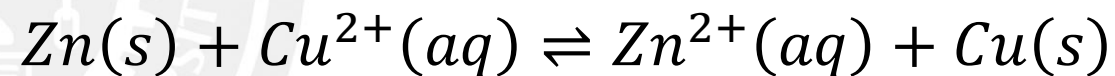


A **redox reaction** is a combination of two separate reactions called **half-reactions**.

The **removal** of electrons is called an **oxidation reaction**, the oxidized substance acts as a **reducing agent**.

The **uptake** of electrons is called a **reduction reaction**, the reduced substance acts as an **oxidizing agent**.

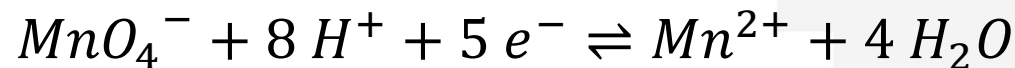
The reactants used in Volta's 1800's battery:



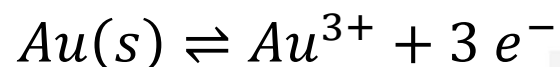
# Example



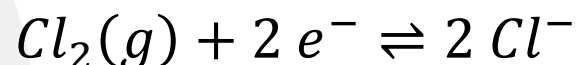
Identify as either an oxidation or a reduction reaction and identify the oxidizing or reducing agents.



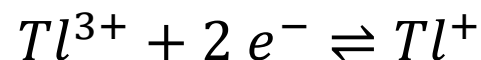
Reduction,  $\text{Mn}^{7+}$  in  $\text{MnO}_4^-$  is the oxidizing agent



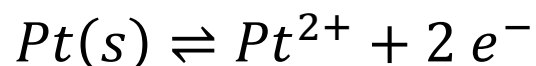
Oxidation,  $\text{Au(s)}$  is the reducing agent



Reduction,  $\text{Cl}_2(\text{g})$  is the oxidizing agent



Reduction,  $\text{Tl}^{3+}$  is the oxidizing agent

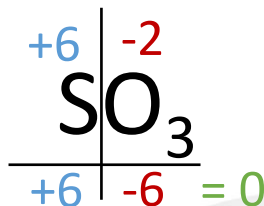


Oxidation,  $\text{Pt(s)}$  is the reducing agent

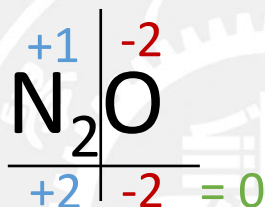
# Oxidation Numbers



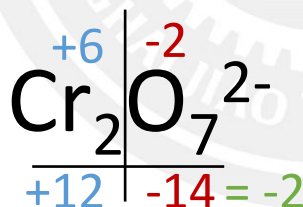
Find the oxidation numbers of the underlined element  $\underline{\text{S}}\text{O}_3$ ,  $\underline{\text{N}}_2\text{O}$  and  $\underline{\text{Cr}}_2\text{O}_7^{2-}$ .



The oxygen side has a total of 6 negative charges. The whole molecule is neutral. Therefore, sulfur needs to have an oxidation number of +6.

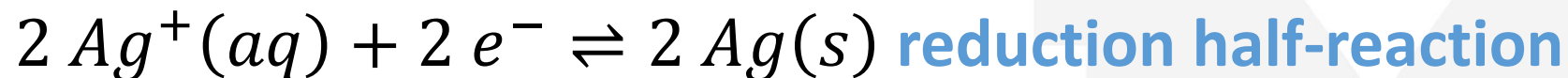
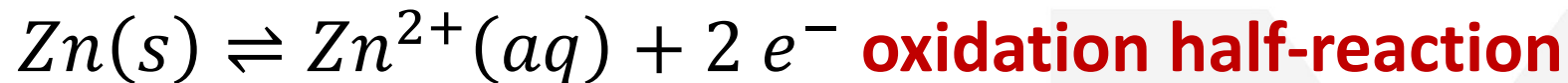


The oxygen side has a total of 2 negative charges. The whole molecule is neutral. Therefore, the nitrogen side needs a total of two positive charges. As there are two nitrogen atoms, they each need to have an oxidation number of +1.



The oxygen side has a total of 14 negative charges. The whole molecule has a charge of -2. Therefore, the chromium side needs a total of twelve positive charges. As there are two chromium atoms, they each need to have an oxidation number of +6.

# Redox Couple



$\text{Zn}(s)$  and  $\text{Zn}^{2+}(aq)$  are **joined** through the oxidation half-reaction, so we refer to these as **couples**, and they are written as  $\text{Zn}^{2+}/\text{Zn}$ .

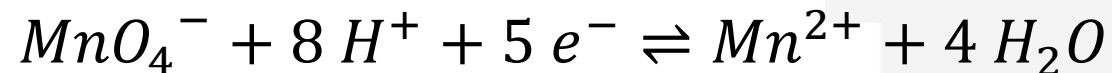
A note on *formalism*: Couples are always written as **reductions**, so  $\text{Zn}^{2+}/\text{Zn}$  implies the reaction  $\text{Zn}^{2+}(aq) + 2 e^{-} \rightleftharpoons \text{Zn}(s)$ .

The silver couple is written as  $\text{Ag}^{+}/\text{Ag}$ .

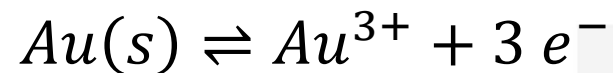
# Example



Write the redox couple for the following half reactions:



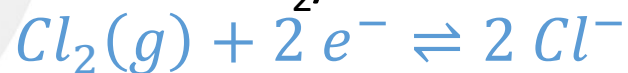
$\text{MnO}_4^-/\text{Mn}^{2+}$



$\text{Au}^{3+}/\text{Au}$

Given these redox couples, what is their half-reaction?

$\text{Cl}_2/\text{Cl}^-$



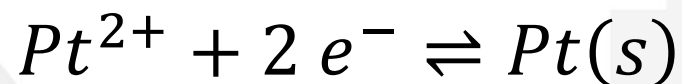
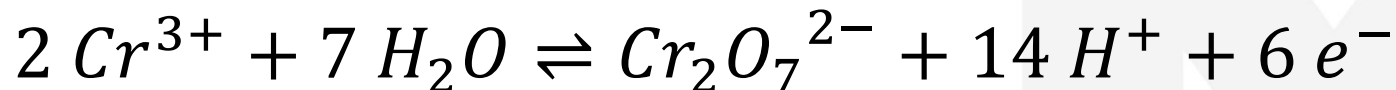
$\text{Tl}^{3+}/\text{Tl}^+$



# Example



What are the redox couples for the following half-reactions:



- A.  $\text{Cr}^{3+}/\text{Cr}_2\text{O}_7^{2-}$  and  $\text{Pt}^{2+}/\text{Pt}$
- B.  $\text{Cr}^{3+}/\text{Cr}_2\text{O}_7^{2-}$  and  $\text{Pt}/\text{Pt}^{2+}$
- C.  $\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$  and  $\text{Pt}/\text{Pt}^{2+}$
- D.  $\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$  and  $\text{Pt}^{2+}/\text{Pt}$

# Balancing Redox Equations



Balancing chemical equations by simple inspection is common.

Now we run across redox chemical equations which we *cannot balance by inspection*.

In aqueous redox reactions, **water** is not an innocent bystander.

Often,  **$\text{H}^+(\text{aq})$**  and  **$\text{OH}^-(\text{aq})$**  participate, so the number of electrons gained or lost is not obvious.

We now learn to balance a redox reaction in either an acidic or basic solution, which is a multi-step process.



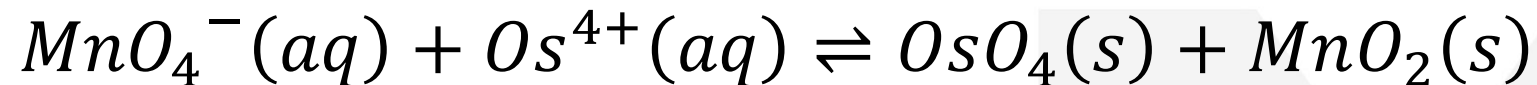
# Balancing Redox Equations



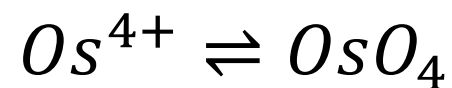
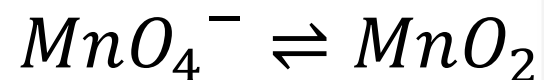
Method for balancing oxidation-reduction reactions in an acidic solution:

- A. Write the equations for the oxidation and reduction half-reactions.
- B. For each half-reaction:
  1. Balance all elements except hydrogen and oxygen
  2. Balance oxygen using  $\text{H}_2\text{O}$
  3. Balance hydrogen using  $\text{H}^+$
  4. Balance the charge using electrons
  5. Cancel like-species and combine remaining species

# Example: Acidic Solution



A. Write the equations for the oxidation and reduction half-reactions.

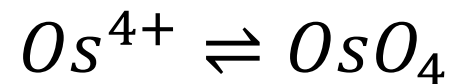
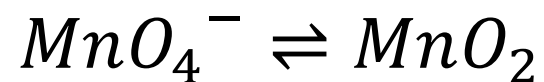


# Example: Acidic Solution



A. For each half-reaction:

1. Balance all elements except hydrogen and oxygen



Since there are the same number of Mn and Os on each side of the reaction, we skip this step.



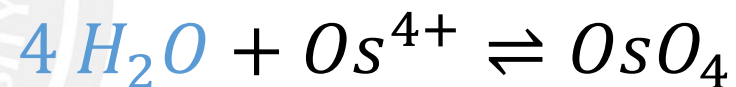
# Example: Acidic Solution



## 2. Balance oxygen using $H_2O$



We balance a total of 4 O atoms on the reactant side by adding  $2 H_2O$ .

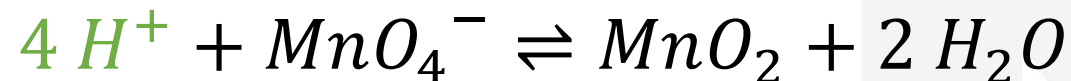


We balance a total of 4 O atoms on the product side by adding  $4 H_2O$ .

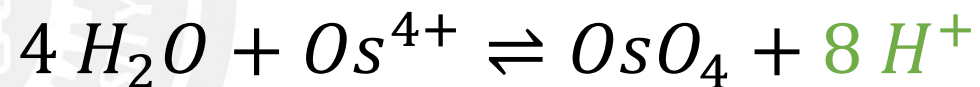
# Example: Acidic Solution



3. Balance hydrogen using  $H^+$



We balance a total of 4 H atoms on the product side by adding  $4 H^+$ .



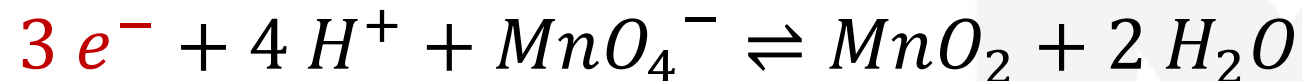
We balance a total of 8 H atoms on the reactant side by adding  $8 H^+$ .

At this point, all *atoms* are balanced.

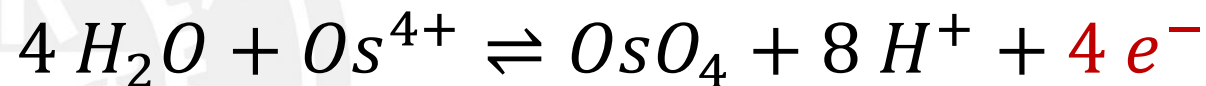
# Example: Acidic Solution



## 4. Balance the charge using electrons



We balance a total of 3 positive charges on the reactant side by adding  $3 e^{-}$ .

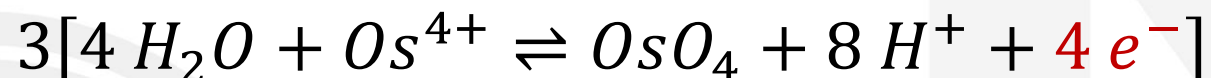
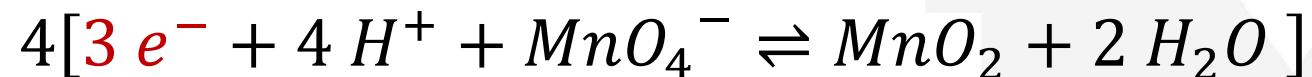


We balance a total of 8 positive charges on the product side by adding  $4 e^{-}$ .

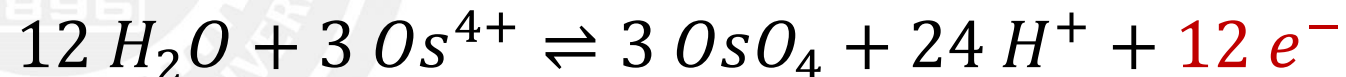
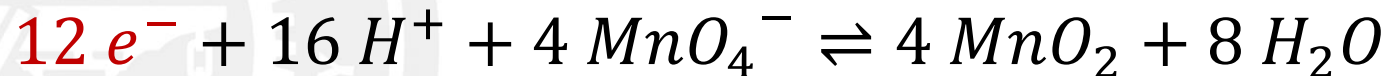
# Example: Acidic Solution



We need the same number of electrons for both half reactions:



Multiplying the stoichiometric coefficients yields:

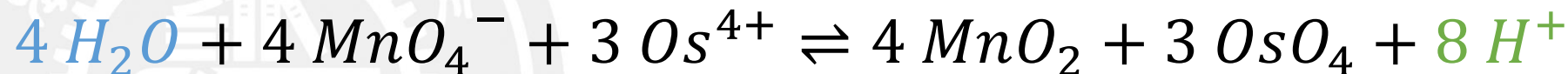
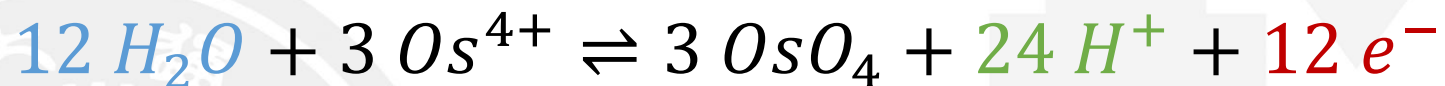
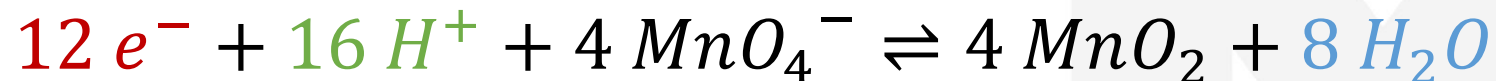


We now have the same number of electrons leaving the oxidation half-reaction and entering the reduction half-reaction.

