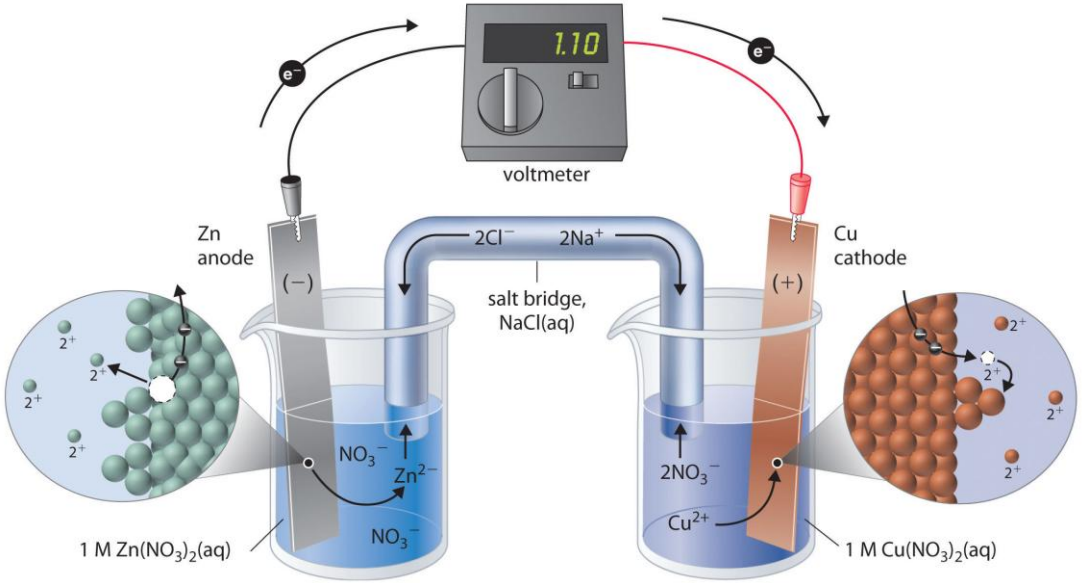
Electrochemistry



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Department of General Science, Faculty of Education,

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Semester 1, Academic year 2025

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Outline

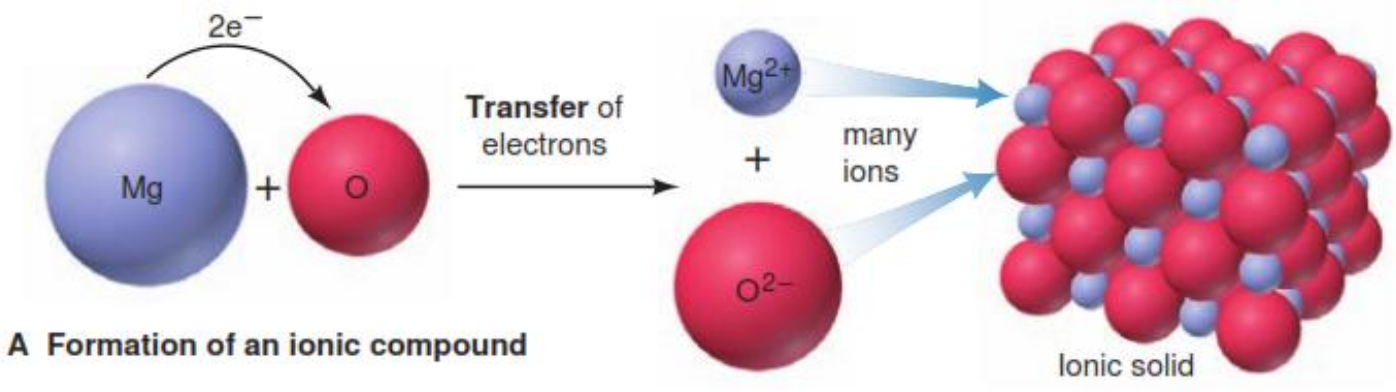
- ❑ Assigning the oxidation state
- ❑ Redox reaction
  - Oxidation reaction
  - Reduction reaction
- ❑ Identifying Redox Reactions
- ❑ Balancing Redox Equations
  - the Oxidation Number Method
  - Half-reaction Method
- ❑ Electrochemical cells
- ❑ Standard potentials and standard electrode (half-cell) potential

Lecture

On demand (Clip)

Using Oxidation Numbers to Monitor the Movement of Electron Charge

Redox reaction



A Formation of an ionic compound

- Oxidation numbers are assigned according to the relative attraction of an atom for electrons, so they are ultimately based on atomic properties

  ประจุไฟฟ้าสมมติของอะตอมในสารประกอบ โดยคำนวณขึ้นจากสมมติฐานที่ว่าอิเล็กตรอนทั้งหมดในพันธะเคมีได้ถูกถ่ายโอนไปยังอะตอมที่มี EN สูงกว่า

- An O.N. has the sign before the number (e.g., +2),

Rules for Assigning an Oxidation Number (O.N.)

General rules

1. For an atom in its elemental form (Na, O_2, Cl_2, etc.): O.N. = 0
2. For a monoatomic ion: O.N. = ion charge
3. The sum of O.N. values for the atoms in a compound equals zero. The sum of O.N. values for the atoms in a polyatomic ion equals the ion's charge.

Rules for specific atoms or periodic table groups

1. For Group 1A(1):	O.N. = +1 in all compounds
2. For Group 2A(2):	O.N. = +2 in all compounds
3. For hydrogen:	O.N. = +1 in combination with nonmetals
4. For fluorine:	O.N. = -1 in combination with metals and boron
5. For oxygen:	O.N. = -1 in peroxides O.N. = -2 in all other compounds(except with F)
6. For Group 7A(17):	O.N. = -1 in combination with metals, nonmetals (except O), and other halogens lower in the group

Silberberg, M. *Chemistry: The Molecular Nature of Matter and Change; McGraw-Hill Education, 2014.*

Sample Problem 4.6 Determining the Oxidation Number of an Element

PROBLEM: Determine the oxidation number (O.N.) of each element in these compounds:

(a) zinc chloride **(b)** sulfur trioxide **(c)** HCO_3^-

PLAN: The O.N.s of the ions in a polyatomic ion add up to the charge of the ion and the O.N.s of the ions in the compound add up to zero.

SOLUTION:

(a) $ZnCl_2$. The O.N. for zinc is +2 and that for chloride is -1.

(b) SO_3. Each oxygen is an oxide with an O.N. of -2. Therefore the O.N. of sulfur must be +6.

(c) HCO_3^-. H has an O.N. of +1 and each oxygen is -2. Therefore the C must have an O.N. of +4.

HCO_3^- $\boxed{+1 + C + 3x(-2) = -1}$

Silberberg, M. *Chemistry: The Molecular Nature of Matter and Change; McGraw-Hill Education, 2014.*

Sample Problem 4.6A **Determining the Oxidation Number of an Element**

PROBLEM: Determine the oxidation number (O.N.) of each element in these compounds

N_2O_5	Cl_2O	Nitric acid
H_2O_2	OF_2	Iodine trifluoride
HPO_4^{2-}	CO_2	$HBrO_3$
$Na_2C_2O_4$	$KMnO_4$	$Cr_2(SO_4)_3$

Highest and lowest oxidation numbers of reactive main group elements

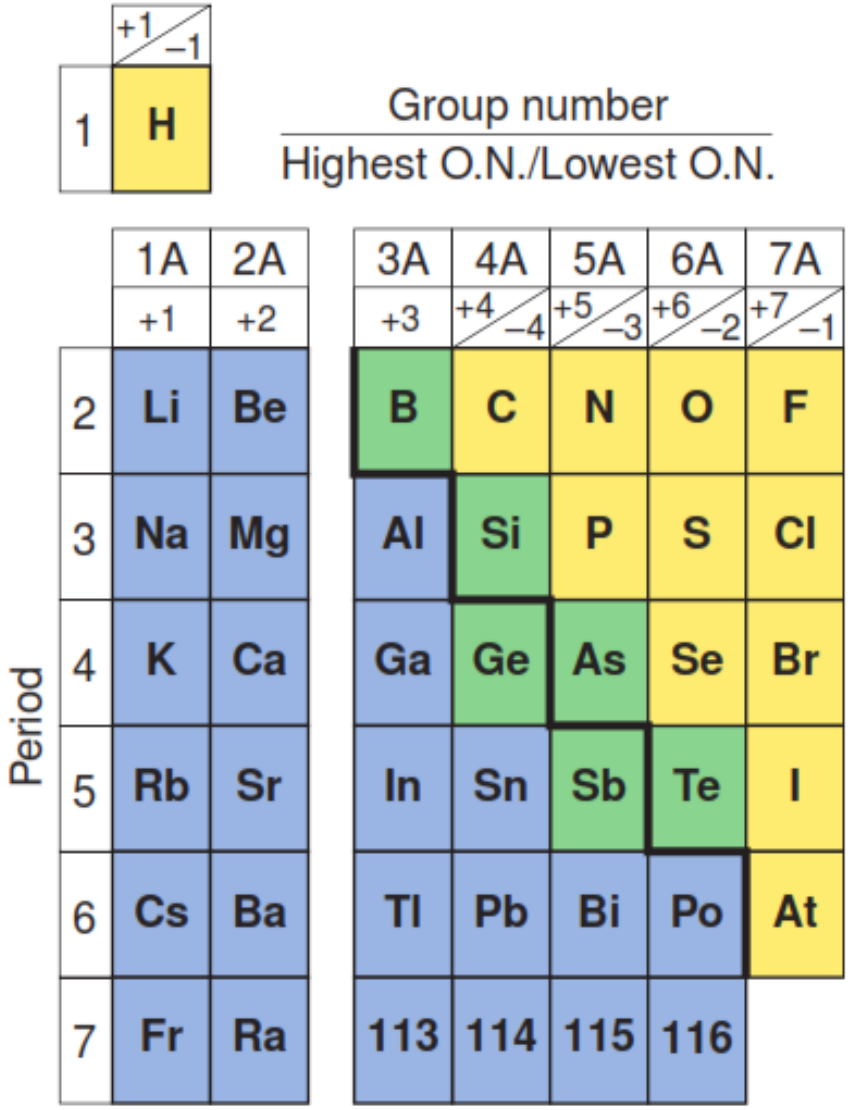
- For main-group nonmetals and some metalloids, the A-group number minus 8 is the lowest oxidation number (always negative) of any element in the group.

+6 6(-1)

SF_6

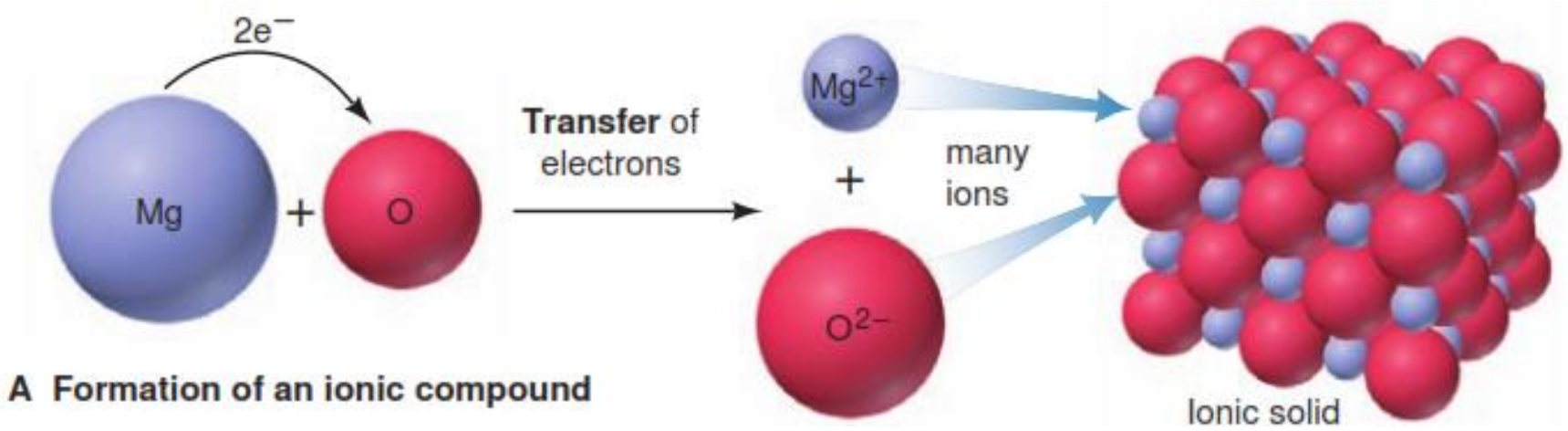
+2 -2

FeS



Silberberg, M. *Chemistry: The Molecular Nature of Matter and Change; McGraw-Hill Education, 2014.*

Redox reaction



A Formation of an ionic compound

- The **Redox reaction** (Oxidation-Reduction) is the net movement of electrons from one reactant to the other.