# Example: Acidic Solution



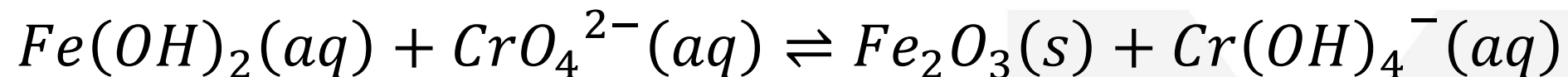
5. Cancel like-species and combine remaining species



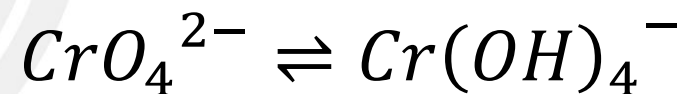
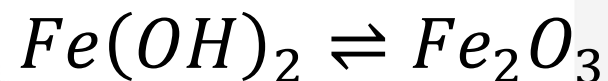
Check to ensure that all elements and charges are balanced.



# Example: Basic Solution



A. Write the equations for the oxidation and reduction half-reactions.

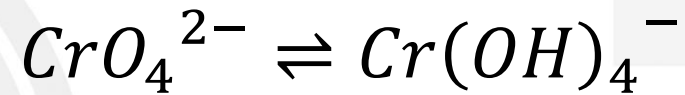
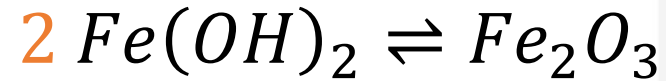


# Example: Basic Solution

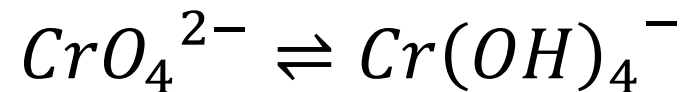
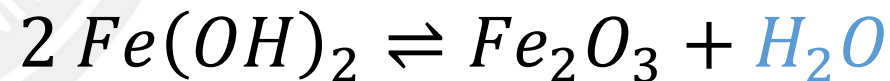


B. For each half-reaction:

1. Balance all elements except hydrogen and oxygen



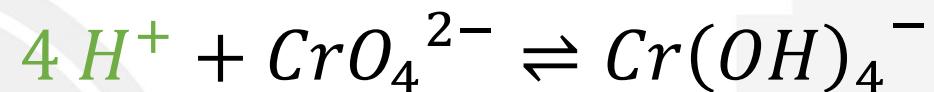
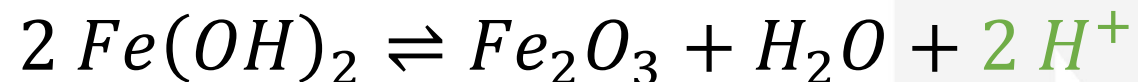
2. Balance oxygen using  $H_2O$



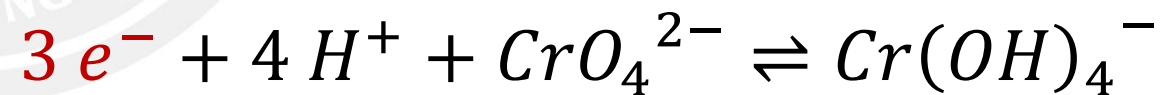
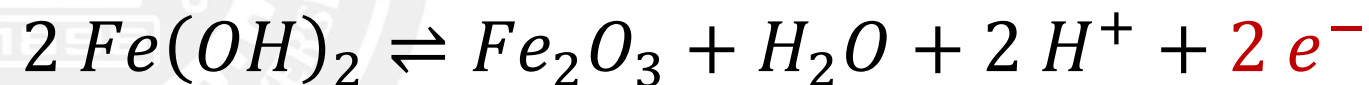
# Example: Basic Solution



3. Balance hydrogen using  $H^+$



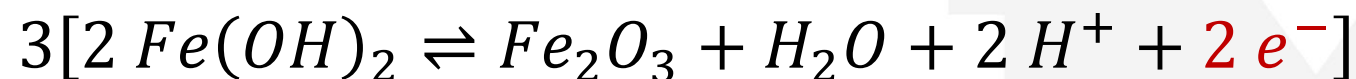
4. Balance the charge using electrons



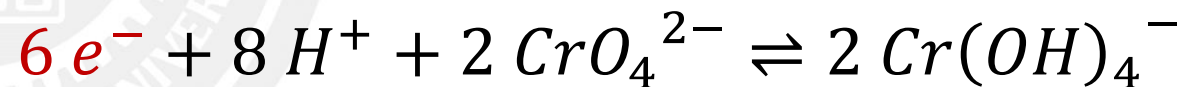
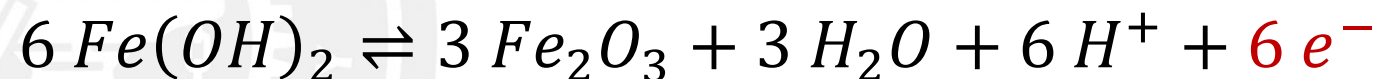
# Example: Basic Solution



We need the same number of electrons for both half reactions:



Multiplying the stoichiometric coefficients yields:

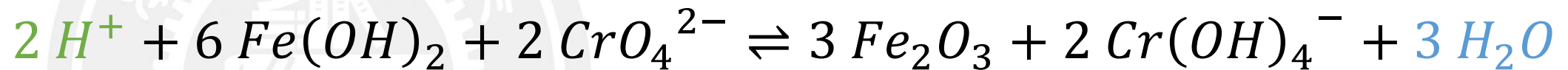
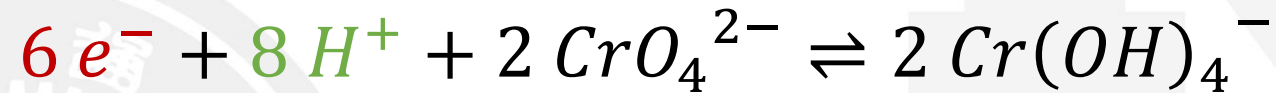
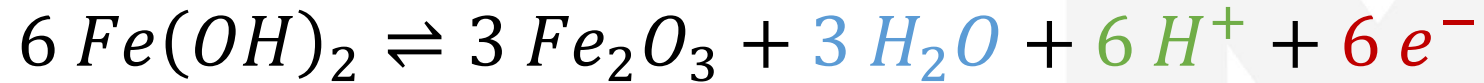


We now have the same number of electrons leaving the oxidation half-reaction and entering the reduction half-reaction.

# Example: Basic Solution



5. Cancel like-species and combine remaining species

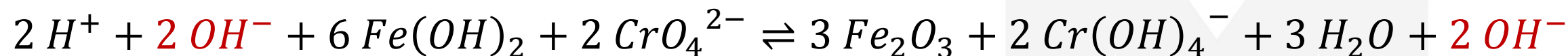


Check to ensure that all elements and charges are balanced.

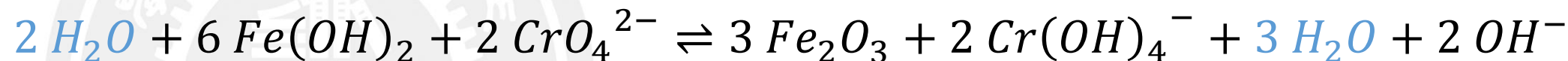
# Example: Basic Solution



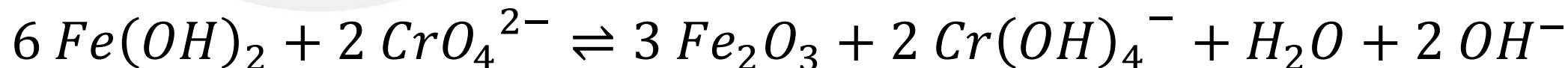
6. Neutralize  $H^+$  with  $OH^-$  (new for basic solutions)



As  $H^+ + OH^- = H_2O$ :



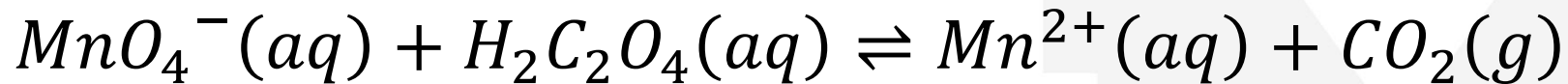
Now we cancel the water molecules that appear on both sides and obtain the final reaction equation, checking that all atoms and charges are balanced:



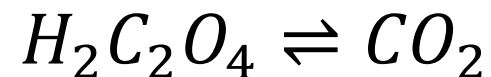
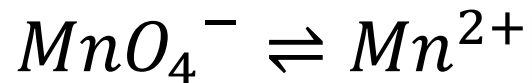
# Example



Balance the redox reaction below in acidic solution and basic solution.

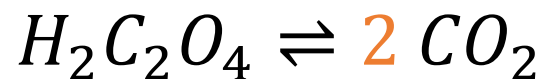
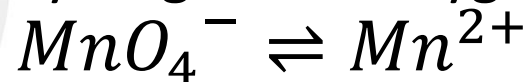


A. Write the equations for the oxidation and reduction half-reactions.

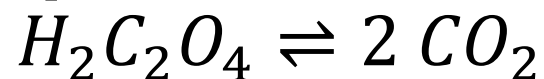


B. For each half-reaction:

1. Balance all elements except hydrogen and oxygen



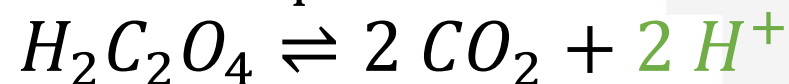
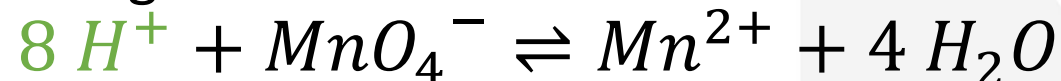
2. Balance oxygen using  $\text{H}_2\text{O}$



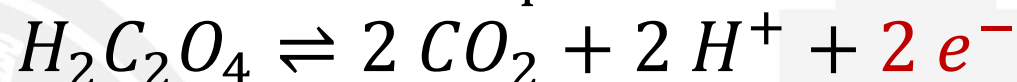
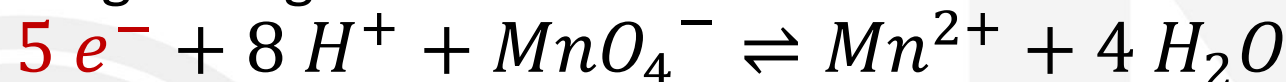
# Example



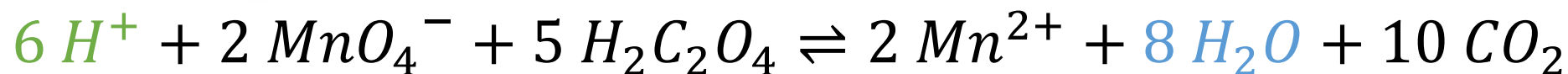
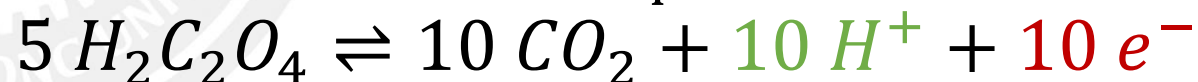
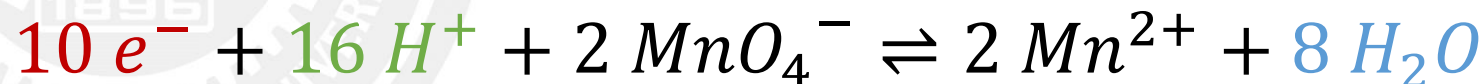
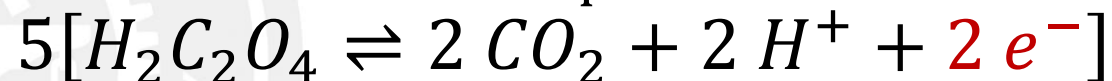
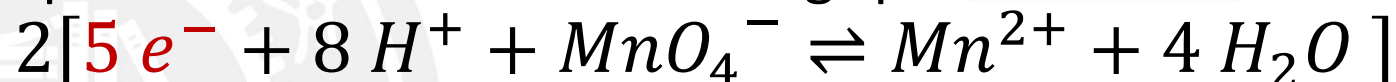
3. Balance hydrogen using  $H^+$



4. Balance the charge using electrons



5. Cancel like-species and combine remaining species

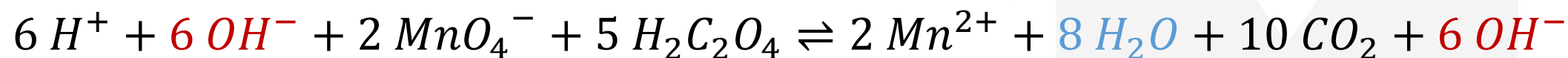




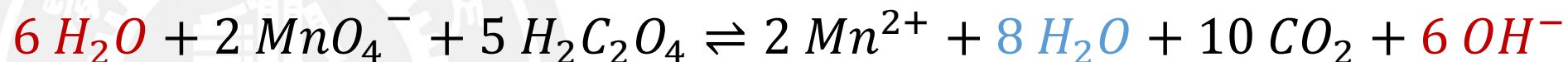
# Example



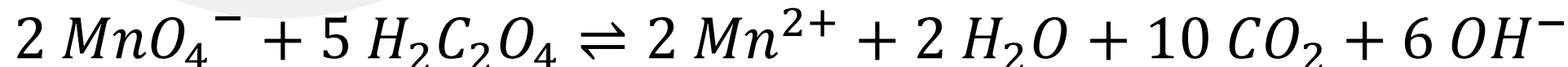
6. Neutralize  $H^+$  with  $OH^-$  (new for basic solutions)



As  $H^+ + OH^- = H_2O$ :



Now we cancel the water molecules that appear on both sides and obtain the final reaction equation, checking that all atoms and charges are balanced:



# Galvanic Cells



Galvanic cells are *spontaneous* reactions generating electric current.

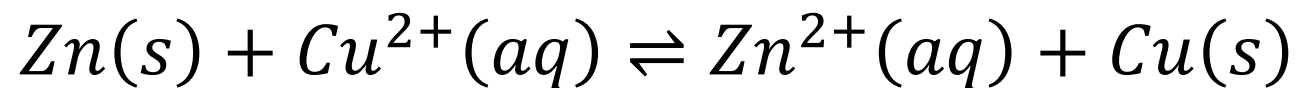
Batteries are a collection of galvanic cells joined in series, where the total voltage is the sum of each cell.

**Voltage** is the **ability** to push an electric current through a circuit.

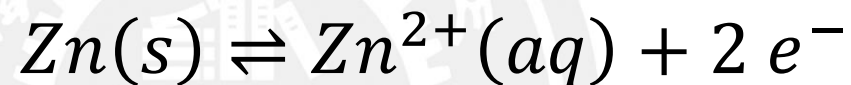
The formal term for “voltage” is potential difference, measured in volts:

$$1 \text{ V} = 1 \frac{\text{J}}{\text{C}} = 1 \frac{\text{N} \cdot \text{m}}{\text{C}} = 1 \frac{\text{kg} \cdot \text{m}^2}{\text{s}^2 \cdot \text{C}}$$

Galvanic cells are also known as voltaic cells.



The **anode** is where the **oxidation** takes place.