Silberberg, M. *Chemistry: The Molecular Nature of Matter and Change; McGraw-Hill Education, 2011.*

Redox reaction

The ***Redox*** reaction (Oxidation-Reduction) is the net *movement of electrons from one reactant to the other*.

This movement of electrons occurs from the reactant with less attraction for electrons to the reactant (or atom) with more attraction for electrons.

Reduction

Oxidation

} Redox

Identifying Redox Reactions

Sample Problem 4.8 **Identifying the Type of Redox Reaction**

PROBLEM: Use the oxidation number to decide which of the following is redox reaction;

(a) magnesium(s) + nitrogen(g) $\longrightarrow$ magnesium nitride (aq)

PLAN: ❑ **assign each atom an O.N. and see if it changes as the reactants become products**

$$\overset{0}{3Mg(s)} + \overset{0}{N_2(g)} \longrightarrow \overset{+2\ -3}{Mg_3N_2\ (aq)}$$

Mg is the reducing agent;

N_2 is the oxidizing agent.

In this case, O.N. of Mg(s) changes from 0 to +2, and O.N. of N changes from 0 to -3

We can conclude that this reaction is **Redox reaction**

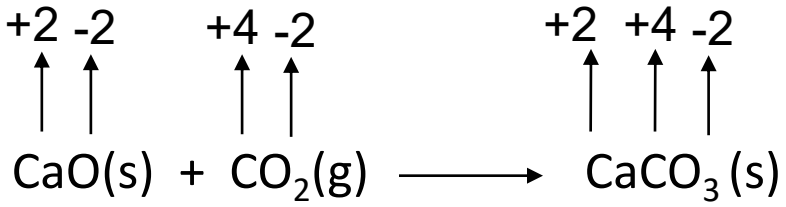
Silberberg, M. *Chemistry: The Molecular Nature of Matter and Change; McGraw-Hill Education, 2011.*

Identifying Redox Reactions

Sample Problem 4.8 **Identifying the Type of Redox Reaction**

PROBLEM: Use the oxidation number to decide which of the following is redox reaction;

(b) $CaO(s) + CO_2(g) \longrightarrow CaCO_3(s)$



Because each atom in the product has the same O.N. that it had in reactant.

We can conclude that this reaction is **not** a Redox reaction

Sample Problem 4.8A Identifying the Type of Redox Reaction

PROBLEM: Use the oxidation number to decide which of the following are redox reaction:

(a) $AgNO_3(aq) + KCl(aq) \longrightarrow AgCl(s) + KNO_3(aq)$

(b) $4KNO_3(s) \longrightarrow 2K_2O(s) + 2N_2(g) + 5O_2(g)$

(c) $5CO(g) + I_2O_5(s) \longrightarrow 5CO_2(g) + I_2(s)$

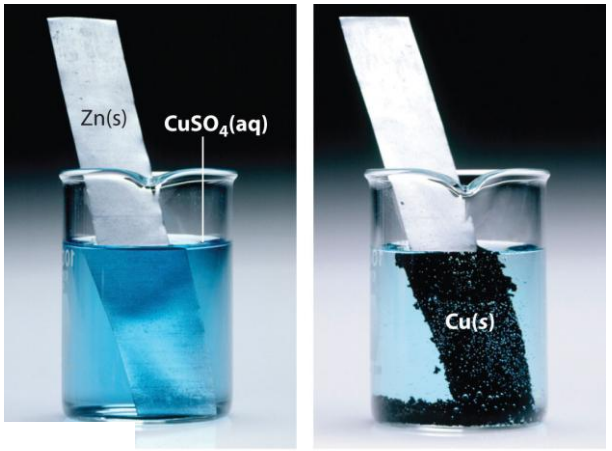
Oxidation-Reduction

Oxidation is the loss of electrons

(oxidation number increase)

Reduction is the gain of electrons.

(oxidation number decrease)



$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

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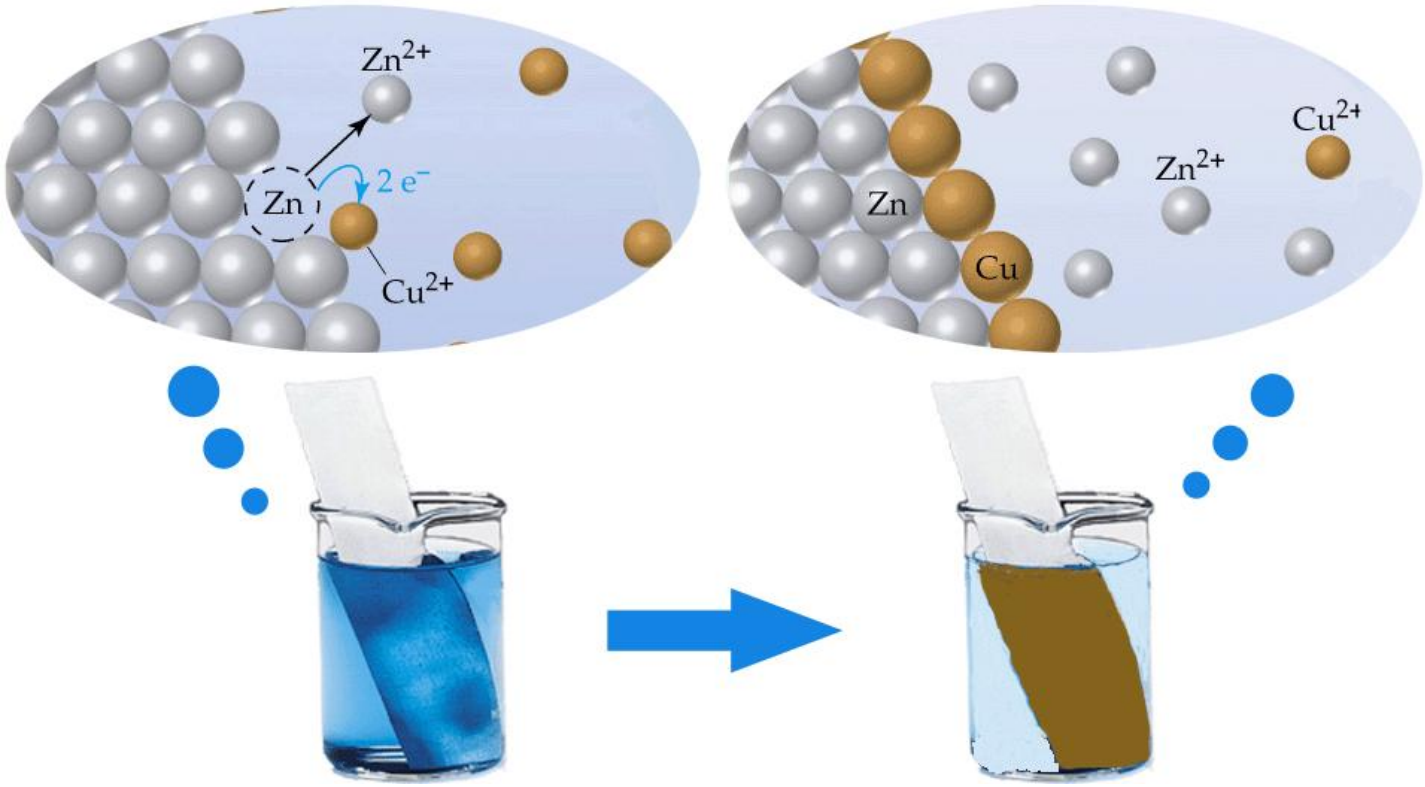
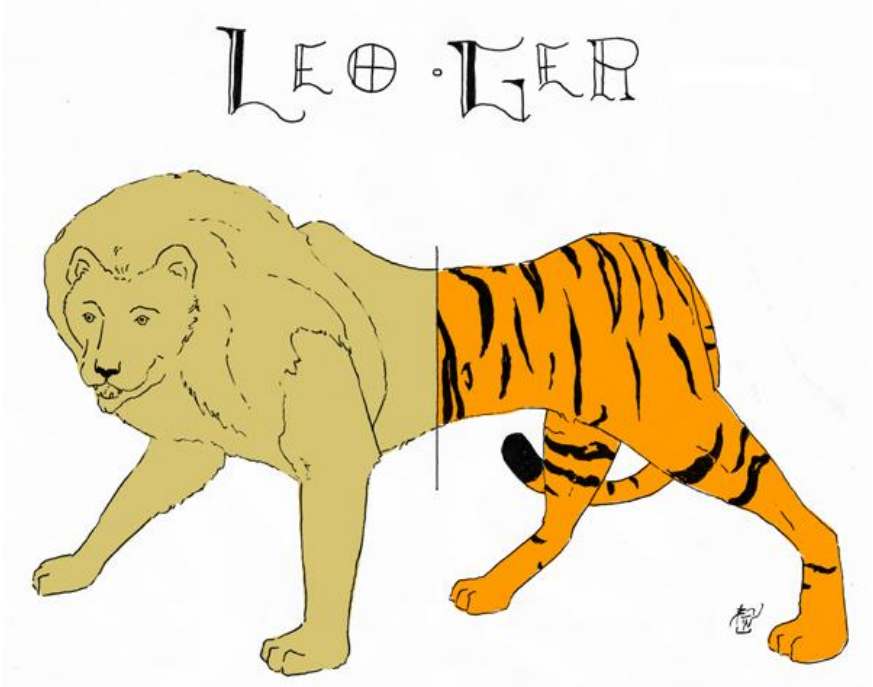


http://merqurycheymii.exteen.com/20110218/oxidation-reduction-reaction-redox

Oxidation-Reduction

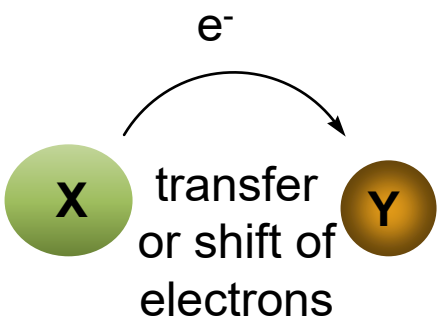
Lose **E**lectrons: **O**xidation, (เพิ่ม Ox ออก)

Gain **E**lectrons: **R**eduction (ลด รับ reduction)



http://learning-laboratory.com/redox-reactions-oxidation-reduction/

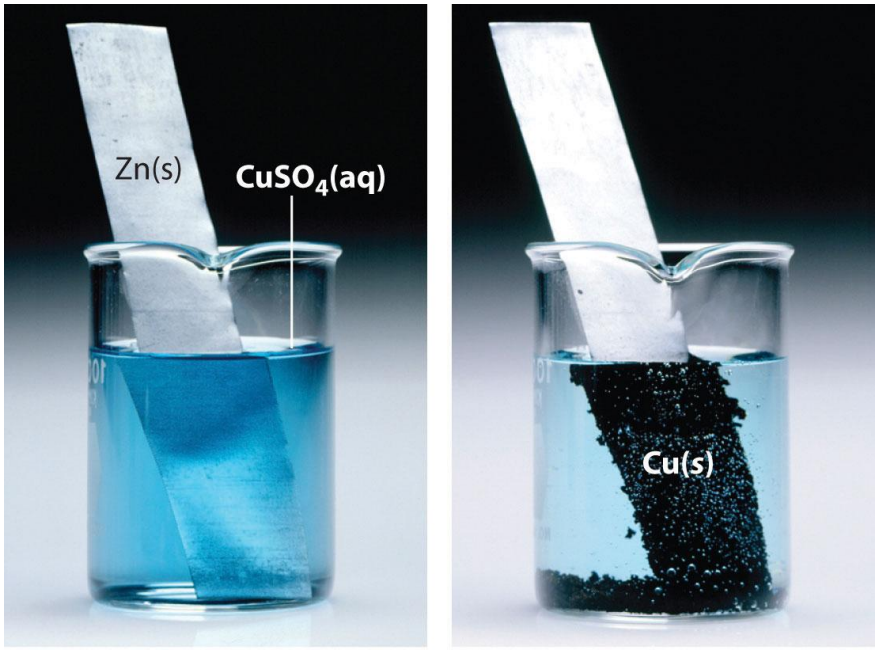
Summary of terminology for oxidation-reduction (redox) reactions.



X loses electron(s)	**Y gains electron(s)**
X is oxidized	Y is reduced
X is the reducing agent	Y is the oxidizing agent
X increases its oxidation number	Y decreases its oxidation number

Silberberg, M. *Chemistry: The Molecular Nature of Matter and Change; McGraw-Hill Education, 2014.*

Example of Oxidation-Reduction



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Oxidation: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

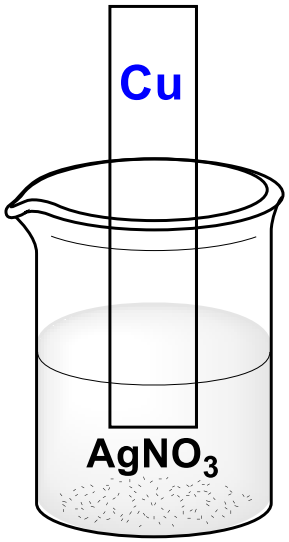
reduction: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

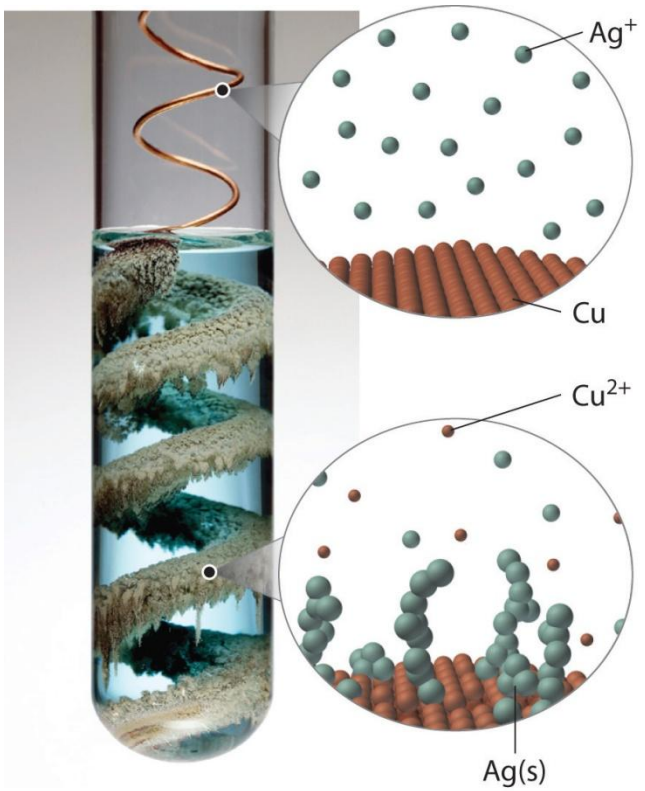
redox: $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

Zn is_____, Zn is _____

Cu^{2+} is _____ Cu^{2+} is _____

Exercise 1





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Metallic copper is added into the silver nitrate solution

1) The oxidizing agent (species that is reduced) is
2) The reducing agent (species that is oxidized) is
3) write the oxidation reaction
4) write the reduction reaction
5) Redox reaction

Sample Problem 4.7 **Recognizing Oxidizing and Reducing Agents**

PROBLEM: Identify the oxidizing agent and reducing agent in each of the following:

(a) $2Al(s) + 3H_2SO_4(aq) \longrightarrow Al_2(SO_4)_3(aq) + 3H_2(g)$

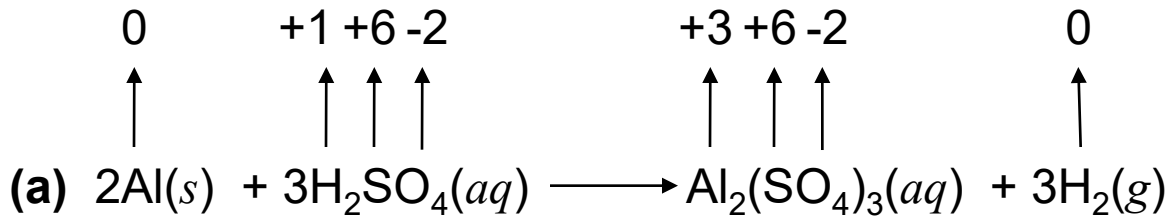
(b) $PbO(s) + CO(g) \longrightarrow Pb(s) + CO_2(g)$

(c) $2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$

PLAN: Assign an O.N. for each atom and see which atom gained and which atom lost electrons in going from reactants to products.

An increase in O.N. means the species was oxidized (and is the reducing agent) and a decrease in O.N. means the species was reduced (is the oxidizing agent).

SOLUTION:



The O.N. of Al increases; it is oxidized; it is the reducing agent.

The O.N. of H decreases; it is reduced; H_2SO_4 is the oxidizing agent.

Sample Problem 4.7 Recognizing Oxidizing and Reducing Agents

(b) $PbO(s) + CO(g) \longrightarrow Pb(s) + CO_2(g)$

(c) $2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$

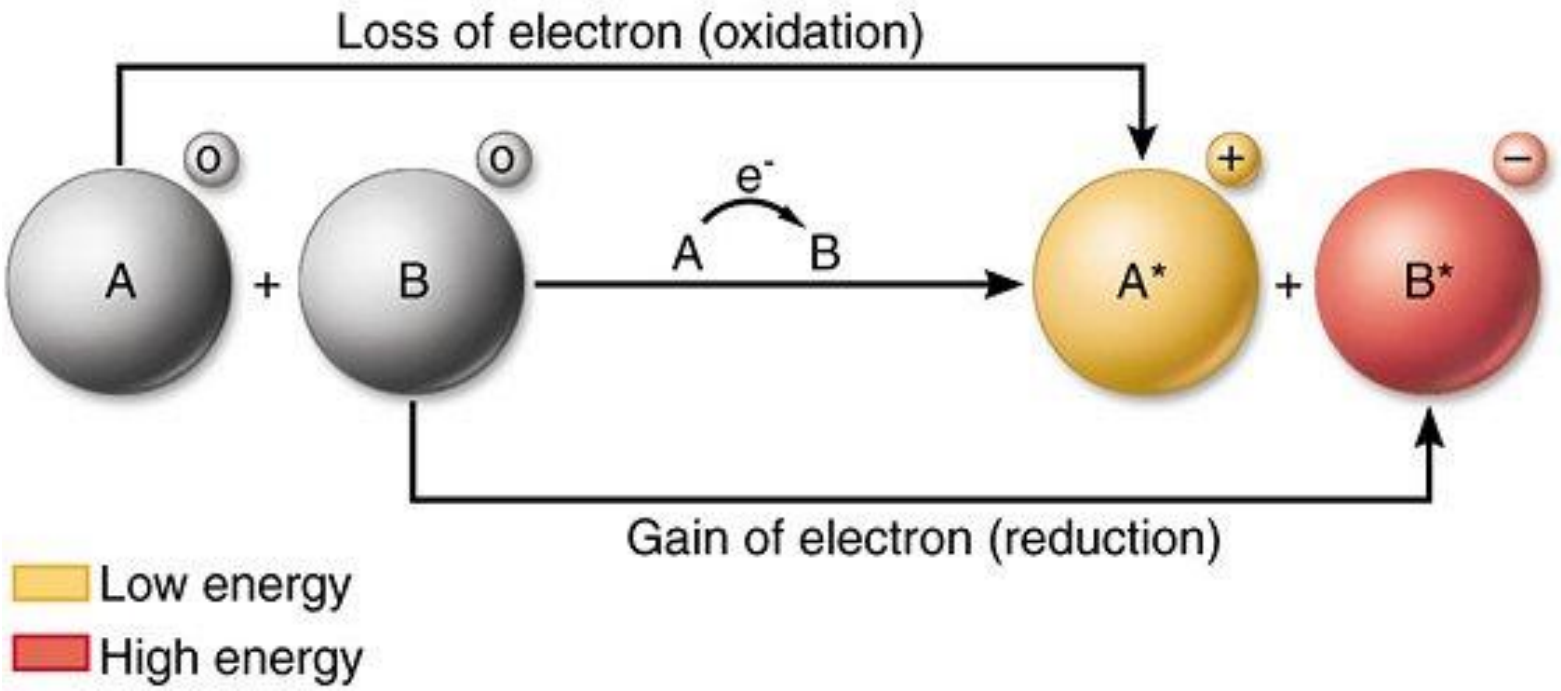
Sample Problem 4.18A

Recognizing Oxidizing and Reducing Agents

PROBLEM: Identify the oxidizing agent and reducing agent in each of the following:

(a) $NCl_3(l) + 3H_2O(l) \longrightarrow NH_3(aq) + 3HOCl(aq)$

Balancing Redox Reaction



Source: http://bioap.wikispaces.com/Ch9+Collaboration

Balancing Redox Equations

Half-Reaction Method for Balancing Redox Reactions

- In acid solution
- In basic solution

The Half-Reaction Method for Balancing Equations for Oxidation–Reduction Reactions Occurring in Acidic Solution

Step 1 Identify and write the equations for the oxidation and reduction half-reactions.

Step 2 For each half-reaction:

a. Balance all of the elements except hydrogen and oxygen.

b. Balance oxygen using H_2O.

c. Balance hydrogen using H^+.

d. Balance the charge using electrons.

Step 3 If necessary, multiply one or both balanced half-reactions by an integer to equalize the number of electrons transferred in the two half-reactions.

Step 4 Add the half-reactions, and cancel identical species that appear on both sides.

Step 5 Check to be sure the elements and charges balance.

Zumdahl, S. S. *World of Chemistry; McDougal Littell, 2007.*

Half-Reaction Method for Balancing Redox Reactions

Balancing Redox Reactions in acid Solution

$$Cr_2O_7^{2-}(aq) + I^-(aq) \longrightarrow Cr^{3+}(aq) + I_2(aq)$$ [acid solution]

STEP 1. Divide the reaction into two half-reactions, one representing oxidation and one representing reduction.

$$Cr_2O_7^{2-} \longrightarrow Cr^{3+} \qquad I^- \longrightarrow I_2$$

Half-Reaction Method for Balancing Redox Reactions

STEP 2. For each half-reaction:

2a) Balance all of elements except H and O

$Cr_2O_7^{2-} \longrightarrow 2\ Cr^{3+}$

2b) Balance O atoms by adding H_2O

$Cr_2O_7^{2-} \longrightarrow 2\ Cr^{3+} + 7H_2O$

2c) Balance H atoms by adding H^+

$Cr_2O_7^{2-} + 14H^+ \longrightarrow 2\ Cr^{3+} + 7H_2O$

2d) Balance charge by adding e^-

$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2\ Cr^{3+} + 7H_2O$

2a) Balance all of elements except H and O

$2\ I^- \longrightarrow I_2$

2b) Balance O atoms by adding H_2O

Not needed; there are no O atoms

2d) Balance charge by adding e^-

Not needed; there are no H atoms

2c) Balance H atoms by adding H^+

$2\ I^- \longrightarrow I_2 + 2e^-$

2a) Balance all of elements except H and O

$Cr_2O_7^{2-} \longrightarrow 2\ Cr^{3+}$

2b) Balance O atoms by adding H_2O

$Cr_2O_7^{2-} \longrightarrow 2\ Cr^{3+} + 7H_2O$

2c) Balance H atoms by adding H^+

$Cr_2O_7^{2-} + 14H^+ \longrightarrow 2\ Cr^{3+} + 7H_2O$

2d) Balance charge by adding e^-

$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2\ Cr^{3+} + 7H_2O$

we see it is the *reduction* because electrons appear on the *left*, as reactants: the reactant $Cr_2O_7^{2-}$ gains electrons (is reduced), so $Cr_2O_7^{2-}$ is the oxidizing agent.