The negative charge of the anode indicates that *electrons are being released in the oxidation reaction.*

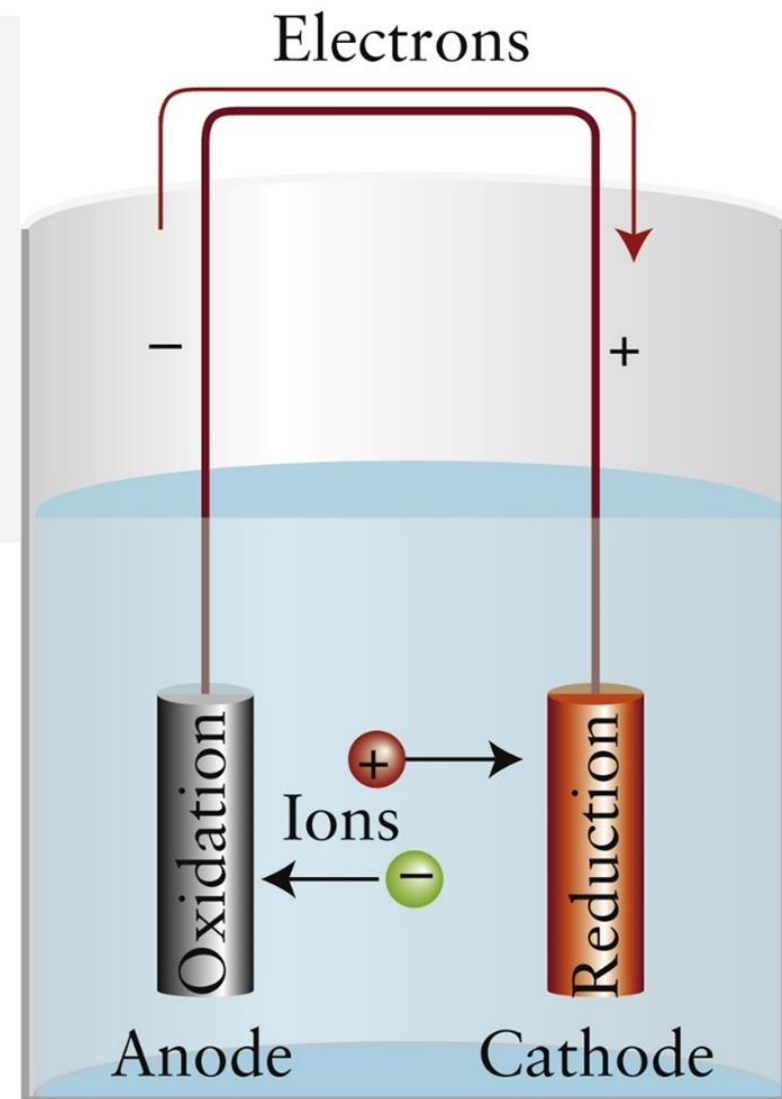
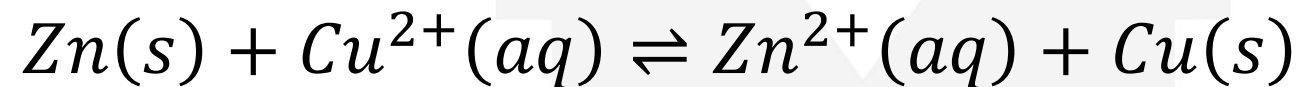
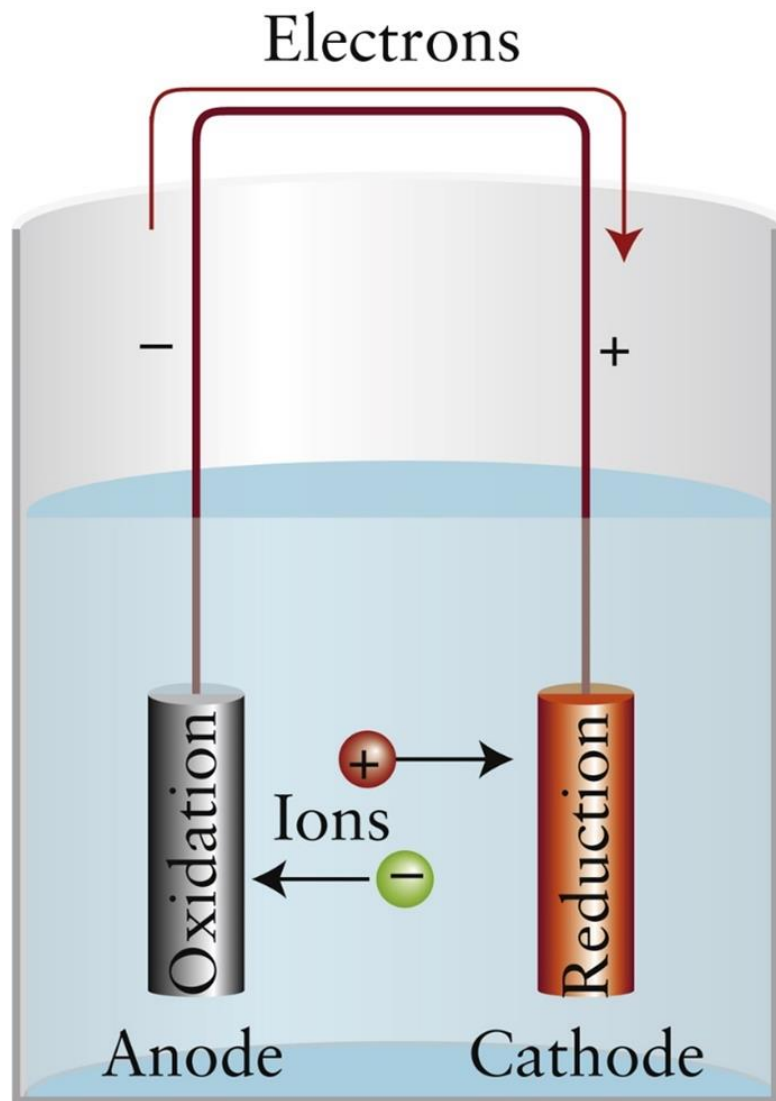


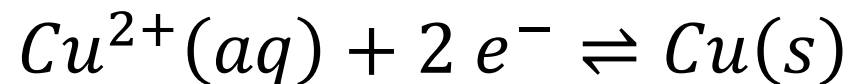
Figure 6L.2

Atkins, *Chemical Principles: The Quest for Insight*, 7e

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The **cathode** is where the **reduction** occurs.



The positive charge of the cathode indicates that *electrons are being attracted here*.

Figure 6L.2  
Atkins, *Chemical Principles: The Quest for Insight*, 7e  
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# The Structure of Daniell Cells

A battery *prevents direct contact* of the **anode** and **cathode** reactions.

Electrons are funneled through a wire from one electrode to another.

Daniell cells contain a **porous pot**, which is a barrier through which ions can travel, but electrons are blocked.

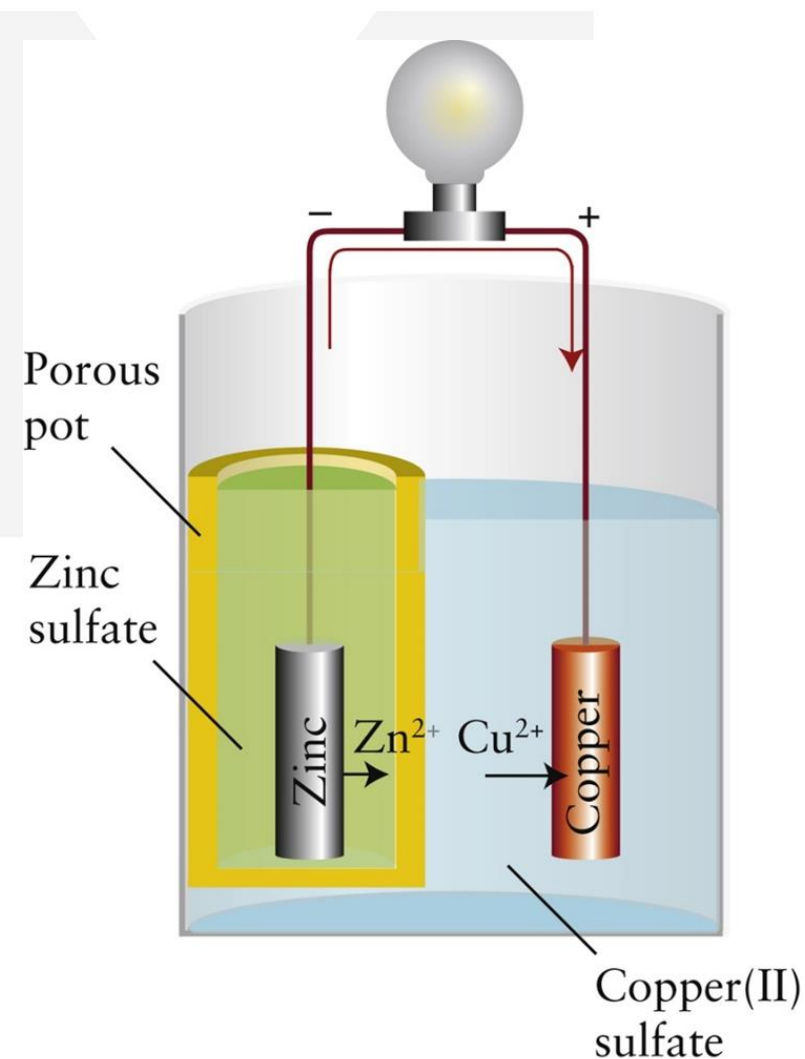
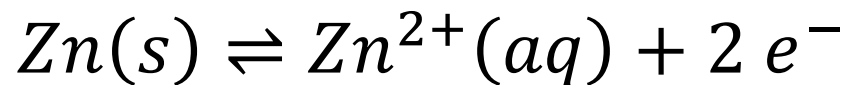


Figure 6L3

Atkins, *Chemical Principles: The Quest for Insight*, 7e

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# The Structure of Daniell Cells: Ion Transport



Zn loses electrons and will therefore build up a **positive** charge (excess  $\text{Zn}^{2+}$ ).



$\text{Cu}^{2+}$  gains electrons and will build up a **negative** charge (depletion of  $\text{Cu}^{2+}$ ).

The **porous pot** allows *ion exchange*, thereby **electrically neutralizing** the anode and cathode.

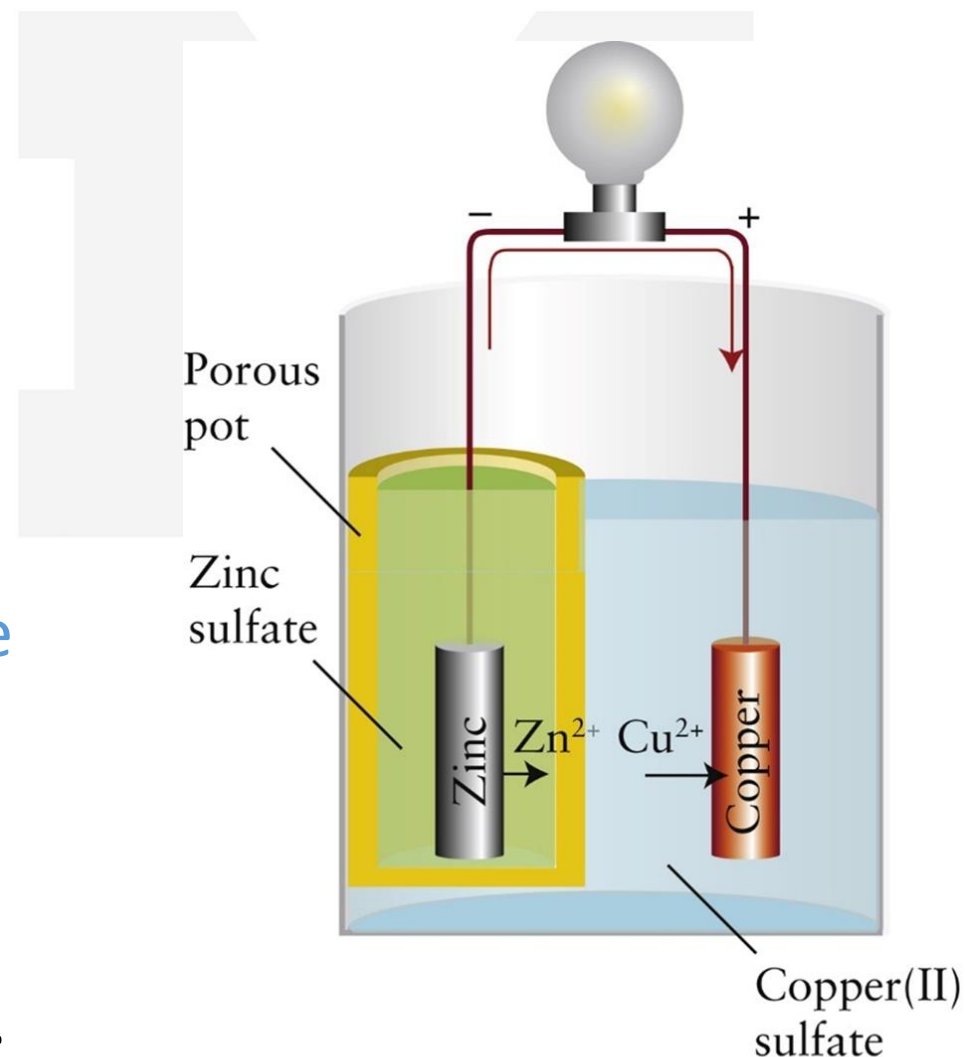


Figure 6L3  
Atkins, *Chemical Principles: The Quest for Insight*, 7e  
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A cell's electrical force is measured by its cell potential,  $E_{cell}$ .

$E_{cell}$  is the *ability* of a cell to *force* electrons through a circuit.

If **both** the **anode** and **cathode** have a **lot** of **pushing** and **pulling** power, this will generate a *high cell potential* (colloquially known as a high voltage).



Exhausted batteries at equilibrium have no pushing or pulling power, and the **cell potential** is zero ( $E_{cell} = 0$ ).

The SI unit of potential is the volt (V) defined as the charge of one coulomb (1 C) falling through a potential difference of one volt (1 V) releasing one joule (1 J) of energy:

$$1 \text{ V} = 1 \frac{\text{J}}{\text{C}}$$

$$e = 1.602 \times 10^{-19} \text{ C}$$

$$C = 6.242 \times 10^{18} e$$

One ampere is the magnitude of charge delivered by one Coloumb flowing per one second:

$$1 \text{ A} = 1 \frac{\text{C}}{\text{s}}$$



Electrical **work** is **neither** a change in pressure nor volume.

Electrical work is **nonexpansion work**.

**Gibbs free energy** is the measure of the **maximum nonexpansion work** that a reaction can do at constant pressure and temperature:

$$\Delta G = W_{\text{nonexpansion,max}} \text{ at } T, p = \text{const.}$$

(as shown in Chapter 08)

*Electrical work* in general is an electron moving through a potential difference (height of a waterfall) called  $E$  (measured in volt, V).

$$W_e = -e \cdot E$$

The *electrical charge* of one electron is  $-e$ .

Therefore, the amount of charge for **one mole of electrons** (Avogadro's constant) is  $-e \cdot N_A$ .

And for a reaction **releasing/taking up  $n$  electrons**, the amount of electrons travelling is  $-n \cdot e \cdot N_A$ .