2a) Balance all of elements except H and O

$2\ I^- \longrightarrow I_2$

2b) Balance O atoms by adding H_2O

Not needed; there are no O atoms

2c) Balance H atoms by adding H^+

Not needed; there are no H atoms

2d) Balance charge by adding e^-

$2\ I^- \longrightarrow I_2 + 2e^-$

This half reaction is the *oxidation* because electrons appear on the *right*, as products: the reactant I^- loses electrons (is oxidized), so I^- is the reducing agent.

STEP 3. Multiply each half-reaction, if necessary, by an integer so that the number of e lost in the oxidation equals the number of e gained in the reduction.

Oxidation $3(2\ I^- \longrightarrow I_2 + 2e^-)$

Oxidation $6\ I^- \longrightarrow 3I_2 + 6e^-$

STEP 4. Add the half-reactions together, canceling substances that appear on both sides, and include states of matter. In this example, only the electrons cancel:

Reduction $Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2\ Cr^{3+} + 7H_2O$

Oxidation $6\ I^- \longrightarrow 3I_2 + 6e^-$

Redox $Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 2\ Cr^{3+} + 3\ I_2 + 7H_2O$

STEP 5. Check to be sure the atoms and charges balance.

Redox $Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 2\ Cr^{3+} + 3\ I_2 + 7H_2O$

Reactants
(6I, 14H, 2Cr, 7O; 6+)

products
(6I, 14H, 2Cr, 7O; 6+)

Exercise 1 — Balancing Redox Reaction

Problem: Balance the following skeleton reactions and identify the oxidizing and reducing agents

Exercise 2

Balancing Redox Reaction

Problem: Balance the following skeleton reactions and identify the oxidizing and reducing agents

Balancing Redox Reactions in basic Solution

- *Balance the reaction in acid and then add OH^- so as to neutralize the H^+ ions in the last step.*
- *Reconcile the number of water molecules*

See example in the next slide

Balancing Redox Reactions in basic Solution

Example: Balancing Redox Reaction in the basic solution

$MnO_4^-(aq) + C_2O_4^{2-}(aq) \longrightarrow MnO_2(s) + CO_3^{2-}(aq)$ [basic solution]

STEP 1. Divide the reaction into two half-reactions, one representing oxidation and one representing reduction.

reduction

$MnO_4^- \longrightarrow MnO_2$

Oxidation

$C_2O_4^{2-} \longrightarrow CO_3^{2-}$

Balancing Redox Reactions in basic Solution

STEP 2. For each half-reaction:

2a) Balance all of elements except H and O

Not need

2b) Balance O atoms by adding H_2O

$$MnO_4^- \longrightarrow MnO_2 + 2H_2O$$

2c) Balance H atoms by adding H^+

$$4H^+ + MnO_4^- \longrightarrow MnO_2 + 2H_2O$$

2d) Balance charge by adding e^-

$$3e^- + 4H^+ + MnO_4^- \longrightarrow MnO_2 + 2H_2O$$

2a) Balance all of elements except H and O

$$C_2O_4^{2-} \longrightarrow 2CO_3^{2-}$$

2b) Balance O atoms by adding H_2O

$$2H_2O + C_2O_4^{2-} \longrightarrow 2CO_3^{2-}$$

2c) Balance H atoms by adding H^+

$$2H_2O + C_2O_4^{2-} \longrightarrow 2CO_3^{2-} + 4H^+$$

2d) Balance charge by adding e^-

$$2H_2O + C_2O_4^{2-} \longrightarrow 2CO_3^{2-} + 4H^+ + 2e^-$$

STEP 3. Multiply each half-reaction, if necessary, by an integer so that the number of e lost in the oxidation equals the number of e gained in the reduction.

Reduction

$$2\,(3e^- + 4H^+ + MnO_4^-) \longrightarrow MnO_2 + 2H_2O)$$

$$6e^- + 8H^+ + 2MnO_4^- \longrightarrow 2MnO_2 + 4H_2O$$

Oxidation

$$3(2H_2O + C_2O_4^{2-} \longrightarrow 2CO_3^{2-} + 4H^+ + 2e^-)$$

$$6H_2O + 3C_2O_4^{2-} \longrightarrow 6CO_3^{2-} + 12H^+ + 6e^-$$

STEP 4. Add the half-reactions together, canceling substances that appear on both sides, and include states of matter. In this example, only the electrons cancel:

Reduction $6e^- + 8H^+ + 2MnO_4^- \longrightarrow 2MnO_2 + 4H_2O$

Oxidation $6H_2O + 3C_2O_4^{2-} \longrightarrow 6CO_3^{2-} + 12H^+ + 6e^-$

$$2MnO_4^- + 2H_2O + 3\,C_2O_4^{2-} \longrightarrow 2MnO_2 + 6CO_3^{2-} + 4\,H^+$$

Balancing Redox Reactions in basic Solution

STEP 4.1 **Basic.** Add OH^- to the both sides to neutralize H^+ and cancel H_2O

$$2MnO_4^- + 2H_2O + 3\,C_2O_4^{2-} + \mathbf{4OH^-} \longrightarrow 2MnO_2 + 6CO_3^{2-} + [\,4H^+ + 4OH^-]$$

$$2MnO_4^- + \cancel{2H_2O} + 3\,C_2O_4^{2-} + \mathbf{4OH^-} \longrightarrow 2MnO_2 + 6CO_3^{2-} + \cancel{2}\,[4\,H_2O]$$

$$2MnO_4^- + 3\,C_2O_4^{2-} + 4OH^- \longrightarrow 2MnO_2 + 6CO_3^{2-} + 2\,H_2O]$$

STEP 5. Check to be sure the atoms and charges balance.

$$2MnO_4^- + 3\,C_2O_4^{2-} + 4OH^- \longrightarrow 2MnO_2 + 6CO_3^{2-} + 2\,H_2O]$$

(2Mn, 24O, 6C, 4H; 12−) (2Mn, 24O, 6C, 4H; 12−)

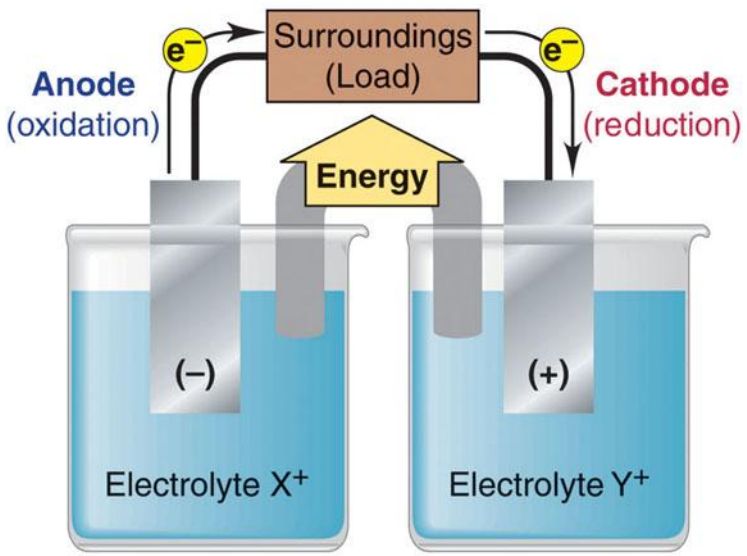
Exercise 3 **Balancing Redox Reaction**

Problem: Write a balanced molecular equation for the reaction between $KMnO_4$ and KI in basic solution.

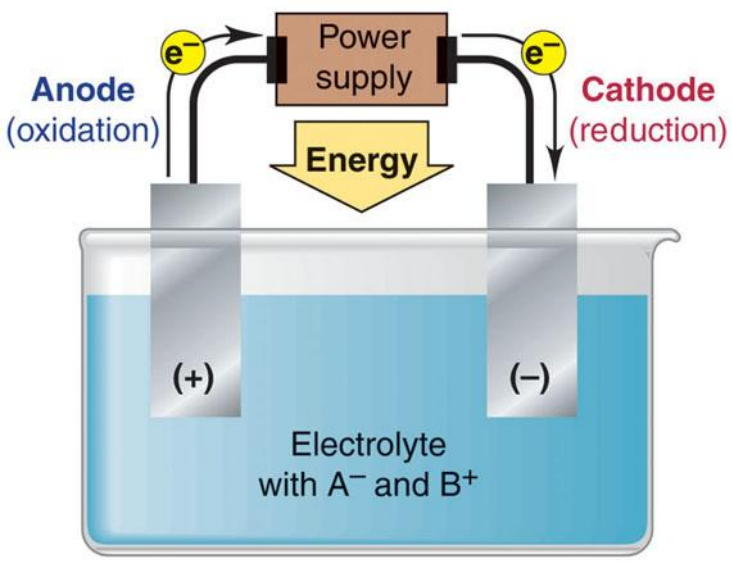
$$MnO_4^-(aq) + I^-(aq) \longrightarrow MnO_4^{2-}(s) + IO_3^-(aq) \quad \text{[basic solution]}$$

Electrochemical Cells

Galvanic cell



Electrolytic cell



OUTLINE

- Electrochemical cells
  - Galvanic cell (Voltaic cell)
  - Electrolytic cell

- Standard potentials and standard electrode (half-cell) potential

Electrochemical Cells

1) A voltaic cell (or ***galvanic cell***) uses a spontaneous reaction ($\Delta G < 0$) to generate electrical energy.

This energy is used to operate the load—flashlight bulb, CD player, car starter motor, or other electrical device.

2) An electrolytic cell uses electrical energy to drive a nonspontaneous reaction ($\Delta G > 0$).

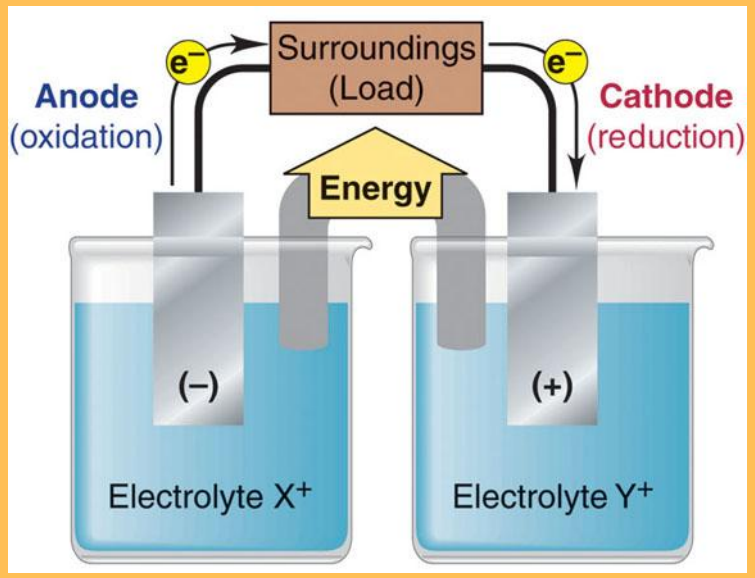
In the cell reaction, electrical energy from an external power supply converts lower energy reactants into higher energy products.

General characteristics of voltaic and electrolytic cells.

GALVANIC CELL

Energy is *released* from spontaneous redox reaction

System does work on its surroundings



Oxidation half-reaction

$X \longrightarrow X^+ + e^-$

Reduction half-reaction

$Y^+ + e^- \longrightarrow Y$

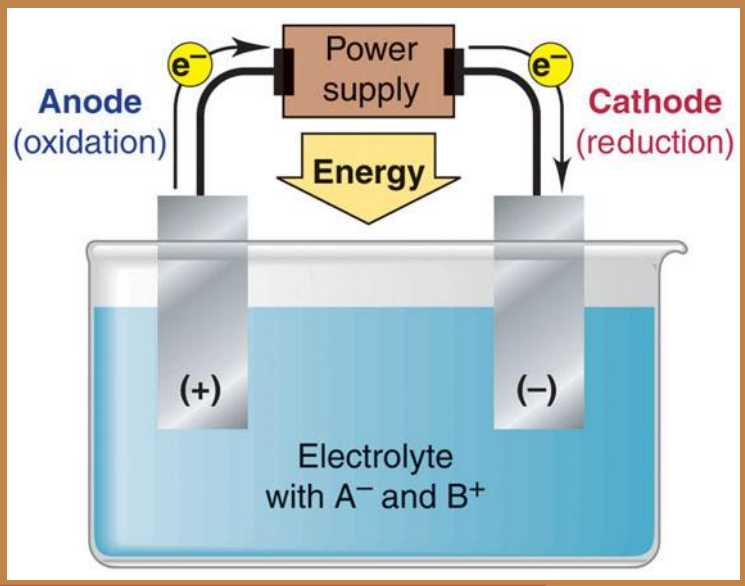
Overall (cell) reaction

$X + Y^+ \longrightarrow X^+ + Y$; $\Delta G < 0$

ELECTROLYTIC CELL

Energy is *absorbed* to drive a nonspontaneous redox reaction

Surroundings (power supply) do work on system(cell)



Oxidation half-reaction

$A^- \longrightarrow A + e^-$

Reduction half-reaction

$B^+ + e^- \longrightarrow B$

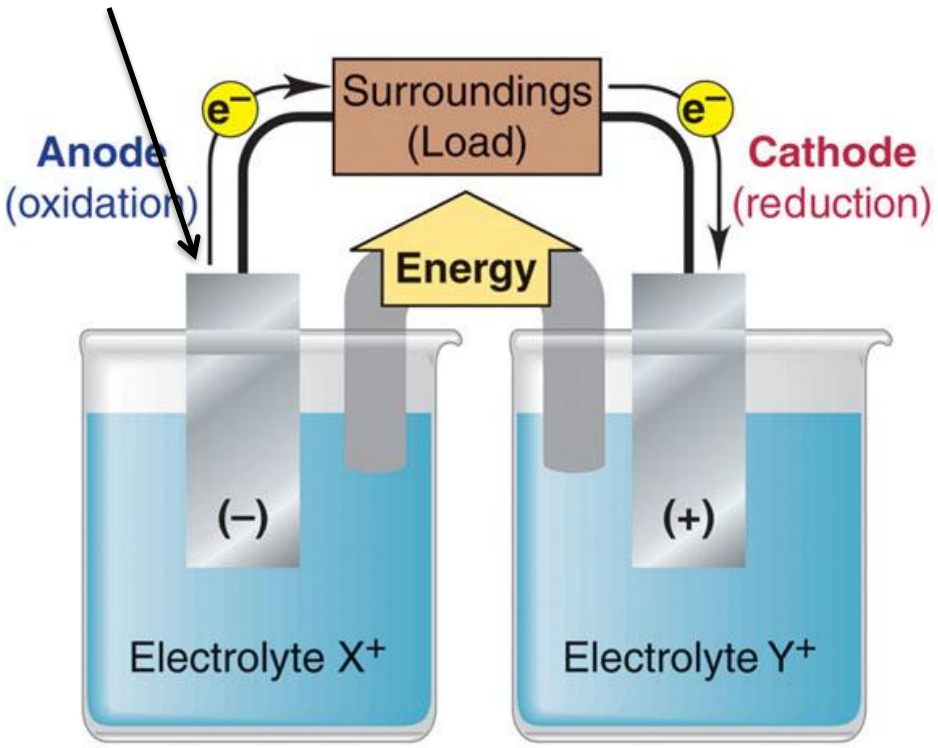
Overall (cell) reaction

$A^- + B^+ \longrightarrow A + B$; $\Delta G > 0$

Consistent features for Electrochemical Cells

The two types of cell have certain design features in common

electrode



Electrode can conduct the electricity between cell and surroundings, are dipped into an electrolyte

The oxidation half-reaction occurs at the anode

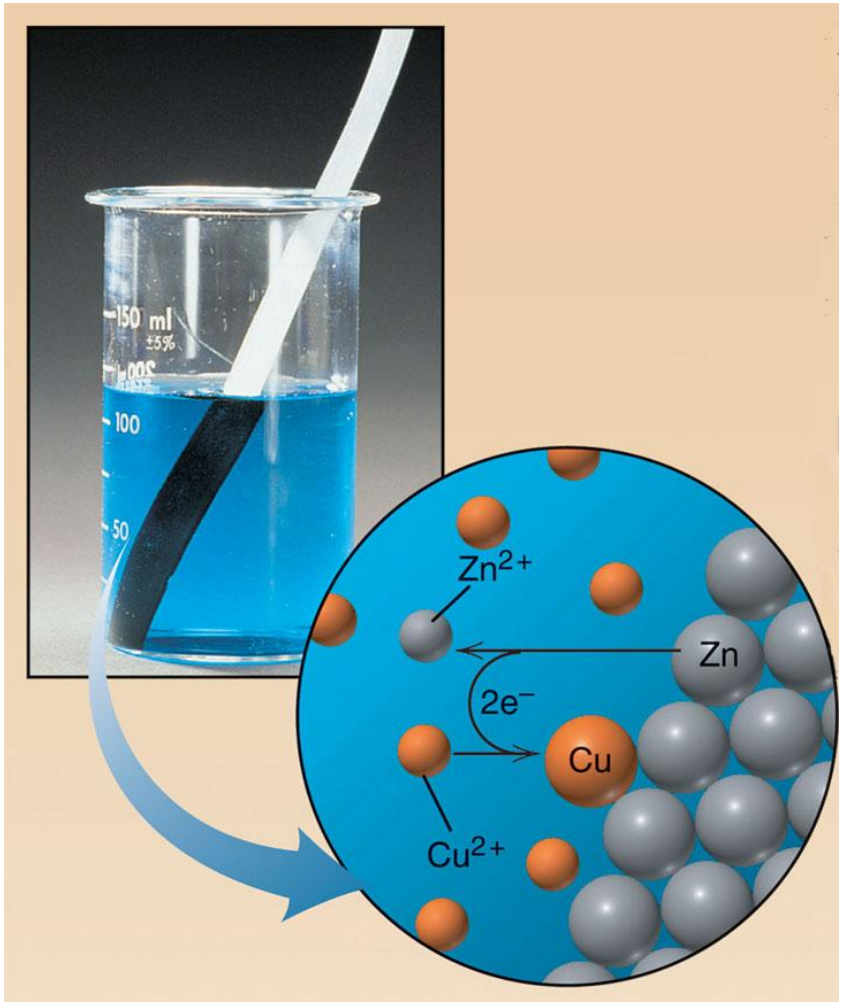
The reduction half-reaction occurs at the cathode

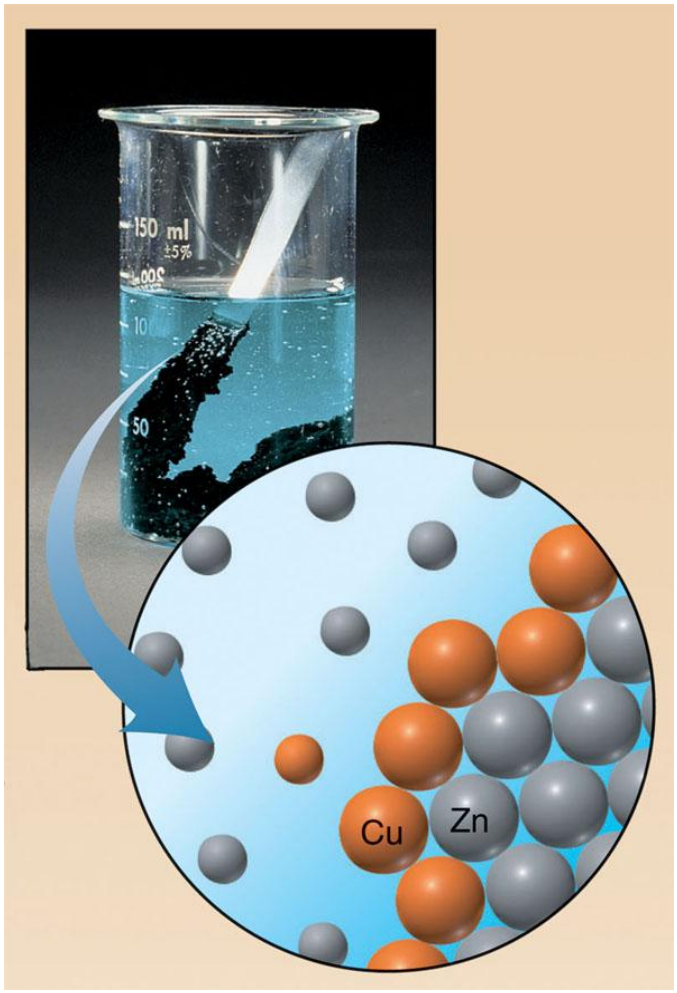
Electrolyte is a mixture of ions (usually in aqueous solution) that are involved in the reaction or that carry the charge.

Electrochemical Cells

1) Galvanic cell
2) Electrolytic cell

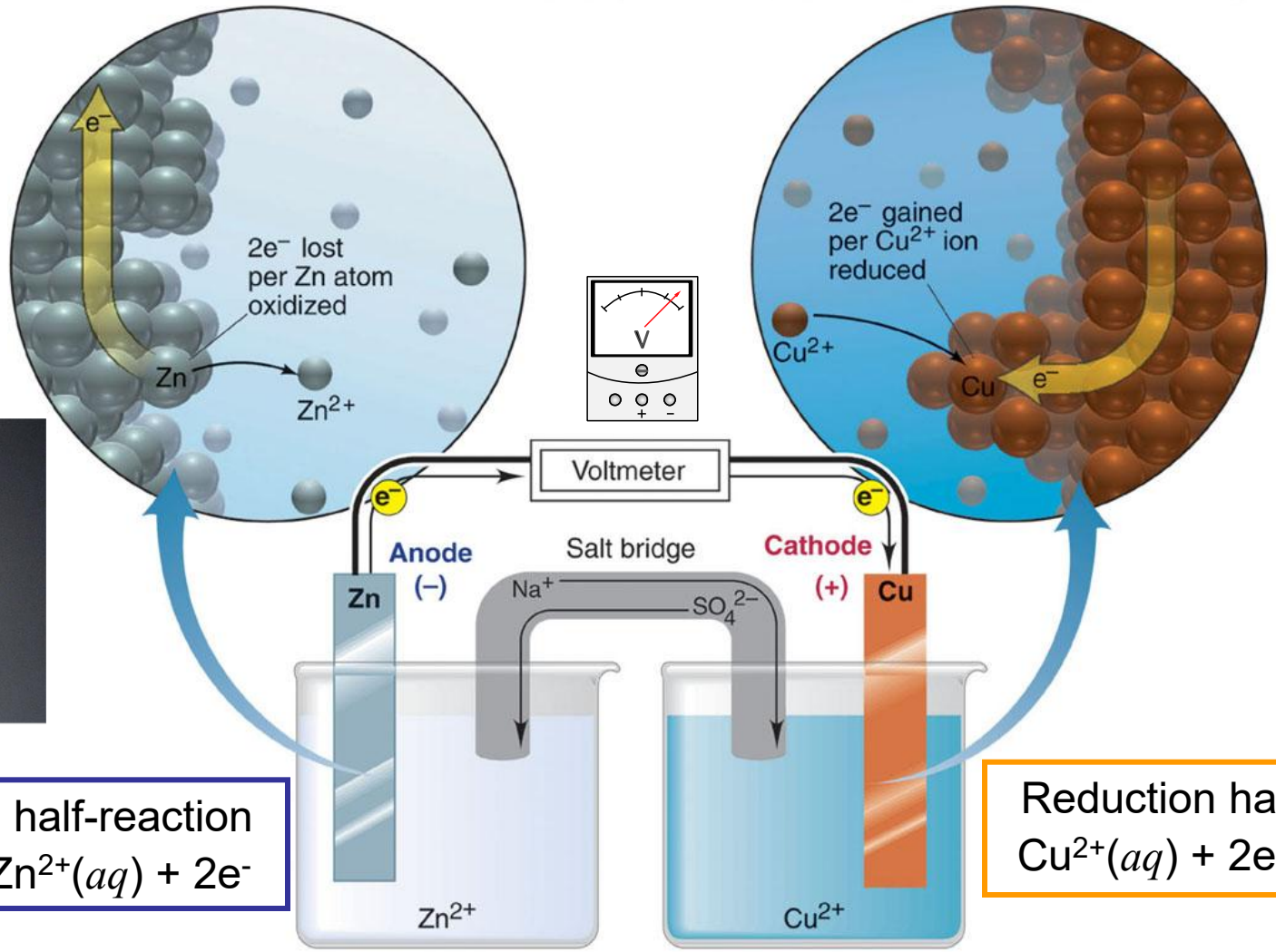
Galvanic cell: The spontaneous reaction between zinc and copper(II) ion.