So, the total *electrical work* done for an electrochemical cell is:

$$\Delta G = W_e = -n \cdot e \cdot N_A \cdot E_{cell}$$

Faraday's constant,  $F$ , is the *magnitude* of the charge *per mole* of electrons (the product of the elementary charge  $-e$  and Avogadro's constant  $N_A$ ):

$$F = e \cdot N_A = 1.602177 \times 10^{-19} \text{ C} \times 6.0223 \times 10^{23} \frac{1}{\text{mol}} = 96,485 \frac{\text{C}}{\text{mol}}$$

$$\Delta G = W_e = -n \cdot e \cdot N_A \cdot E_{\text{cell}} = -nF E_{\text{cell}}$$

$$\Delta G = -nFE_{cell}$$

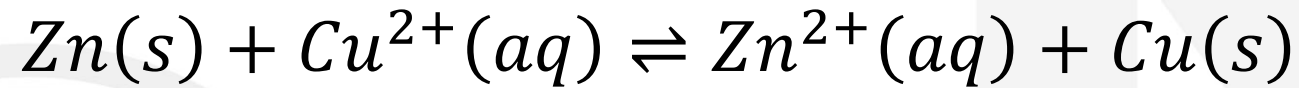
The maximum amount of work is the maximum cell potential produced in the reaction and is called the electromotive force, **emf**, of a cell.

From now on,  $E_{cell}$  will always be taken to represent this emf.

# Example



The emf of the Daniell cell for certain concentrations of copper and zinc ions is 1.04 V. What is the reaction Gibbs free energy under those conditions?



$$\Delta G = -nFE = -2 \text{ mol} \times 96,485 \frac{\text{C}}{\text{mol}} \times 1.04 \text{ V} = -2.01 \times 10^5 \text{ C} \cdot \text{V}$$

We remember that  $1 \text{ V} = 1 \frac{\text{J}}{\text{C}}$ , so this reaction has a Gibbs free energy of -201 kJ. This also means that this reaction is **spontaneous**.

# Example



The reaction taking place in the silver cell used in some cameras and wristwatches is  $Ag_2O(s) + Zn(s) \rightleftharpoons 2 Ag(s) + ZnO(s)$ , and the emf of the cell when new is 1.6 V. What is the reaction's Gibbs free energy?

Anode:  $Zn(s) + 2 OH^-(aq) \rightleftharpoons ZnO(s) + H_2O(l) + 2 e^-$

Cathode:  $Ag_2O(s) + H_2O(l) + 2 e^- \rightleftharpoons 2 Ag(s) + 2 OH^-(aq)$

This is a two-electron process.

$$\Delta G = -nFE = -2 \text{ mol} \times 96,485 \frac{\text{C}}{\text{mol}} \times 1.6 \text{ V} = -3.09 \times 10^5 \text{ C} \cdot \text{V}$$

The reaction's Gibbs free energy is -309 kJ, making this a spontaneous reaction.

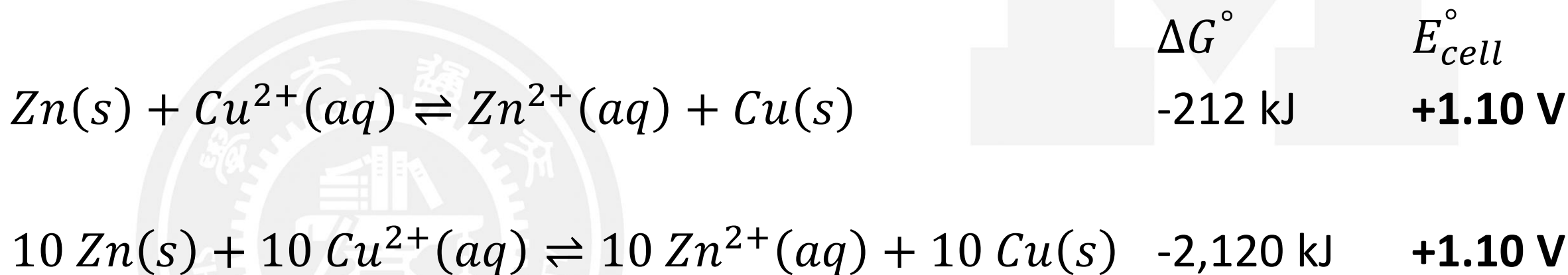
For the standard emf ( $E_{cell}^{\circ}$ ) under standard conditions (298.15 K,  $10^5$  Pa pressure,  $1 \text{ mol}\cdot\text{L}^{-1}$  solutions) we can write:

$$\Delta G^{\circ} = -nFE_{cell}^{\circ}$$

# The Meaning of $E$



The value of  $E_{cell}$  is the same, regardless of how we write the equation, but the value of  $\Delta G^\circ$  depends on the stoichiometric coefficients in the chemical equation.



You would get the same voltage if you had a battery that could fit in your hand or that was the size of an Olympic-sized swimming pool (only capacity would change).



# IUPAC Cell Notation

Anode electrode | anode electrolyte || cathode electrolyte | cathode electrode



“|” represents a phase change, like between an electrode and a solution.

“||” represents a salt bridge.

The anode is also called the anodic compartment, and cathodic compartment is used for the cathode.

The salt bridge allows ions to move back and forth.

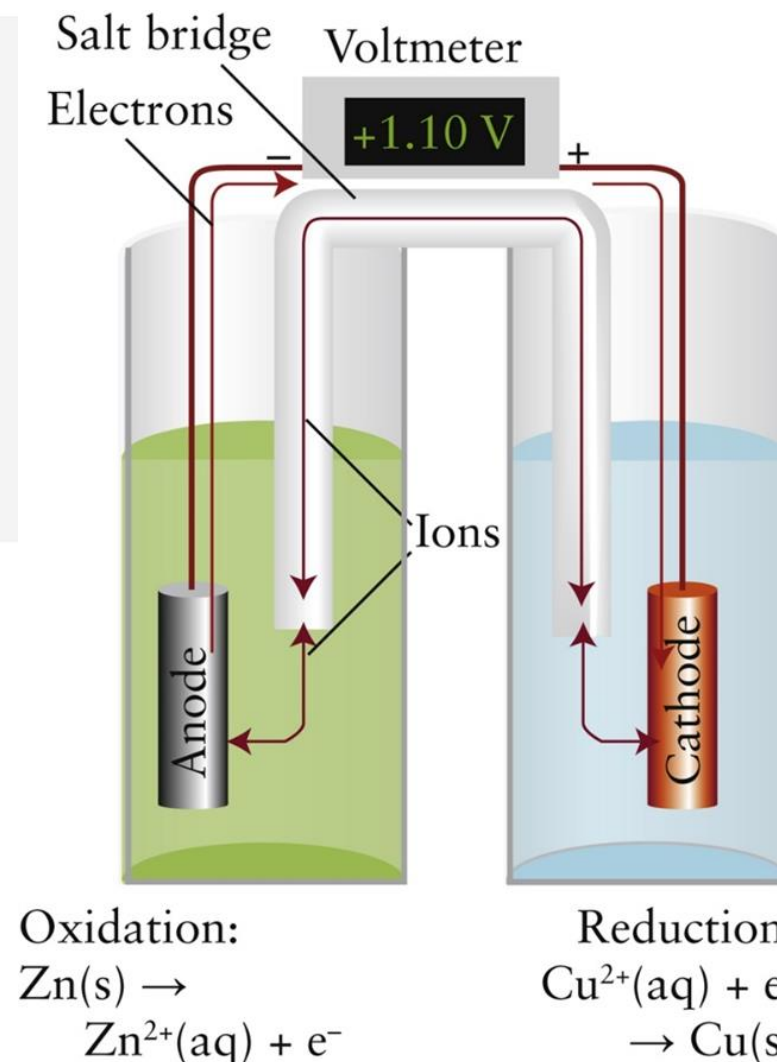


Figure 6L.4  
Atkins, *Chemical Principles: The Quest for Insight*, 7e  
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The field of electrochemistry would be very small if we only had metallic electrodes. How about gases?

Inert electrodes allow electrons to pass yet will not react with any ions; e.g., platinum, gold, and carbon.

For instance, measuring the potential of two aqueous ions:



or a gas:



Only the species in the electrolyte and not the electrode undergo a redox reaction.

# Example



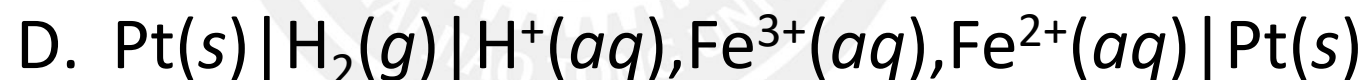
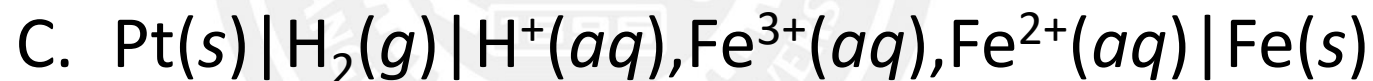
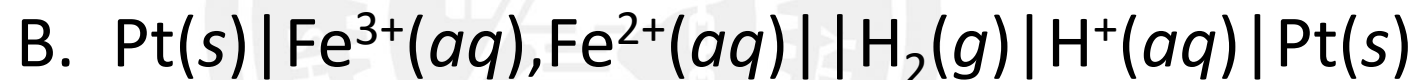
Write the diagram for a cell that has an electrode consisting of a manganese wire dipping into a solution of manganese(II) ions on the left, a salt bridge, and a copper(II)/copper(I) electrode on the right with a platinum wire.



# Short Quiz



Which of the diagrams below is the correct one for a cell with a hydrogen electrode on the left and an iron(III)/iron(II) electrode on the right. The two electrode compartments are connected by a salt bridge, and platinum is used as the conductor at each electrode.



All of the following statements concerning key features of a voltaic cell are true EXCEPT:

- A. A salt bridge must connect the two half-cells.
- B. Electrons flow from the anode to the cathode.
- C. Oxidation occurs at the cathode.
- D. The cathode is the positive electrode.

# Electronic Voltmeter



Voltmeters (aka potentiometer) measure voltage.

The Voltage for  $\text{Zn(s)}|\text{Zn}^{2+}(\text{aq})||\text{Cu}^{2+}(\text{aq})|\text{Cu(s)}$  is  $E_{\text{cell}}^{\circ} = +1.10 \text{ V}$ . Zn is the anode, (-), and Cu is the cathode (+).

Here  $E_{\text{cell}}^{\circ} > 0$ , so  $\Delta G^{\circ} < 0$ , making this a **spontaneous** cell.  
( $\Delta G^{\circ} = -nFE_{\text{cell}}^{\circ}$ )

Switching the wires around would read electrons flowing in the opposite direction:

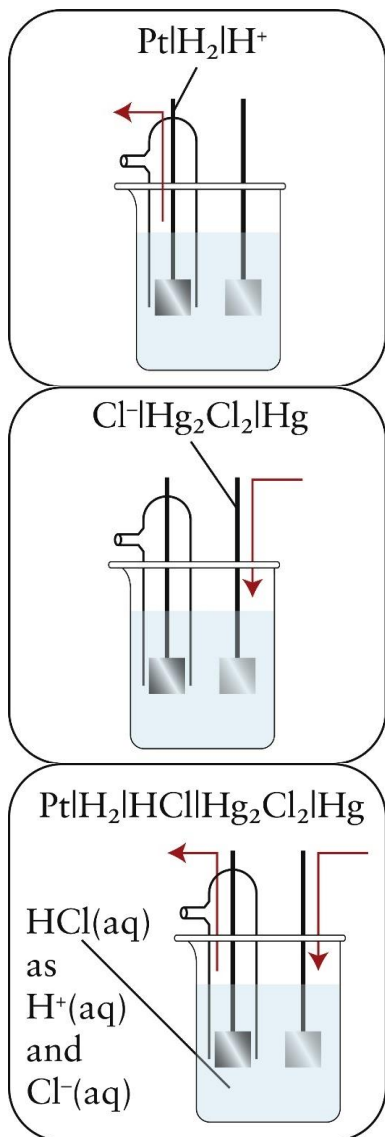
$\text{Cu(s)}|\text{Cu}^{2+}(\text{aq})||\text{Zn}^{2+}(\text{aq})|\text{Zn(s)}$  with  $E_{\text{cell}}^{\circ} = -1.10 \text{ V}$

Here  $E_{\text{cell}}^{\circ} < 0$ , so  $\Delta G^{\circ} > 0$  and this is a **nonspontaneous** cell.  
( $\Delta G^{\circ} = -nFE_{\text{cell}}^{\circ}$ )



Figure 6L.5  
Atkins, *Chemical Principles: The Quest for Insight*, 7e  
W. H. Freeman photo by Ken Karp.

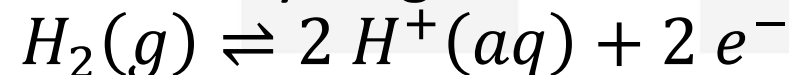
# Example



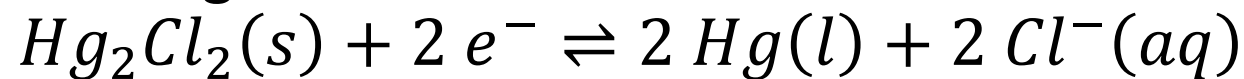
Write the cell reaction for the cell:



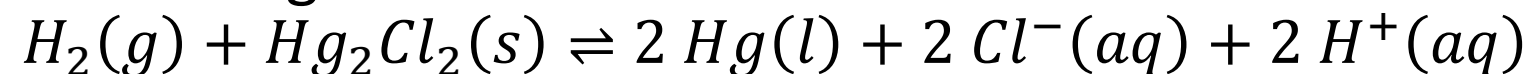
We note there is **no salt bridge**, so this is done in a single beaker. The anode is where the oxidation takes place, and this is the hydrogen electrode:



The cathode is where the reduction takes place, and this is the Hg electrode:



Combining the two half-reactions:

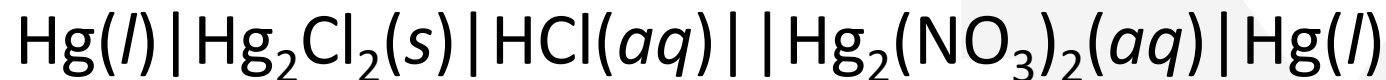




# Example

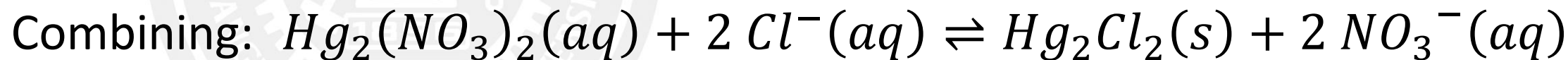
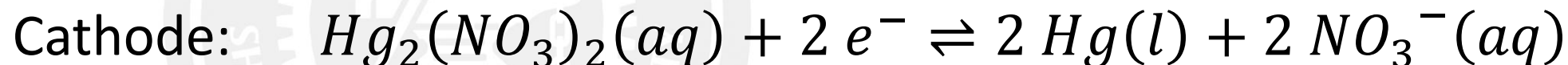
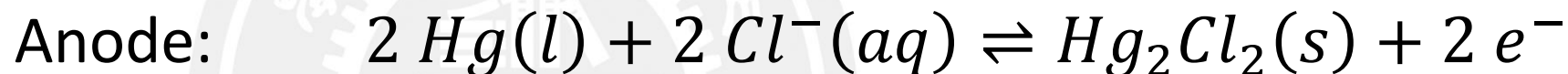


a) Write the chemical equation for the reaction corresponding to the cell



b) Given that the cell emf is reported as positive, is the cell reaction spontaneous as written?

a)



b) Here  $E_{\text{cell}}^\circ > 0$ , so  $\Delta G^\circ < 0$ , making this a **spontaneous** cell.  
( $\Delta G^\circ = -nFE^\circ$ )



Each **electrode** makes its own characteristic contribution to the cell potential, called its standard potential,  $E_{electrode}^{\circ}$ , a measure of its **electron-pulling power**.

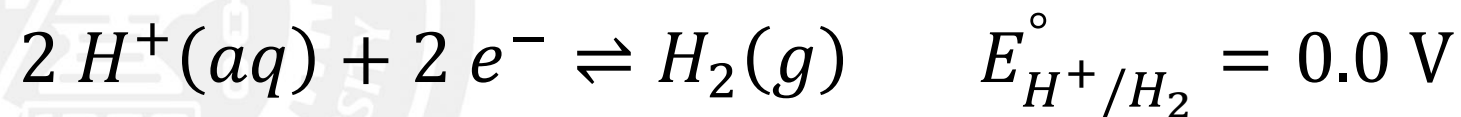
Galvanic cells measure the overall pulling power of the cell, called the **cell's standard emf** ( $E_{cell}^{\circ}$ ); a **difference** of the **standard potentials of the two electrodes**.

The difference is written as:

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

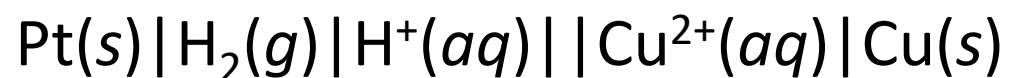
The standard potential,  $E^\circ$ , is only measuring a **difference**.

Therefore, **one** electrode is chosen to be the standard against which all other electrodes are measured—the hydrogen electrode.



This is called the **Standard Hydrogen Electrode** (SHE).

# Standard Potentials: SHE



$$E_{\text{cell}}^{\circ} = +0.34 \text{ V}$$

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

$$E_{\text{cathode}}^{\circ} = E_{\text{cell}}^{\circ} + E_{\text{anode}}^{\circ}$$

$$E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} = E_{\text{cell}}^{\circ} + E_{\text{H}^+/\text{H}_2}^{\circ} = +0.34 \text{ V} + 0.0 \text{ V} = +0.34 \text{ V}$$

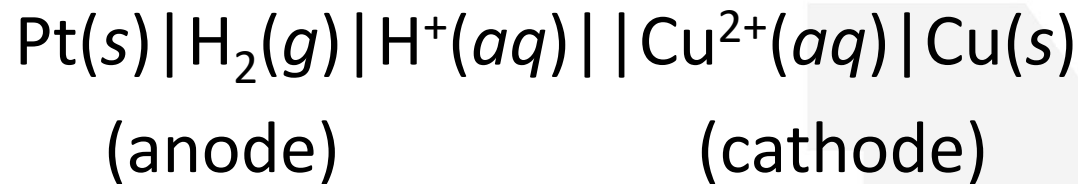
Since the hydrogen electrode is zero, the emf is **attributed entirely to the copper** electrode, and we write:



$$E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} = +0.34 \text{ V}$$

Additionally, the hydrogen electrode is ***always*** the anode.

# Meaning of Standard Potentials

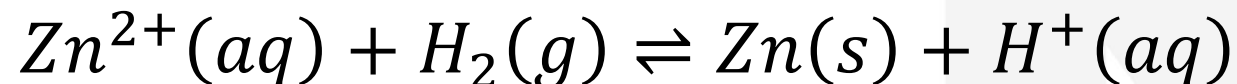
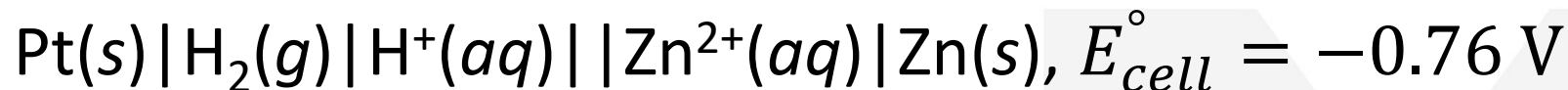


Since the standard emf is +0.34 V, the reaction is **spontaneous**  $E_{cell}^{\circ} > 0$   
( $\Delta G^{\circ} = -nFE_{cell}^{\circ}$ )

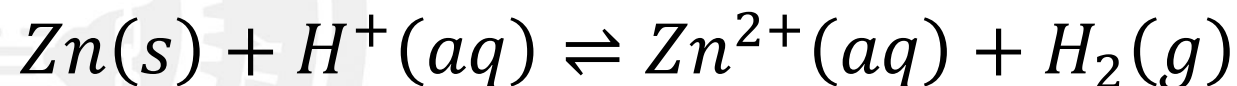
$$E_{cell}^{\circ} = E_{cathode}^{\circ} - E_{anode}^{\circ} = +0.34 \text{ V} - 0.0 \text{ V}$$

The *more positive the potential is*:

1. The greater the **electron-pulling power** of the reduction half-reaction;
2. The stronger it is as an oxidizing agent.



The reaction is **nonspontaneous**  $E_{cell}^{\circ} < 0$  ( $\Delta G^{\circ} = -nF E_{cell}^{\circ}$ ). The zinc ion has a poor electron-pulling ability; therefore, it is a poor oxidizing agent when compared to  $\text{H}^+$ .



For the reverse of the cell reaction,  $E_{cell}^{\circ} = +0.76 \text{ V}$ . This is **spontaneous**. Therefore, zinc is a better reducing agent when compared to hydrogen ( $\text{H}_2$ ).

# Standard Electrode Potentials at 25 °C



## Strongest Oxidizing Potential

Electrode reaction	$E^\circ_{\text{electrode}} / \text{V}$
$F_2(g) + 2 e^- \rightleftharpoons 2 F^-(aq)$	+2.87
$MnO_4^-(aq) + 4 H^+(aq) + 3 e^- \rightleftharpoons MnO_2(s) + 2 H_2O(l)$	+2.09
$O_3(g) + 2 H^+(aq) + 2 e^- \rightleftharpoons O_2(g) + H_2O(l)$	+2.075
$Fe_3O_4(s) + 8 H^+(aq) + 8 e^- \rightleftharpoons 3 Fe(s) + 4 H_2O(l)$	+0.085
$S_4O_6^{2-}(aq) + 2 e^- \rightleftharpoons 2 S_2O_3^{2-}$	+0.08
<b><math>2 H^+(aq) + 2 e^- \rightleftharpoons H_2(g)</math></b>	<b>0.0000</b>
$SnO_2(s) + 2 H^+(aq) + 2 e^- \rightleftharpoons SnO(s) + H_2O(l)$	-0.09
$SnO(s) + 2 H^+(aq) + 2 e^- \rightleftharpoons Sn(s) + H_2O(l)$	-0.10
$CO_2(g) + 2 H^+(aq) + 2 e^- \rightleftharpoons CO(g) + H_2O(l)$	-0.11
$Se(s) + 2 H^+(aq) + 2 e^- \rightleftharpoons H_2Se(g)$	-0.11

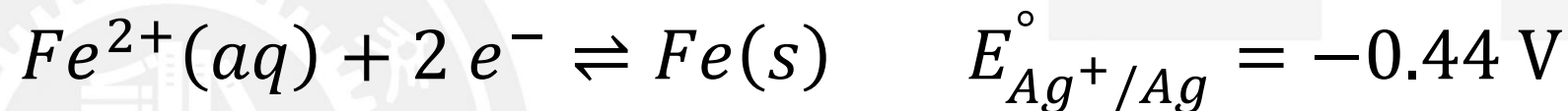
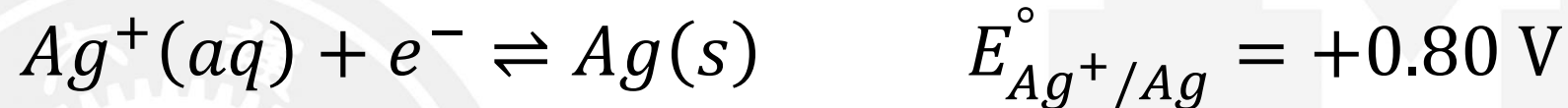
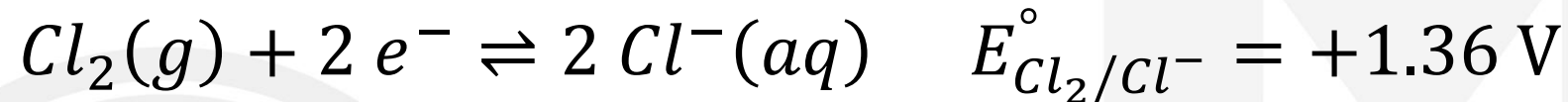
## Strongest Reducing Potential

1. Written as reductions
2. Ranked from **highest** to **lowest** oxidizing potential

# Short Quiz



Use the standard reduction potentials below to determine which compound or ion is the best oxidizing agent?



A.  $\text{Cl}_2$

B.  $\text{Cl}^-$

C. Ag

D.  $\text{Fe}^{2+}$

# Oxidizing and Reducing Agents



Electrode reaction	$E^\circ_{\text{electrode}} / \text{V}$
$F_2(g) + 2 e^- \rightleftharpoons 2 F^-(aq)$	+2.87
$MnO_4^-(aq) + 4 H^+(aq) + 3 e^- \rightleftharpoons MnO_2(s) + 2 H_2O(l)$	+2.09
$O_3(g) + 2 H^+(aq) + 2 e^- \rightleftharpoons O_2(g) + H_2O(l)$	+2.075
$Fe_3O_4(s) + 8 H^+(aq) + 8 e^- \rightleftharpoons 3 Fe(s) + 4 H_2O(l)$	+0.085
$S_4O_6^{2-}(aq) + 2 e^- \rightleftharpoons 2 S_2O_3^{2-}$	+0.08
$2 H^+(aq) + 2 e^- \rightleftharpoons H_2(g)$	<b>0.0000</b>
$SnO_2(s) + 2 H^+(aq) + 2 e^- \rightleftharpoons SnO(s) + H_2O(l)$	-0.09
$SnO(s) + 2 H^+(aq) + 2 e^- \rightleftharpoons Sn(s) + H_2O(l)$	-0.10
$CO_2(g) + 2 H^+(aq) + 2 e^- \rightleftharpoons CO(g) + H_2O(l)$	-0.11
$Se(s) + 2 H^+(aq) + 2 e^- \rightleftharpoons H_2Se(g)$	-0.11

At the top are the strongest oxidizing ( $e^-$  pulling) agents, and the bottom lists the strongest reducing ( $e^-$  pushing) agents.

$F_2(g)$  pulls electrons strongly, so it is a strong oxidizing element. It can oxidize any other species below it in the table.



# Oxidizing and Reducing Agents



Electrode reaction	$E^\circ_{\text{electrode}} / \text{V}$
$F_2(g) + 2 e^- \rightleftharpoons 2 F^-(aq)$	+2.87
$MnO_4^-(aq) + 4 H^+(aq) + 3 e^- \rightleftharpoons MnO_2(s) + 2 H_2O(l)$	+2.09
$O_3(g) + 2 H^+(aq) + 2 e^- \rightleftharpoons O_2(g) + H_2O(l)$	+2.075
$Fe_3O_4(s) + 8 H^+(aq) + 8 e^- \rightleftharpoons 3 Fe(s) + 4 H_2O(l)$	+0.085
$S_4O_6^{2-}(aq) + 2 e^- \rightleftharpoons 2 S_2O_3^{2-}$	+0.08
$2 H^+(aq) + 2 e^- \rightleftharpoons H_2(g)$	<b>0.0000</b>
$SnO_2(s) + 2 H^+(aq) + 2 e^- \rightleftharpoons SnO(s) + H_2O(l)$	-0.09
$SnO(s) + 2 H^+(aq) + 2 e^- \rightleftharpoons Sn(s) + H_2O(l)$	-0.10
$CO_2(g) + 2 H^+(aq) + 2 e^- \rightleftharpoons CO(g) + H_2O(l)$	-0.11
<div><div><math>Se(s)</math></div><div><math>+ 2 H^+(aq) + 2 e^- \rightleftharpoons H_2Se(g)</math></div></div>	-0.11

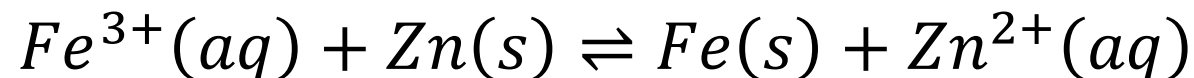
Se(s) cannot oxidize any species above it

# Example



Can you make iron metal by reacting iron(III) with zinc metal to produce aqueous zinc ions under standard conditions?

Electrode reaction	$E^\circ_{\text{electrode}} / \text{V}$
$2 \text{H}^+(\text{aq}) + 2 \text{e}^- \rightleftharpoons \text{H}_2(\text{g})$	0.0000
$\text{Fe}^{3+}(\text{aq}) + 3 \text{e}^- \rightleftharpoons \text{Fe}(\text{s})$	-0.04
$\text{O}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) + 2 \text{e}^- \rightleftharpoons \text{HO}_2^-(\text{aq}) + \text{OH}^-(\text{aq})$	-0.08
$\text{Pb}^{2+}(\text{aq}) + 2 \text{e}^- \rightleftharpoons \text{Pb}(\text{s})$	-0.13
$\text{Sn}^{2+}(\text{aq}) + 2 \text{e}^- \rightleftharpoons \text{Sn}(\text{s})$	-0.14
$\text{Fe}^{2+}(\text{aq}) + 2 \text{e}^- \rightleftharpoons \text{Fe}(\text{s})$	-0.44
$\text{Zn}^{2+}(\text{aq}) + 2 \text{e}^- \rightleftharpoons \text{Zn}(\text{s})$	-0.76
$2 \text{H}_2\text{O}(\text{l}) + 2 \text{e}^- \rightleftharpoons \text{H}_2(\text{g}) + 2 \text{OH}^-(\text{aq})$	-0.83
$\text{Al}^{3+}(\text{aq}) + 3 \text{e}^- \rightleftharpoons \text{Al}(\text{s})$	-1.66



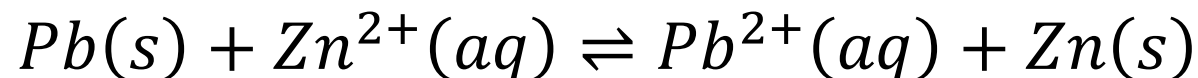
Yes,  $\text{Fe}^{3+}$  is a stronger oxidizing agent than  $\text{Zn}^{2+}$ .

# Example



Can lead metal produce zinc metal from aqueous zinc sulfate under standard conditions?