$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

A Galvanic cell based on the zinc-copper reaction.



Oxidation half-reaction

$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$

Reduction half-reaction

$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

Overall (cell) reaction

$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$

Construction and Operation of a Voltaic Cell

1. The oxidation half-cell.

The ***anode*** compartment consists of a zinc bar (the anode) immersed in a Zn^{2+} electrolyte (such as a solution of zinc(II)sulfate, ($ZnSO_4$). The zinc bar is the reactant in the oxidation half-reaction, and it conducts the released electrons out of its half-cell.

2. The reduction half-cell.

the cathode compartment consists of a copper bar (the cathode) immersed in a Cu^{2+} electrolyte [such as a solution of copper(II) sulfate, $CuSO_4$]. Copper metal is the product in the reduction halfreaction, and the bar conducts electrons into its half-cell.

3. Relative charges on the electrodes.

The electrode charges are determined by the source of electrons and the direction of electron flow through the circuit

In any voltaic cell, the anode is negative and the cathode is positive

Construction and Operation of a Voltaic Cell

4. The purpose of the salt bridge

salt bridge acts as a "liquid wire," allowing ions to flow through both compartments and complete the circuit. The solution cannot pour out, but ions can diffuse through it into or out of the half-cells.

To maintain neutralityin the reduction half-cell

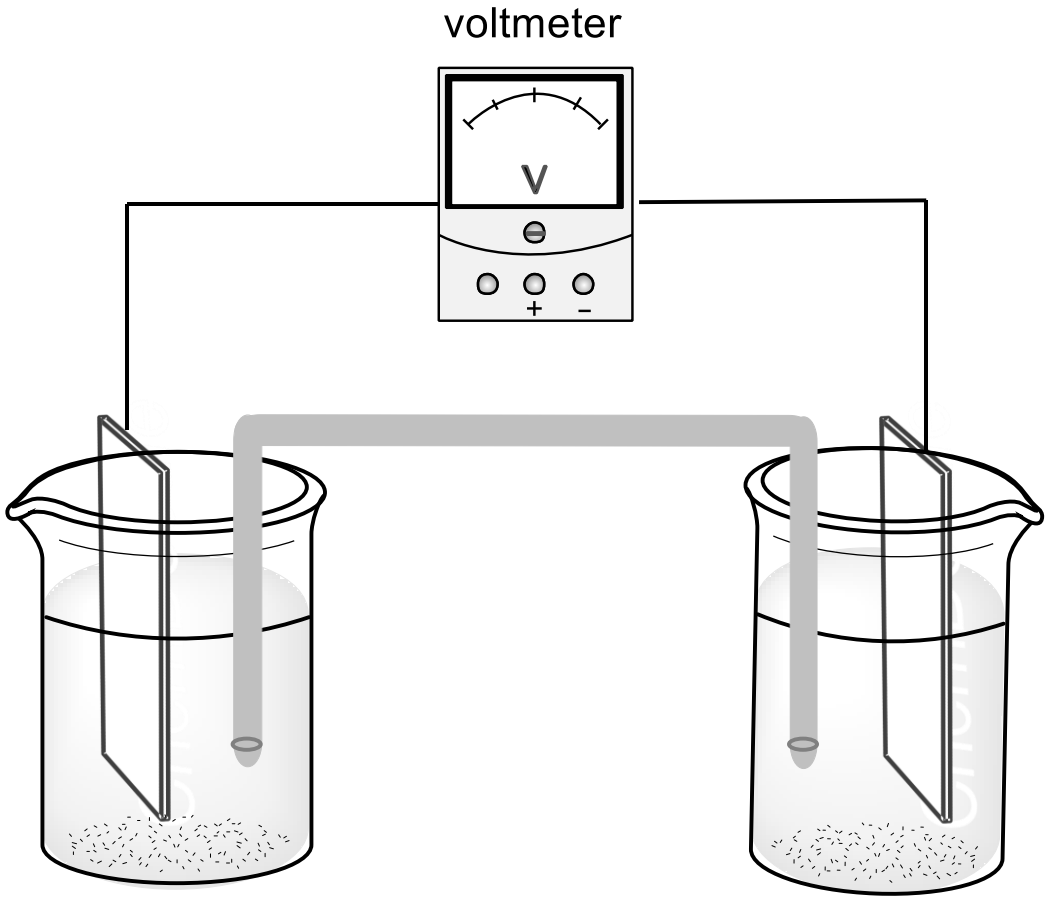
Na^+ ions move from the salt bridge into the solution (and some SO_4^{2-} ions move from the solution into the salt bridge)

To maintain neutrality in the oxidation half-cell

SO_4^{2-} ions move from the salt bridge into that solution (and some Zn^{2+} ions move from the solution into the salt bridge).

Exercise 1

Draw a diagram and show balanced equations that consists of one half-cell with a Cr bar in a $Cr(NO_3)_3$ solution, another half-cell with an Ag bar in an $AgNO_3$ solution, and a KNO_3 salt bridge. Measurement indicates that the Cr electrode is negative relative to the Ag electrode.



Exercise 2

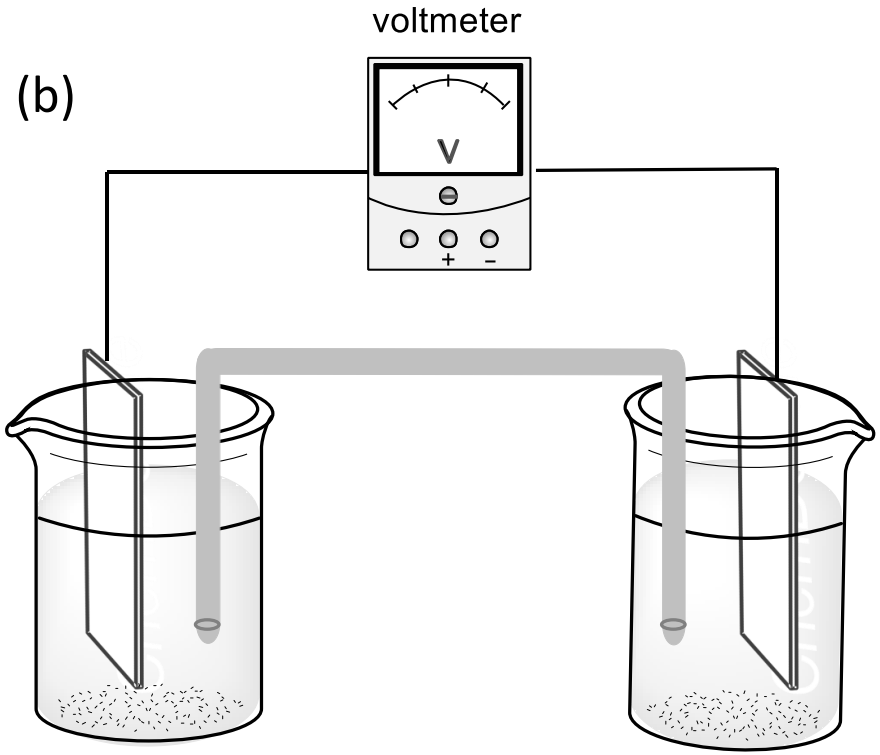
A voltaic cell is constructed with an Sn/Sn^{2+} half-cell and a Zn/ Zn^{2+} half-cell. The zinc electrode is negative.

(a) Write balanced half-reactions and the overall reaction.

(b) Diagram the cell, labeling electrodes with their charges and showing the directions of electron flow in the circuit and of cation and anion flow in the salt bridge.

(a)

(b)



Notation for a Galvanic Cell

components of anode compartment

(oxidation half-cell)

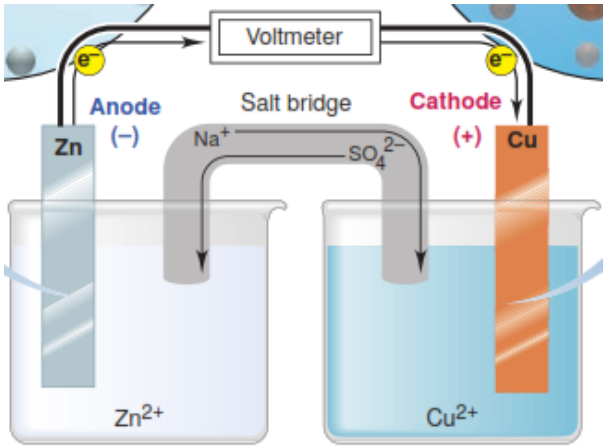
components of cathode compartment

(reduction half-cell)

phase of lower oxidation state | phase of higher oxidation state || phase of higher oxidation state | phase of lower oxidation state

act as a salt bridge
phase boundary between half-cells

Examples:



$Zn(s) \mid Zn^{2+}(aq) \;||\; Cu^{2+}(aq) \mid Cu\,(s)$

$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$ $\qquad$ $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

$Zn(s) \mid Zn^{2+}(aq,\ 1\ M) \;||\; Cu^{2+}(aq,\ 1\ M) \mid Cu\,(s)$

Exercise 2

Write a Notation for Galvanic cell in the exercise 1 (slide NO. 47)

Exercise 3

Write the cell reaction for the following voltaic cell

(a) $Tl(s)|Tl^{+}(aq, 1\ mol/L)||Sn^{2+}(aq, 1\ mol/L)|Sn(s)$

(b) $Mn(s)|Mn^{2+}(aq)||Cd^{2+}(aq)|Cd(s)$

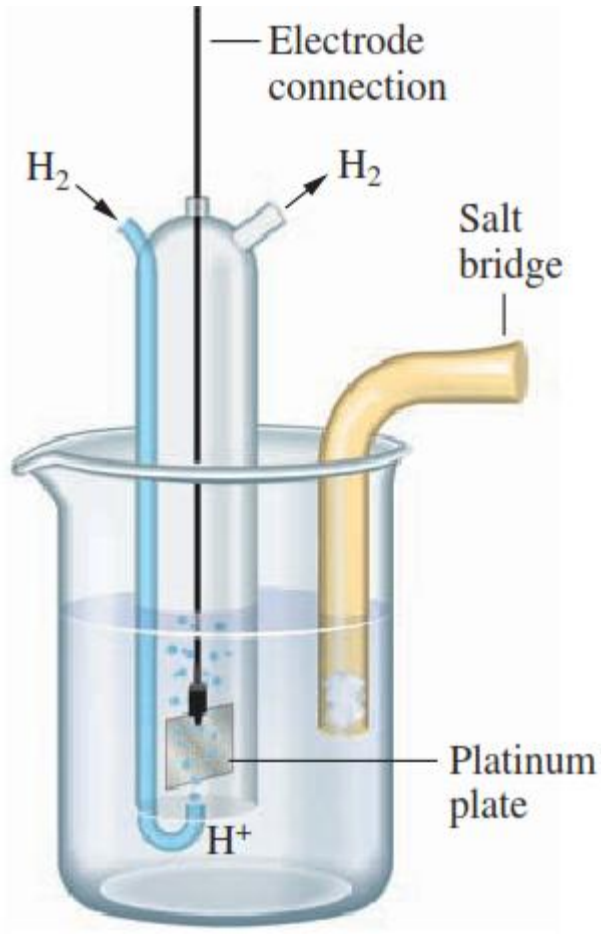
A Galvanic cell using inactive electrodes.