Electrode reaction	$E^\circ_{\text{electrode}} / \text{V}$
$2 \text{H}^+(\text{aq}) + 2 \text{e}^- \rightleftharpoons \text{H}_2(\text{g})$	0.0000
$\text{Fe}^{3+}(\text{aq}) + 3 \text{e}^- \rightleftharpoons \text{Fe}(\text{s})$	-0.04
$\text{O}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) + 2 \text{e}^- \rightleftharpoons \text{HO}_2^-(\text{aq}) + \text{OH}^-(\text{aq})$	-0.08
$\text{Pb}^{2+}(\text{aq}) + 2 \text{e}^- \rightleftharpoons \text{Pb}(\text{s})$	-0.13
$\text{Sn}^{2+}(\text{aq}) + 2 \text{e}^- \rightleftharpoons \text{Sn}(\text{s})$	-0.14
$\text{Fe}^{2+}(\text{aq}) + 2 \text{e}^- \rightleftharpoons \text{Fe}(\text{s})$	-0.44
$\text{Zn}^{2+}(\text{aq}) + 2 \text{e}^- \rightleftharpoons \text{Zn}(\text{s})$	-0.76
$2 \text{H}_2\text{O}(\text{l}) + 2 \text{e}^- \rightleftharpoons \text{H}_2(\text{g}) + 2 \text{OH}^-(\text{aq})$	-0.83
$\text{Al}^{3+}(\text{aq}) + 3 \text{e}^- \rightleftharpoons \text{Al}(\text{s})$	-1.66



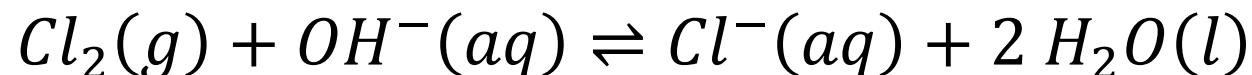
No,  $\text{Zn}^{2+}$  is a weaker oxidizing agent than  $\text{Pb}^{2+}$ .

# Example



Can chlorine gas oxidize water to oxygen gas under standard conditions in *basic* solution?

Electrode reaction	$E^\circ_{\text{electrode}} / \text{V}$
$\text{MnO}_4^-(\text{aq}) + 8 \text{H}^+(\text{aq}) + 5 \text{e}^- \rightleftharpoons \text{Mn}^{2+}(\text{aq}) + 4 \text{H}_2\text{O}(\text{l})$	+1.51
$\text{Cl}_2(\text{g}) + 2 \text{e}^- \rightleftharpoons 2 \text{Cl}^-(\text{aq})$	+1.36
$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14 \text{H}^+(\text{aq}) + 6 \text{e}^- \rightleftharpoons 2 \text{Cr}^{3+}(\text{aq}) + 7 \text{H}_2\text{O}(\text{l})$	+1.33
$\text{O}_2(\text{g}) + 4 \text{H}^+(\text{aq}) + 4 \text{e}^- \rightleftharpoons 2 \text{H}_2\text{O}(\text{l})$	+1.23
$\text{Br}_2(\text{l}) + 2 \text{e}^- \rightleftharpoons 2 \text{Br}^-(\text{aq})$	+1.09
$\text{NO}_3^-(\text{aq}) + 4 \text{H}^+(\text{aq}) + 3 \text{e}^- \rightleftharpoons \text{NO}(\text{g}) + 2 \text{H}_2\text{O}(\text{l})$	+0.96
$\text{Ag}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Ag}(\text{s})$	+0.80
$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{Fe}^{2+}(\text{aq})$	+0.77
$\text{I}_2(\text{s}) + 2 \text{e}^- \rightleftharpoons 2 \text{I}^-(\text{aq})$	+0.54
$\text{O}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l}) + 4 \text{e}^- \rightleftharpoons 4 \text{OH}^-(\text{aq})$	+0.40

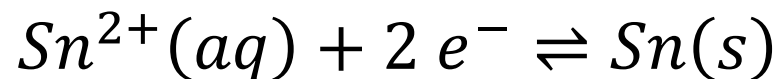
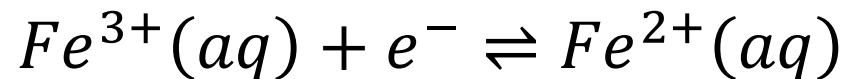


Yes,  $\text{Cl}_2$  is a stronger oxidizing agent.

# Short Quiz



Consider the following half-reactions.



$$E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\circ} = +0.77 \text{ V}$$

$$E_{\text{Sn}^{2+}/\text{Sn}}^{\circ} = -0.14 \text{ V}$$

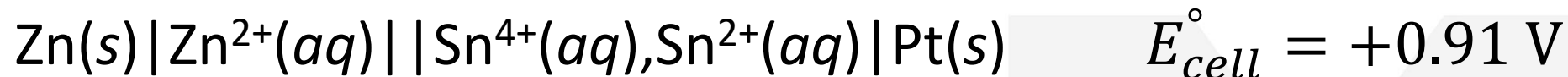
$$E_{\text{Fe}^{2+}/\text{Fe}}^{\circ} = -0.44 \text{ V}$$

$$E_{\text{Al}^{3+}/\text{Al}}^{\circ} = -1.66 \text{ V}$$

$$E_{\text{Fe}^{2+}/\text{Fe}}^{\circ} = -2.37 \text{ V}$$

Which of the above metals or metal ions are able to oxidize Al(s)?

- A.  $\text{Fe}^{3+}$  and  $\text{Sn}^{2+}$
- B.  $\text{Fe}^{3+}$ ,  $\text{Sn}^{2+}$ , and  $\text{Fe}^{2+}$
- C.  $\text{Fe}^{2+}$ , Sn, and Fe
- D. Mg and  $\text{Mg}^{2+}$



The standard potential of a zinc electrode is -0.76 V. What is the standard potential of the  $\text{Sn}^{4+}/\text{Sn}^{2+}$  electrode?

This is written as anode || cathode, so  $\text{Sn}^{4+}/\text{Sn}^{2+}$  is our cathode.

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

$$E_{\text{cathode}}^{\circ} = E_{\text{cell}}^{\circ} + E_{\text{anode}}^{\circ}$$

$$E_{\text{Sn}^{4+}/\text{Sn}^{2+}}^{\circ} = E_{\text{cell}}^{\circ} + E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} = +0.91 \text{ V} + (-0.76 \text{ V}) = +0.15 \text{ V}$$

# Example



$$E_{\text{cell}}^{\circ} = +0.31 \text{ V}$$

The standard potential of a  $\text{Fe}^{2+}/\text{Fe}$  electrode is  $-0.44 \text{ V}$ . What is the standard potential of the  $\text{Pb}^{2+}/\text{Pb}$  electrode?

This is written as anode || cathode, so  $\text{Pb}^{2+}/\text{Pb}$  is our cathode.

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

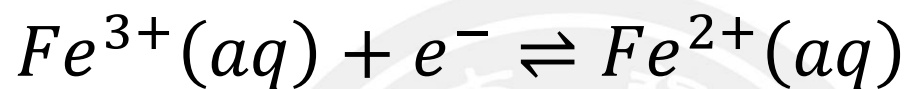
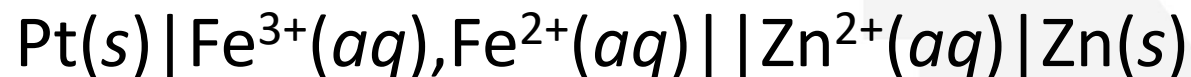
$$E_{\text{cathode}}^{\circ} = E_{\text{cell}}^{\circ} + E_{\text{anode}}^{\circ}$$

$$E_{\text{Pb}^{2+}/\text{Pb}}^{\circ} = E_{\text{cell}}^{\circ} + E_{\text{Fe}^{2+}/\text{Fe}}^{\circ} = +0.31 \text{ V} + (-0.44 \text{ V}) = -0.13 \text{ V}$$

# Short Quiz



Calculate  $E_{cell}^{\circ}$  for the following electrochemical cell:



$$E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\circ} = +0.771 \text{ V}$$

$$E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} = -0.763 \text{ V}$$

A.  $-1.534 \text{ V}$

B.  $-0.008 \text{ V}$

C.  $+0.008 \text{ V}$

D.  $+1.802 \text{ V}$

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

$$E_{cell}^{\circ} = -0.763 \text{ V} - (+0.771 \text{ V})$$

$$E_{cell}^{\circ} = -1.534 \text{ V}$$



# Main Group Standard Potentials



								18 He
	1	2	13	14	15	16	17	
2	Li -3.05	Be -1.85	B	C	N	O +1.23	F +2.87	Ne
3	Na -2.71	Mg -2.36	Al -1.66	Si	P	S -0.48	Cl +1.36	Ar
4	K -2.93	Ca -2.87	Ga -0.53	Ge	As	Se -0.67	Br +1.09	Kr
5	Rb -2.93	Sr -2.89	In -0.34	Sn -0.14	Sb	Te -0.84	I +0.54	Xe
6	Cs -2.92	Ba -2.91	Tl -0.34	Pb -0.13	Bi +0.20	Po	At	Rn
	Fr	Ra -2.92						

Hardest to oxidize  
Strongest oxidizing agents

Note that the most negative values are in the s-block and that the most positive values are close to fluorine.

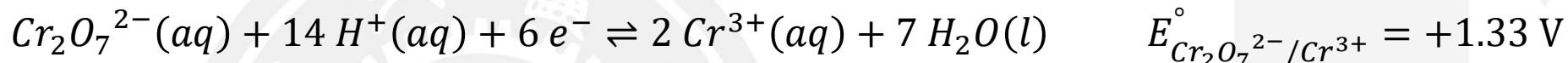
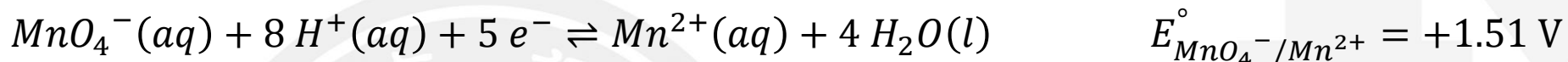
Easiest to oxidize  
Strongest reducing agents

# Prediction of Spontaneous Direction



Which is the more powerful oxidizing agent under standard conditions, an acidified aqueous permanganate solution or an acidified aqueous dichromate solution? Specify the cell for the spontaneous reaction of the two couples by writing a cell diagram that under standard conditions has a positive emf. Determine the standard emf of the cell.

First, we look at the reactions for these electrodes and their standard potentials:



As  $\Delta G^\circ = -nFE_{\text{cell}}^\circ$  requires  $E_{\text{cell}}^\circ > 0$  for a spontaneous reaction, we need the larger value of  $E_{\text{cell}}^\circ$  as our cathode ( $E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ$ ). Here,  $E_{\text{MnO}_4^-/\text{Mn}^{2+}}^\circ > E_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}}^\circ$ , so  $\text{MnO}_4^-/\text{Mn}^{2+}$  will be our cathode.

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

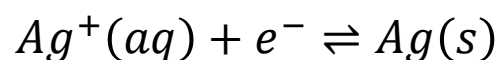
$$E_{\text{cell}}^\circ = E_{\text{MnO}_4^-/\text{Mn}^{2+}}^\circ - E_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}}^\circ = +1.51 \text{ V} - (+1.33 \text{ V}) = +0.18 \text{ V}$$



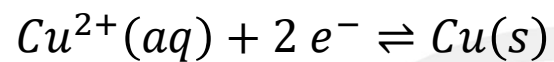
# Example



Which is the stronger oxidizing agent,  $\text{Cu}^{2+}$  or  $\text{Ag}^+$ , in aqueous solution under standard conditions? Evaluate the standard emf of the appropriate spontaneous cell, specify the cell with a cell diagram, and write the net ionic equation for the corresponding cell reaction.



$$E_{\text{Ag}^+/\text{Ag}}^\circ = +0.7996 \text{ V}$$

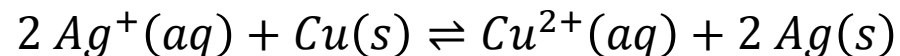
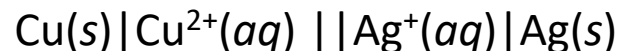


$$E_{\text{Cu}^{2+}/\text{Cu}}^\circ = +0.340 \text{ V}$$

As  $\Delta G^\circ = -nFE_{\text{cell}}^\circ$  requires  $E_{\text{cell}}^\circ > 0$  for a spontaneous reaction, we need the larger value of  $E_{\text{cell}}^\circ$  as our cathode ( $E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ$ ). Here,  $E_{\text{Ag}^+/\text{Ag}}^\circ > E_{\text{Cu}^{2+}/\text{Cu}}^\circ$ , so  $\text{Ag}^+/\text{Ag}$  will be our cathode.

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

$$E_{\text{cell}}^\circ = E_{\text{Ag}^+/\text{Ag}}^\circ - E_{\text{Cu}^{2+}/\text{Cu}}^\circ = +0.7996 \text{ V} - (+0.340 \text{ V}) = +0.460 \text{ V}$$



# Standard Potentials and Equilibrium Constants



The standard reaction Gibbs free energy,  $\Delta G_r^\circ$ , is related to the *equilibrium constant*:  $\Delta G_r^\circ = -RT \cdot \ln(K)$

In this chapter, the standard reaction Gibbs free energy is related to the *standard emf*:  $\Delta G_r^\circ = -nFE_{cell}^\circ$

We can combine these two concepts to the following:

$$\Delta G_r^\circ = -nFE_{cell}^\circ = -RT \cdot \ln(K)$$

$$\ln(K) = \frac{nFE_{cell}^\circ}{RT}$$

$$\text{At } 25^\circ\text{C}, \frac{RT}{F} = \frac{8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}} \times (273.15 + 25)\text{K}}{96,485 \text{ C}} = 0.025693 \frac{\text{V}}{\text{mol}}$$

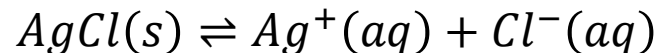
$$\ln(K) = \frac{nE_{cell}^\circ}{0.025693 \frac{\text{V}}{\text{mol}}}$$

$K$  increases exponentially with  $E_{cell}^\circ$ . A large  $E_{cell}^\circ$  means  $K > 1$  (product favoured).

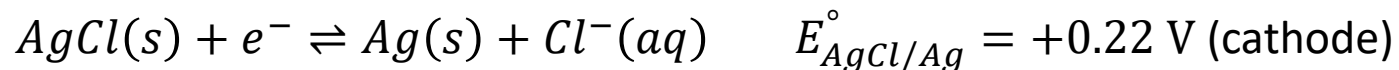
# Example



Calculate the equilibrium constant at 25.00 °C for the reaction:



The equilibrium constant is the solubility product,  $K_{sp} = [\text{Ag}^+][\text{Cl}^-]$ .



First, we need to determine  $E_{\text{cell}}^\circ$ :

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

$$E_{\text{cell}}^\circ = E_{\text{AgCl}/\text{Ag}}^\circ - E_{\text{Ag}^+/\text{Ag}}^\circ = +0.22 \text{ V} - (+0.80 \text{ V}) = -0.58 \text{ V}$$

$$\ln(K) = \frac{nE_{\text{cell}}^\circ}{0.025693 \frac{\text{V}}{\text{mol}}}$$

$$K = e^{\frac{nE_{\text{cell}}^\circ}{0.025693 \frac{\text{V}}{\text{mol}}}} = e^{\frac{1 \text{ mol} \times (-0.58 \text{ V})}{0.025693 \frac{\text{V}}{\text{mol}}}} = 1.6 \times 10^{-10}$$

When the concentration is very low, measuring these precisely is a challenge.

Measuring  $E_{\text{cell}}^\circ$  is easier.

# The Nernst Equation



As a reaction proceeds, reactants are consumed, the concentrations change and eventually the battery becomes “dead.” This happens when  $\Delta G$  approaches zero, or “at equilibrium, zero potential is generated”.

The Nernst equation is a quantitative measure of a cell potential at different concentrations.

We know  $\Delta G_r = \Delta G_r^\circ + RT \cdot \ln(Q)$  ( $Q$  is the reaction quotient).

Since  $\Delta G_r = -nFE_{cell}$  and  $\Delta G_r^\circ = -nFE_{cell}^\circ$ , we can substitute these two into the equation above.

# The Nernst Equation



$$\Delta G_r = \Delta G_r^\circ + RT \cdot \ln(Q)$$

$$-nFE_{cell} = -nFE_{cell}^\circ + RT \cdot \ln(Q)$$

$$E_{cell} = E_{cell}^\circ - \frac{RT}{nF} \cdot \ln(Q)$$

$$\text{At } 25^\circ\text{C}, \frac{RT}{F} = \frac{8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}} \times (25 + 273.15)\text{K}}{96,485 \text{ C}} = 0.025693 \frac{\text{V}}{\text{mol}}:$$

$$E_{cell} = E_{cell}^\circ - \frac{0.025693 \frac{\text{V}}{\text{mol}}}{n} \cdot \ln(Q)$$

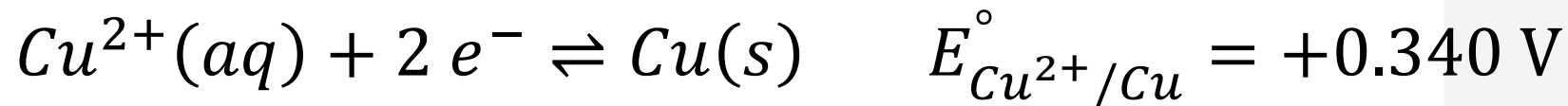
The Nernst equation is widely used to estimate the emf of cells under nonstandard conditions. Concentration difference gives potential difference.



# Example



Calculate the emf at 25 °C of a Daniell cell in which the concentration of  $\text{Zn}^{2+}$  ions is  $0.10 \text{ mol}\cdot\text{L}^{-1}$  and that of the  $\text{Cu}^{2+}$  ions is  $0.0010 \text{ mol}\cdot\text{L}^{-1}$ .



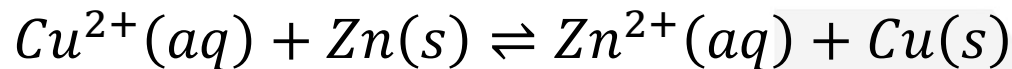
For a Daniell cell,  $E_{\text{cell}}$  is positive. Since  $\text{Cu}^{2+}$  is a stronger oxidizing agent, Zn will get oxidized (anode).

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

$$E_{\text{cell}}^{\circ} = E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} - E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} = +0.340 \text{ V} - (-0.7618 \text{ V}) = +1.102 \text{ V}$$



# Example



We can see that this is a two-electron process and that  $\text{Zn}^{2+}$  will be formed, while  $\text{Cu}^{2+}$  is consumed.

$$Q = \frac{[\text{Products}]}{[\text{Reactants}]} = \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = \frac{0.10 \frac{\text{mol}}{\text{L}}}{0.0010 \frac{\text{mol}}{\text{L}}}$$

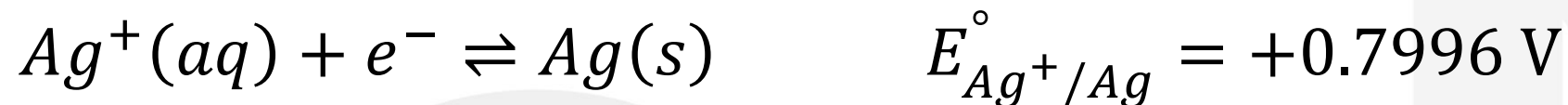
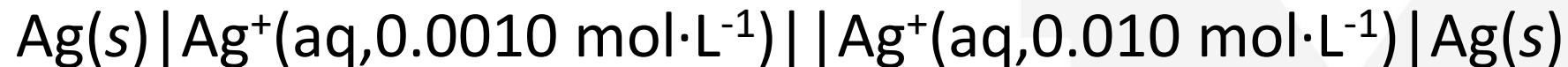
$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.025693 \frac{\text{V}}{\text{mol}}}{n} \cdot \ln(Q)$$

$$E_{\text{cell}} = +1.102 \text{ V} - \frac{0.025693 \frac{\text{V}}{\text{mol}}}{2 \text{ mol}} \cdot \ln\left(\frac{0.10 \frac{\text{mol}}{\text{L}}}{0.0010 \frac{\text{mol}}{\text{L}}}\right) = +1.04 \text{ V}$$

# Example



Calculate the emf of the concentration cell:

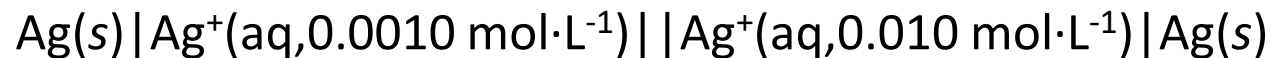


For a Daniell cell,  $E_{\text{cell}}$  is positive. In this case:

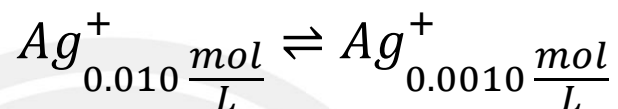
$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ$$

$$E_{\text{cell}}^\circ = E_{\text{Ag}^+/\text{Ag}}^\circ - E_{\text{Ag}^+/\text{Ag}}^\circ = +0.7996 \text{ V} - (+0.7996 \text{ V}) = +0.0 \text{ V}$$

# Example



At the anode,  $\text{Ag}(s)$  will be oxidized to  $\text{Ag}^+$ , while at the cathode  $\text{Ag}^+$  will be reduced to  $\text{Ag}(s)$ . As the cell notation is written as anode || cathode, we can deduce:



$$Q = \frac{[\text{Products}]}{[\text{Reactants}]} = \frac{\left[ \text{Ag}_{0.0010 \frac{\text{mol}}{\text{L}}}^+ \right]}{\left[ \text{Ag}_{0.010 \frac{\text{mol}}{\text{L}}}^+ \right]} = \frac{0.0010 \frac{\text{mol}}{\text{L}}}{0.010 \frac{\text{mol}}{\text{L}}}$$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.025693 \frac{\text{V}}{\text{mol}}}{n} \cdot \ln(Q)$$

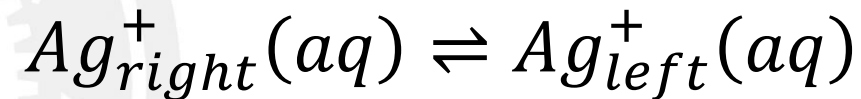
$$E_{\text{cell}} = +0.0 \text{ V} - \frac{0.025693 \frac{\text{V}}{\text{mol}}}{1 \text{ mol}} \cdot \ln\left(\frac{0.0010 \frac{\text{mol}}{\text{L}}}{0.010 \frac{\text{mol}}{\text{L}}}\right) = +0.059 \text{ V}$$

This is an interesting cell driven only by a difference in concentration.

# Finding Concentration in a Precipitation Reaction



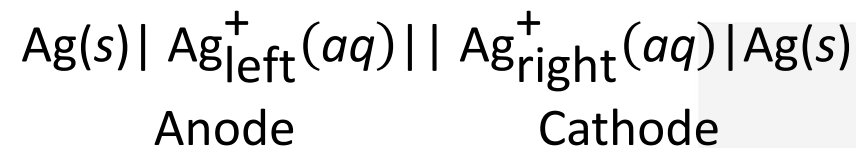
Each electrode compartment of a galvanic cell contains a silver electrode and 10.0 mL of 0.10 M  $\text{AgNO}_3(aq)$ ; they are connected by a salt bridge. You now add 10.0 mL of 0.10 M  $\text{NaCl}(aq)$  to the *left-hand electrode compartment*. Almost all the silver ions precipitate as silver chloride, but some remain in solution as a saturated solution of  $\text{AgCl}$ . The measured emf is +0.42 V. What is the concentration of  $\text{Ag}^+$  in the saturated solution?



Anode

Cathode

# Finding Concentration in a Precipitation Reaction



$$Q = \frac{[\text{Products}]}{[\text{Reactants}]} = \frac{[\text{Ag}_{\text{left}}^+]}{[\text{Ag}_{\text{right}}^+]}$$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.025693 \frac{\text{V}}{\text{mol}}}{n} \cdot \ln(Q) = E_{\text{cell}}^{\circ} - \frac{0.025693 \frac{\text{V}}{\text{mol}}}{n} \cdot \ln\left(\frac{[\text{Ag}_{\text{left}}^+]}{[\text{Ag}_{\text{right}}^+]}\right)$$

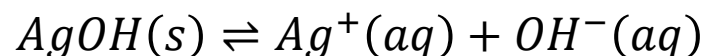
$$[\text{Ag}_{\text{left}}^+] = [\text{Ag}_{\text{right}}^+] \cdot e^{\frac{E_{\text{cell}}}{\frac{0.025693 \frac{\text{V}}{\text{mol}}}{n}}}$$

$$[\text{Ag}_{\text{left}}^+] = 0.10 \frac{\text{mol}}{\text{L}} \times e^{\frac{+0.42 \text{ V}}{+0.0 \text{ V} - \frac{0.025693 \frac{\text{V}}{\text{mol}}}{1 \text{ mol}}}} = 8.0 \times 10^{-9} \frac{\text{mol}}{\text{L}}$$

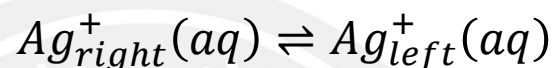
# Example



Calculate the emf of a cell constructed with two silver electrodes. The electrolyte in one compartment is 1.0 M  $\text{AgNO}_3(aq)$ . In the left compartment, NaOH has been added to an  $\text{AgNO}_3$  solution until the pH = 12.5 at 298 K.



$$K_{sp} = [\text{Ag}^+][\text{OH}^-] = 1.5 \times 10^{-8}$$



Anode

Cathode

$$[\text{Ag}_{\text{left}}^+] = \frac{K_{sp}}{[\text{OH}^-]} = \frac{K_{sp}}{10^{-(14-\text{pH})}} = \frac{1.5 \times 10^{-8}}{10^{-(14-12.5)}} = 4.7 \times 10^{-7} \frac{\text{mol}}{\text{L}}$$

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.025693 \frac{\text{V}}{\text{mol}}}{n} \cdot \ln(Q) = E_{\text{cell}}^\circ - \frac{0.025693 \frac{\text{V}}{\text{mol}}}{n} \cdot \ln\left(\frac{[\text{Ag}_{\text{left}}^+]}{[\text{Ag}_{\text{right}}^+]}\right)$$

$$E_{\text{cell}} = +0.0 \text{ V} - \frac{0.025693 \frac{\text{V}}{\text{mol}}}{1 \text{ mol}} \cdot \ln\left(\frac{4.7 \times 10^{-7} \frac{\text{mol}}{\text{L}}}{0.1 \frac{\text{mol}}{\text{L}}}\right) = +0.37 \text{ V}$$

# Ion-Selective Electrodes

The pH of a solution can be measured electrochemically with a **pH meter**.

To measure the concentration of  $\text{H}_3\text{O}^+$  ions, we select an electrode sensitive to these ions.

Each different ion is measured with its own ion-selective electrode.



Figure 6B.1  
Atkins, *Chemical Principles: The Quest for Insight*, 7e  
Charles D. Winters/Science Source



# Electrolytic Cells



Electrolytic cells are nonspontaneous cells, where a current is forced in the opposite direction to drive the reaction.

This process is called electrolysis and is the opposite of a Galvanic cell.

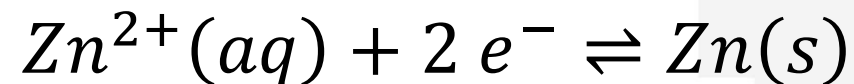
Whereas electrons flow spontaneously in a Galvanic cell from the anode to cathode, electrolytic cells apply an emf at the cathode, making the **cathode negative** and the **anode positive**.



# Electrolytic Cells

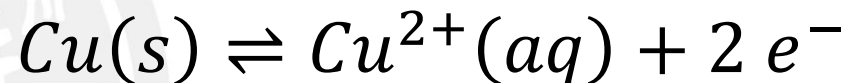


**Reduction** still takes place at the **cathode**



But the electrons are supplied (pumped in) by an **external power source**. They are not coming from the anode.

**Oxidation** still takes place at the **anode**



Except now the electrons are being pulled toward the higher potential. They are “flowing” *upstream*, in order to create new  $\text{Cu}^{2+}$ .

[The new  $\text{Cu}^{2+}$  serves both to create neutrality as well as to migrate toward the cathode to be plated.]

# The Dow Process

The following is an example of a nonspontaneous reaction, driven by an external power supply.

Anode:  $2 \text{Cl}^-(\text{melt}) \rightleftharpoons \text{Cl}_2(\text{g}) + 2 \text{e}^-$

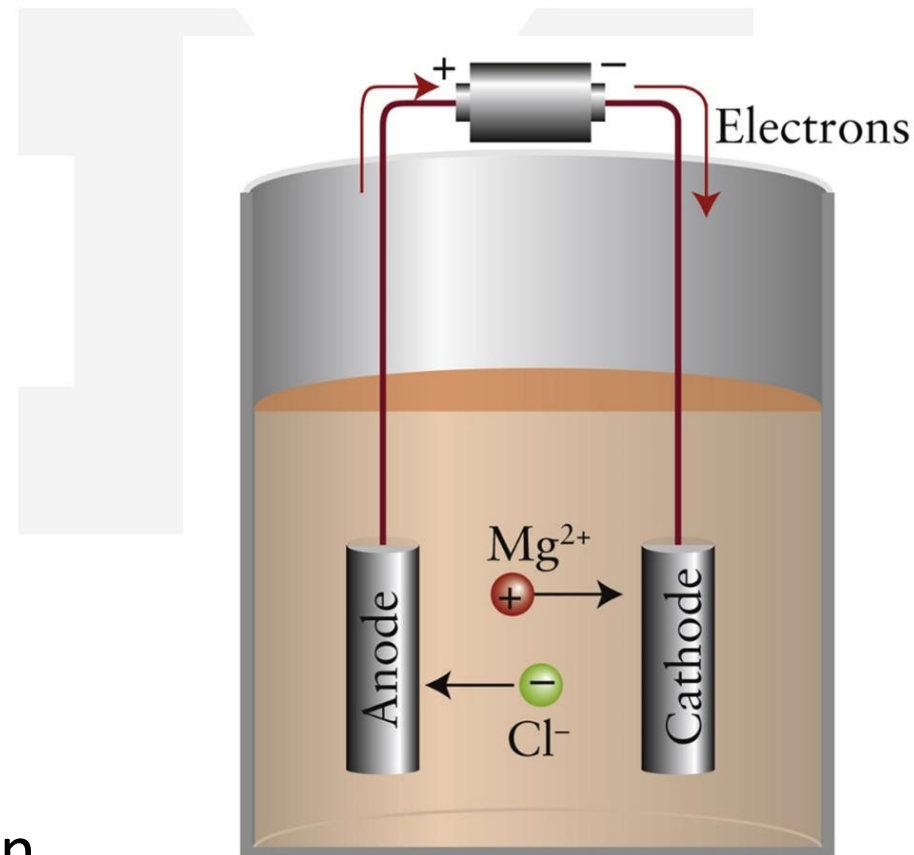
Cathode:  $\text{Mg}^{2+}(\text{melt}) + 2 \text{e}^- \rightleftharpoons \text{Mg}(\text{l})$

(The “melt” signifies molten salt.)