The electrodes in the Zn/Cu^{2+} cell are active electrode

For many redox reactions, there are no reactants or products capable of serving as electrodes, so inactive electrodes are used.

Most commonly, inactive electrodes are rods of graphite or platinum: they conduct electrons into or out of the half-cells but cannot take part in the half-reactions

Hydrogen electrodes.



hydrogen bubbles over a platinum plate that is immersed in an acidic solution

The platinum catalyzes the half-reaction but otherwise is not involved in it

The cathode half-reaction is

$$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$$

The notation for the hydrogen electrode

Cathode: $H^+(aq)|H_2(g)|Pt(s)$

Anode: $Pt(s)|H_2(g)|H^+(aq)$

Exercise 4

1) Write the notation for a cell in which the electrode reactions are

$2H^+(aq) + 2e^- \rightarrow H_2(g)$ $\quad E^0 = 0\ V$

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ $\quad E^0 = -0.76\ V$

2) Write the redox reaction for the following voltaic cell

$$Cd(s)|Cd^{2+}(aq)||H^+(aq),H_2(g)|Pt(s)$$

Standard cell Potentials
and
Standard electrode (Half-cell)Potentials

Standard Cell Potentials

The standard cell potential is the difference between the standard electrode potential of the cathode (reduction) half-cell and the standard electrode potential of the anode (oxidation) half-cell

$$E^{\circ}_{cell} = E^{\circ}_{cathode(reduction)} - E^{\circ}_{anode(oxidation)}$$

$E_{cell} > o$ For a spontaneous process

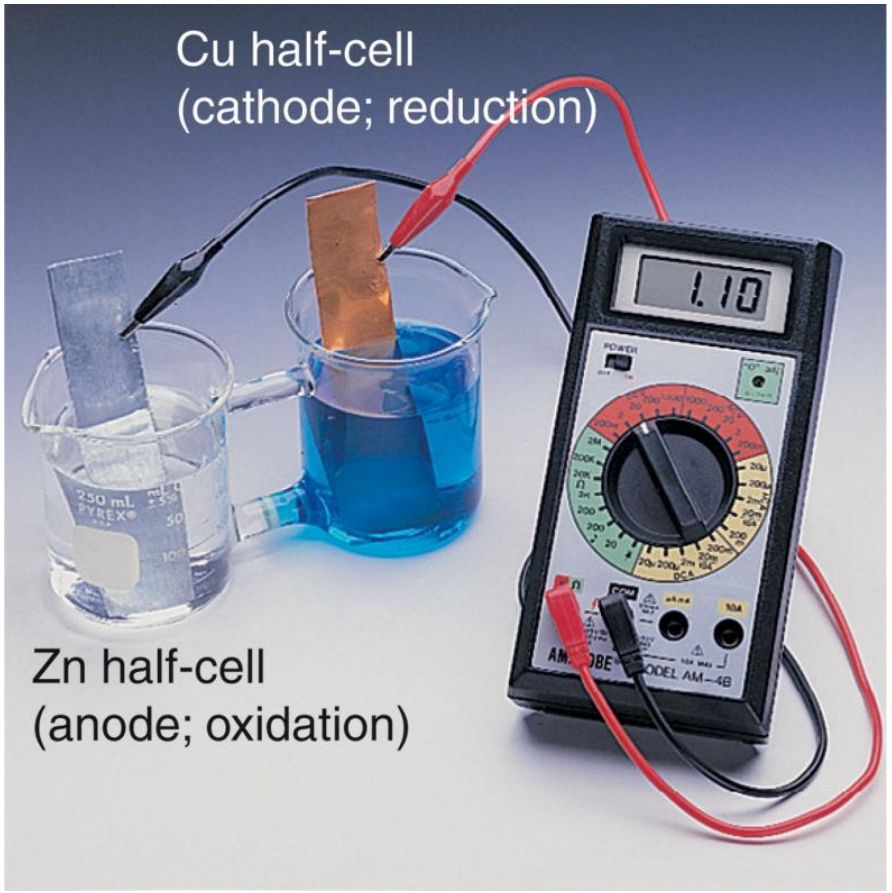
The standard cell potential is the potential measured at a specified

temperature (298 K)

1 atm for gas

1 M for solution

Standard Cell Potentials



The standard cell potential can be measured by an electronic digital voltmeter

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

Standard electrode (half-cell) Potentials

The standard electrode potential ($E^0_{half\text{-}cell}$) is the potential associated with a given half-reaction (electrode compartment) when all the components are in their standard states

❑ a standard electrode potential always refers to the half-reaction written as a **reduction**

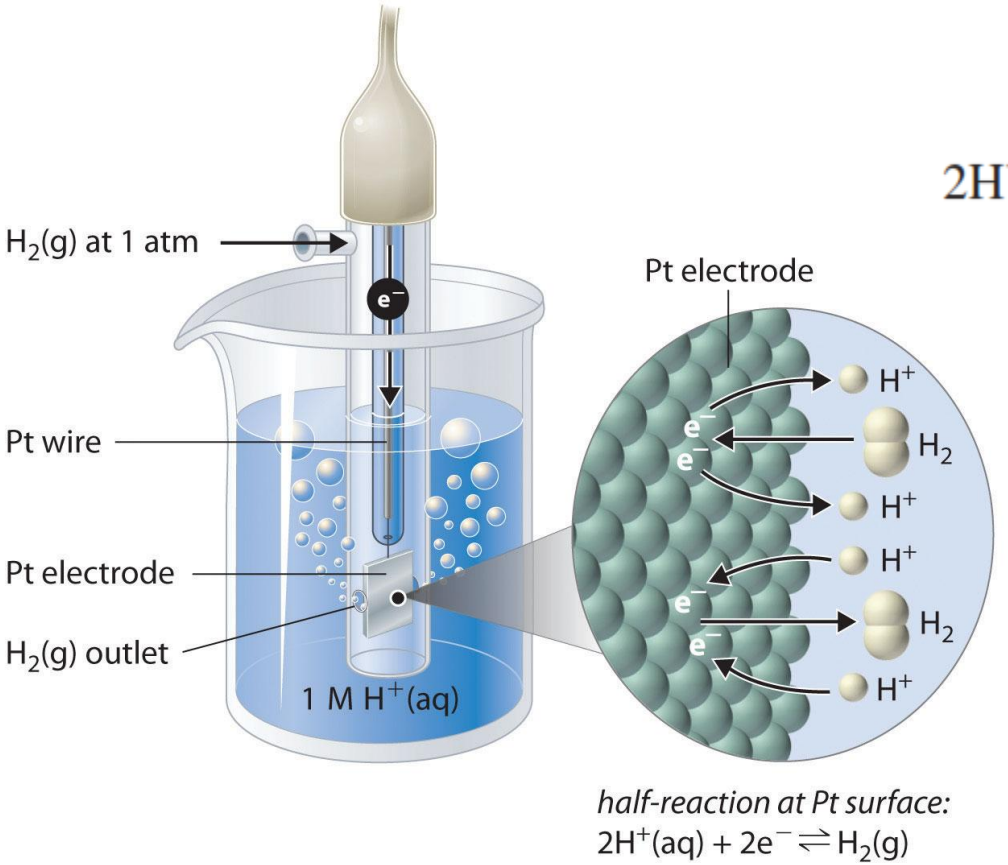
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$ E^o_{zinc} [reduction]

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $E^o_{zcopper}$ [reduction]

$$E^\circ_{cell} = E^\circ_{cathode(reduction)} - E^\circ_{anode(oxidation)}$$

Determining $E^0_{\text{half-cell}}$: The Standard Hydrogen Electrode

The standard reference half-cell is a standard hydrogen electrode, which consists of a specially prepared platinum electrode immersed in a 1 M aqueous solution of a strong acid, through with H_2 gas at 1 atm is bubbled.



$$2H^+(aq;\ 1\ M) + 2e^- \rightleftharpoons H_2(g;\ 1\ \text{atm})$$

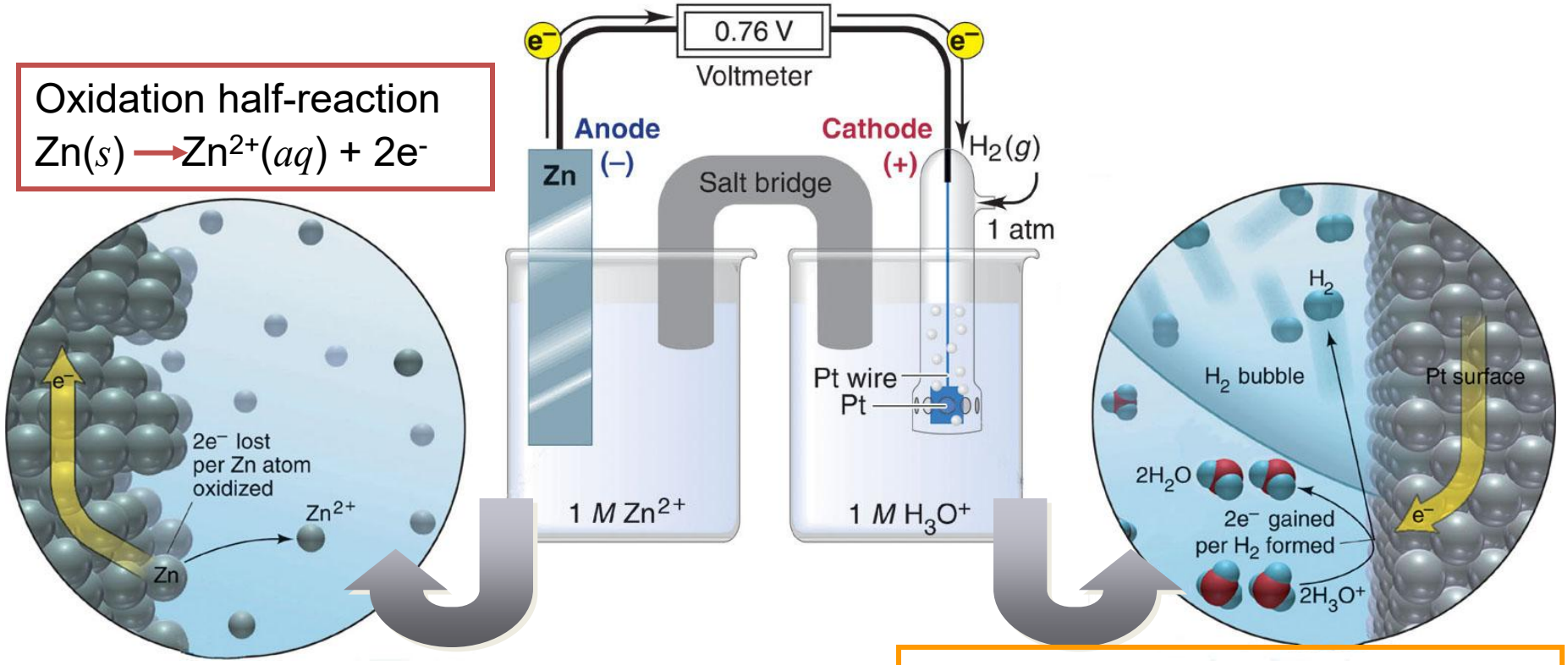
$$E^\circ_{\text{reference}} = 0.00\ \text{V}$$

http://chemwiki.ucdavis.edu/Analytical_Chemistry/Electrochemistry/Standard_Potentials

Determining an unknown $E^0_{\text{half-cell}}$ with the standard reference (hydrogen) electrode.

Oxidation half-reaction

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$



Overall (cell) reaction

$Zn(s) + 2H_3O^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g) + 2H_2O(l)$

Reduction half-reaction

$2H_3O^+(aq) + 2e^- \rightarrow H_2(g) + 2H_2O(l)$

Determining an unknown $E^0_{\text{half-cell}}$ with the standard reference (hydrogen) electrode.