Note that only the **sign changes**.

Electrons are forced into the cathode and are drawn toward a higher potential from the anode.

Notice the **lack of a salt bridge**.



Oxidation:  
 $2 \text{Cl}^-(\text{aq}) \rightarrow$   
 $\text{Cl}_2(\text{g}) + 2 \text{e}^-$

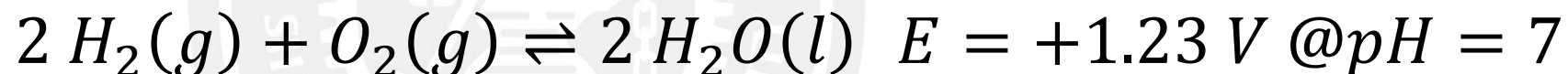
Reduction:  
 $\text{Mg}^{2+}(\text{melt}) + 2 \text{e}^-$   
 $\rightarrow \text{Mg}(\text{s})$

Figure 60.1

Atkins, *Chemical Principles: The Quest for Insight*, 7e  
W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman

**Overpotential** is having to apply a higher voltage than the potential cited in a table.

In practice, the applied potential must be substantially greater than the cell emf. The **additional potential** is called the **overpotential**. This is common for many reactions.

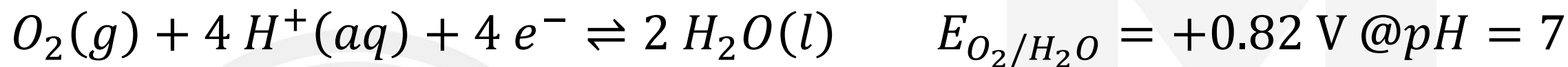


Frequently, water is a problem. For platinum electrodes, the overpotential for the **production of water** from hydrogen and oxygen is **0.6 V**. So, it requires about  $1.23 V + 0.6 V = 1.8 V$ .

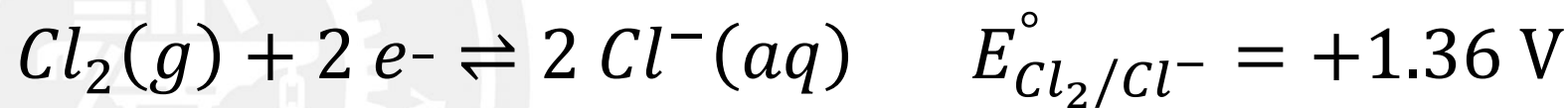
# Other Electrolytic Considerations



Pure water will not conduct electricity but if a solute is added, the ionic solution will conduct electricity. So, we might think we can electrolyse seawater to obtain oxygen:



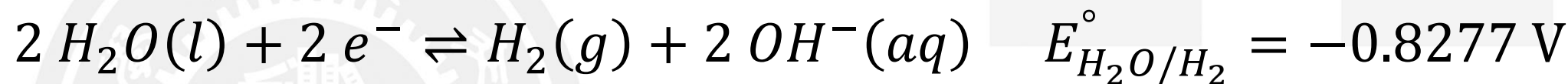
The problem is that seawater also has chloride:



At first glance, these values appear far enough apart to electrolyse oxygen from seawater. However, taking the overpotential of water into consideration ( $0.82 \text{ V} + 0.6 \text{ V} = 1.4 \text{ V}$ ), the production of  $Cl_2(g)$  will begin before the production of oxygen.

Seawater also has a considerable amount of  $\text{Na}^+$ . It would be optimal to produce sodium metal,  $\text{Na}(s)$ , from seawater.

Compare the standard potentials for water and sodium.



Even taking the overpotential of water into account, water still has a lower reduction potential than sodium. Therefore, in the reduction of seawater, hydrogen gas is produced before sodium metal.

# Example

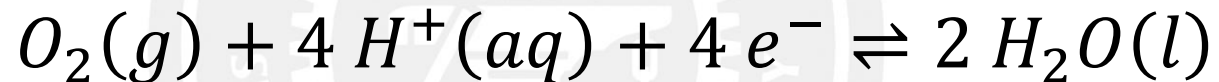


Suppose that an aqueous solution with  $\text{pH} = 7$  and containing  $\text{I}^-$  ions at  $1 \text{ mol}\cdot\text{L}^{-1}$  is being electrolysed.

Will  $\text{O}_2$  or  $\text{I}_2$  be produced at the anode?



$$E_{\text{I}_2/\text{I}^-}^\circ = +0.54 \text{ V}$$

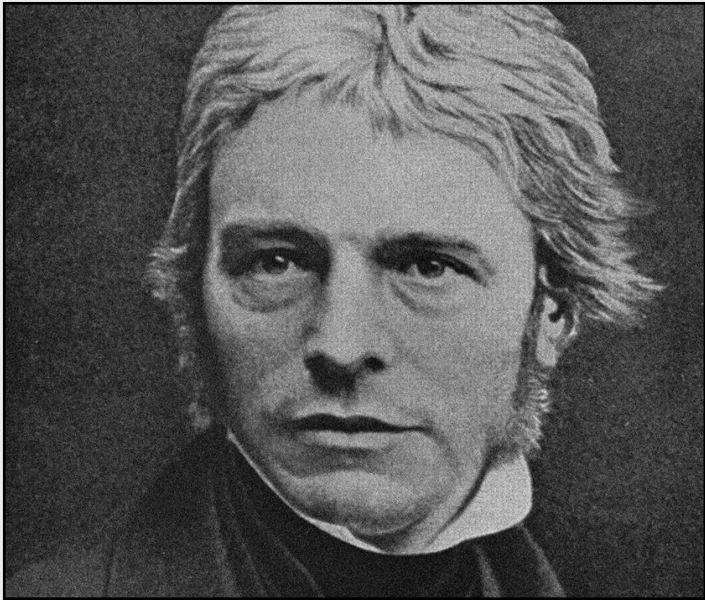


$$E_{\text{O}_2/\text{H}_2\text{O}} = +0.82 \text{ V @pH} = 7$$

Since  $E_{\text{I}_2/\text{I}^-}^\circ < E_{\text{O}_2/\text{H}_2\text{O}}$ , we expect it to be oxidized at the anode first. Therefore,  $\text{I}_2$  will be produced at the anode.



# The Products of Electrolysis



Michael Faraday

Michael Faraday was the first to calculate quantities from electrolysis experiments.

Two key observations were made:

- 1) connection between amount (moles) and charge (coulombs)
- 2) connection between charge (coulombs) and current (amperes)

$$F = 96,485 \frac{\text{C}}{\text{mol}} = 96,485 \frac{\text{A} \cdot \text{s}}{\text{mol}}$$

# Recycling of Copper

Copper is refined electrolytically by using an impure form of copper metal called **blister copper** as the anode in an electrolytic cell. Supplied current drives the oxidation of the blister copper to copper(II) ions,  $\text{Cu}^{2+}$ , which are then reduced to pure copper metal at the cathode.



**Copper is 100% recyclable!**

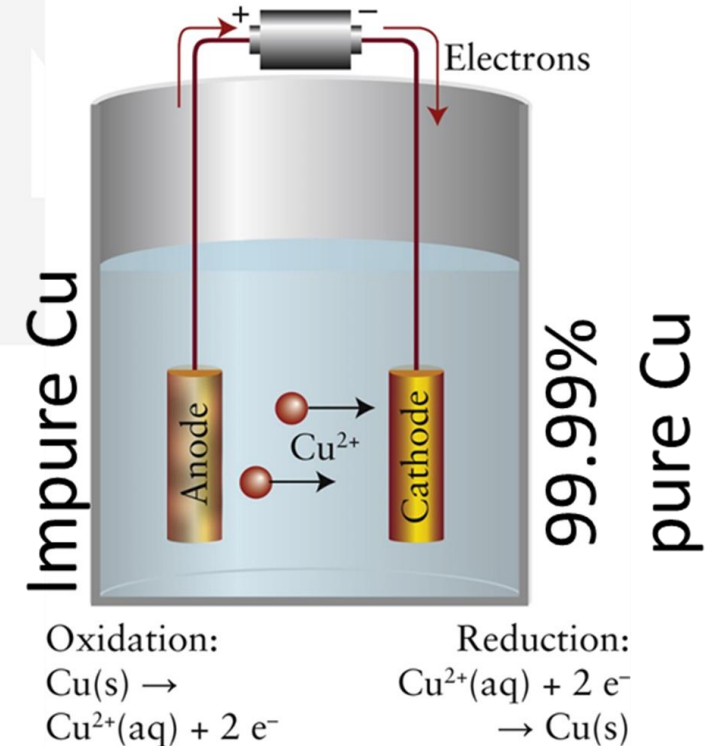


Figure 60.3  
Atkins, *Chemical Principles: The Quest for Insight*, 7e  
W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman



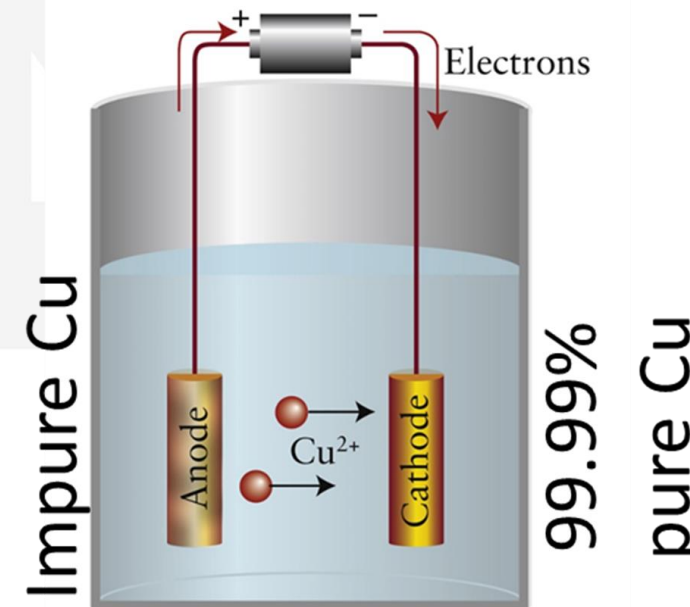
# Example

What amount of copper (in moles) can be produced by supplying 4.0 mol  $e^-$ ?

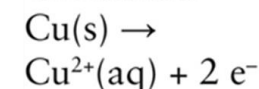


As it is a two-electron process ( $n = 2$ ):

$$n_{Cu} = \frac{n_{e^-}}{n} = \frac{4.0 \text{ mol}}{2} = 2.0 \text{ mol}$$



Oxidation:



Reduction:

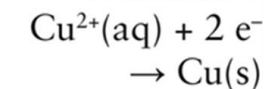


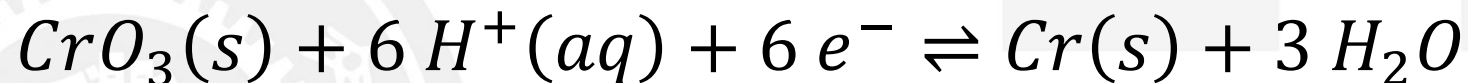
Figure 60.3  
Atkins, *Chemical Principles: The Quest for Insight*, 7e  
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# Example



What amount (in moles) of  $\text{Cr}(s)$  can be produced from  $\text{CrO}_3$  if  $12.0 \text{ mol } e^-$  are supplied?

First, we determine the reaction equation as discussed earlier in this chapter:



As it is a six-electron process ( $n = 6$ ):

$$n_{\text{Cr}} = \frac{n_{e^-}}{n} = \frac{12.0 \text{ mol}}{6} = 2.0 \text{ mol}$$

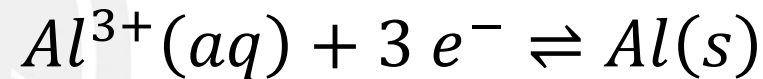
# Example



Aluminium is produced by electrolysis of its oxide dissolved in molten cryolite ( $\text{Na}_3\text{AlF}_6$ ). Find the mass of aluminium that can be produced in 1.00 d in an electrolytic cell operating continuously at  $1.00 \times 10^5$  A. The cryolite does not react.

$$M_{\text{Al}} = 26.98 \frac{\text{g}}{\text{mol}}$$

$\text{Al}_2\text{O}_3$  means that the Al has an oxidation number of +3. Therefore:



As it is a three-electron process ( $n = 3$ ):

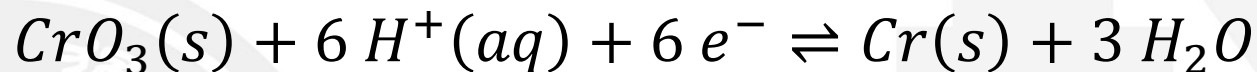
$$m_{\text{Al}} = M_{\text{Al}} \cdot \frac{n_{e^-}}{n} = \frac{M_{\text{Al}} \cdot A \cdot t}{n \cdot F} = \frac{26.98 \frac{\text{g}}{\text{mol}} \times 1.00 \times 10^5 \frac{\text{C}}{\text{s}} \times (24 \times 3600)\text{s}}{3 \times 96,485 \frac{\text{C}}{\text{mol}}} = 8.05 \times 10^5 \text{ g} = 805 \text{ kg}$$

# Example



How many hours are required to plate 12.00 g of chromium metal from a 1 M solution of  $\text{CrO}_3$  in dilute sulfuric acid by using a current of 6.20 A?

$$M_{\text{Cr}} = 52.00 \frac{\text{g}}{\text{mol}}$$



As it is a six-electron process ( $n = 6$ ):

$$m_{\text{Cr}} = M_{\text{Cr}} \cdot \frac{n_{\text{e}^-}}{n} = \frac{M_{\text{Cr}} \cdot A \cdot t}{n \cdot F}$$

$$t = \frac{m_{\text{Cr}} \cdot n \cdot F}{M_{\text{Cr}} \cdot A} = \frac{12.00 \text{ g} \times 6 \times 96,485 \frac{\text{C}}{\text{mol}}}{52.00 \frac{\text{g}}{\text{mol}} \times 6.20 \frac{\text{C}}{\text{s}}} = 21,547 \text{ s} = 5.99 \text{ h}$$