$2H^+ + 2e^- \rightarrow H_2$ $\quad E°_{reference} = 0.0\ V$ [cathode; reduction]

$Zn \rightarrow Zn^{2+} + 2e^-$ $\quad E°_{zinc} = ?\ V$ [anode; oxidation]

$Zn + 2H^+ \rightarrow Zn^{2+} + H_2$ $\quad E°_{cell} = 0.76\ V$

$$E^\circ_{cell} = E^\circ_{cathode(reduction)} - E^\circ_{anode(oxidation)}$$

$$0.76 = 0.0 - E^\circ_{anode(zinc)}$$

$$E^\circ_{anode(zinc)} = -0.76 \quad V$$

Analog Multimeter

Table 21.2 Selected Standard Electrode Potentials (298K)

Half-Reaction	E^0(V)
$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$	+2.87
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$	+1.36
$MnO_2(g) + 4H^+(aq) + 2e^- \rightleftharpoons Mn^{2+}(aq) + 2H_2O(l)$	+1.23
$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightleftharpoons NO(g) + 2H_2O(l)$	+0.96
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+0.80
$Fe^{3+}(g) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H_2O(l) + 4e^- \rightleftharpoons 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	**0.00**
$N_2(g) + 5H^+(aq) + 4e^- \rightleftharpoons N_2H_5^+(aq)$	-0.23
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	-0.44
$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$	-0.83
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	-2.71
$Li^+(aq) + e^- \rightleftharpoons Li(s)$	-3.05

strength of oxidizing agent ↑

strength of reducing agent ↓

Silberberg, M. *Chemistry: The Molecular Nature of Matter and Change; McGraw-Hill Education, 2011.*

Calculating an Unknown $E^0_{half\text{-}cell}$ from E^0_{cell}

Problem: A voltaic cell houses the reaction between aqueous bromine and zinc metal:

$$Br_2(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + 2Br^-(aq) \qquad E^0_{cell} = 1.83V$$

Calculate $E^0_{bromine}$ given $E^0_{zinc} = -0.76V$

Anode: $Zn \rightarrow Zn^{2+}(aq) + 2e^-$

Cathode: $Br_2 + 2e^- \rightarrow 2Br^-$

E^0_{Zn} is -0.76V; $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$

$$E^0_{cell} = E^0_{cathode} - E^0_{anode}$$
$$1.83 = E^0_{bromine} - (-0.76)$$
$$E^0_{bromine} = 1.07\ V$$

Problem: A voltaic cell based on the reaction between aqueous Br_2 and vanadium(III) ions has $E^0_{cell} = 1.39V$

$$Br_2(aq) + 2V^{3+}(aq) + H_2O(l) \rightarrow VO^{2+}(aq) + 4H^+(aq) + 2Br^-(aq)$$

What is $E^0_{vanadium,}$ the standard electrode potential for reduction of VO^{2+} to V^{3+}?

Problem 2: In acidic solution, O_3 and Mn^{2+} ion react spontaneously:

$O_3(g) + Mn^{2+}(aq) + H_2O(l) \rightarrow O_2(g) + MnO_2(s) + 2H^+(aq)$ $\quad E^o_{cell} = 0.84$ V

What is $E^0_{manganese}$?

The use of Standard electrode (half-cell) potentials

1. Strengths of Oxidizing and Reducing Agents
2. Calculating Cell Potentials
3. Determining the Direction of Spontaneity from Electrode Potentials

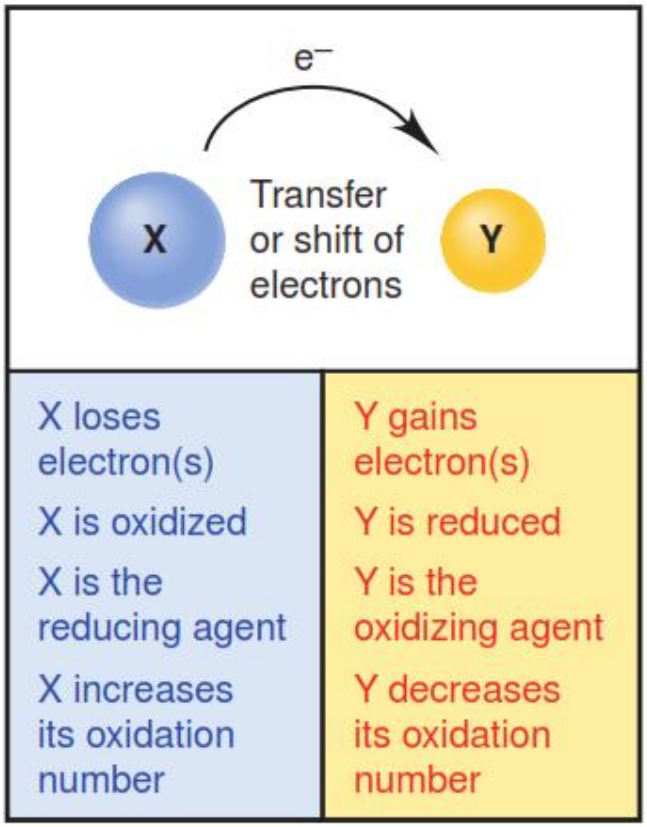
1) Relative Strengths of Oxidizing and Reducing Agents

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s) \qquad E^\circ = 0.34\ V$$
$$2H^+(aq) + 2e^- \longrightarrow H_2(g) \qquad E^\circ = 0.00\ V$$
$$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s) \qquad E^\circ = -0.76\ V$$

more positive the E^0 value

↓

the more readily the reaction (as written) occurs



Strengths of oxidizing agent: $Cu^{2+} > H^+ > Zn^{2+}$

Strengths of reducing agent: $Zn > H_2 > Cu$

Example 1: Order the following oxidizing agents by increasing strength under standard-state conditions: $Cl_2(g)$, $H_2O_2(aq)$, $Fe^{3+}(aq)$.

$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	0.77 V
$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$	1.36 V
$H_2O_2(aq) + 2H^+(aq) + 2e^- \longrightarrow 2H_2O(l)$	1.78 V

Example 2: Order the following reducing agents by increasing strength under standard-state conditions:

$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$	−1.66 V
$2H^+(aq) + 2e^- \longrightarrow H_2(g)$	0.00 V
$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	0.34 V

Example 3: Which is the stronger oxidizing agent, NO_3^- (*aq) in acidic solution (to NO) or* Ag^+(*aq)?*

2. Calculating Cell Potentials

Calculation of Cell Potentials Using Standard Reduction Potentials

$$Cd(s) \mid Cd^{2+}(aq) \mid\mid Ag^{+}(aq) \mid Ag\,(s$$

In the case of the cadmium–silver cell above

$$E^{\circ}_{cell} = E^{\circ}_{cathode(reduction)} - E^{\circ}_{anode(oxidation)}$$

See E^{0}_{cell} Table

$Cd^{2+}(aq) + 2e^{-} \rightarrow Cd(s)$ $\quad E^{o}_{Cd} = -0.40$ V

$Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$ $\quad E^{o}_{Ag} = 0.80$ V

Reaction at cathode: _____

Reaction at anode: _____

2. Calculating Cell Potentials

$$Cd(s) \mid Cd^{2+}(aq) \mid\mid Ag^{+}(aq) \mid Ag\,(s$$

$Cd^{2+}(aq) + 2e^{-} \rightarrow Cd(s)$ $\quad E^{o}_{Cd} = -0.40\ V$

$Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$ $\quad E^{o}_{Ag} = 0.80\ V$

$$E^{\circ}_{cell} = E^{\circ}_{cathode(reduction)} - E^{\circ}_{anode(oxidation)}$$

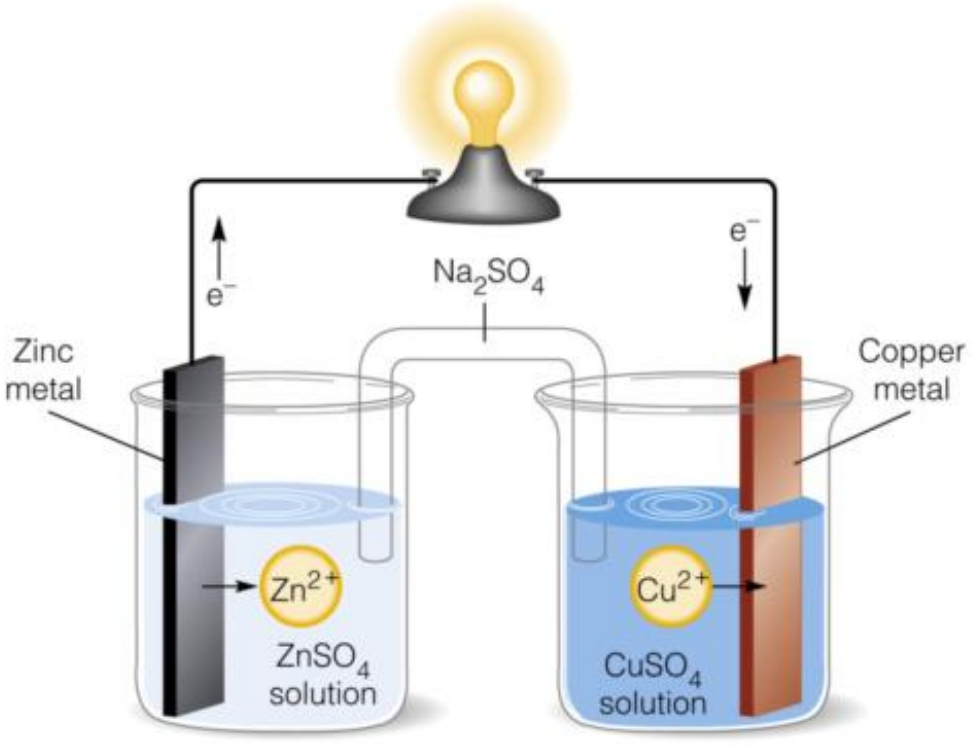
$$= 0.80 - (-0.40)$$

$$E^{\circ}_{cell} = 1.20V$$

Example 1: Calculate the standard cell potential of the following voltaic cell at 25°C using standard electrode potentials.

$$Al(s)|Al^{3+}(aq)||Fe^{2+}(aq)|Fe(s)$$

Example 2: Calculate the standard cell potential of the following galvanic cell below at 25°C using standard electrode potentials.



http://chemistry.stackexchange.com/questions/28637/whats-the-source-of-electrical-energy-in-galvanic-cells

3. Determining the Direction of Spontaneity from Electrode Potentials

E^0_{cell} is *positive,* the redox reaction is a ***spontaneous*** **reaction**

E^0_{cell} will be *zero* for a redox reaction at *equilibrium*

E^0_{cell} is *negative,* the **reverse reaction** is spontaneous

Example 1: Consider the reaction

$$Zn^{2+}(aq) + 2Fe^{2+}(aq) \rightarrow Zn(s) + 2Fe^{3+}(aq)$$

Does the reaction go spontaneously in the direction indicated, under standard conditions?

Step 1: Identify the equation for oxidation and reduction reaction

Oxidation [**anode**] is $Fe^{2+} \rightarrow Fe^{3+} + e^{-}$

Reduction [**cathode**] is $Zn^{2+} + 2e^{-} \rightarrow Zn$

The corresponding standard electrode potentials are

$$Zn^{2+}(aq) + 2e^{-} \longrightarrow Zn(s);\ E^{\circ} = -0.76\ V$$

$$Fe^{3+}(aq) + e^{-} \longrightarrow Fe^{2+}(aq);\ E^{\circ} = 0.77\ V$$

Example 1: Consider the reaction

$$Zn^{2+}(aq) + 2Fe^{2+}(aq) \rightarrow Zn(s) + 2Fe^{3+}(aq)$$

Does the reaction go spontaneously in the direction indicated, under standard conditions?

Step 2: Calculate the E^0_{cell}

$$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s);\ E^\circ = -0.76\ V$$
$$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq);\ E^\circ = 0.77\ V$$

$$E^\circ_{cell} = E^\circ_{cathode(reduction)} - E^\circ_{anode(oxidation)}$$

$$E^\circ_{cell} = (-0.76) - (0.77)$$

$$E^\circ_{cell} = -1.53V$$

A *negative* voltage indicates that this reaction is nonspontaneous reaction but the reverse reaction is spontaneous

$$Zn(S) + 2Fe^{3+}(aq) \rightarrow Zn^{2+}(aq) + 2Fe^{2+}(aq)$$

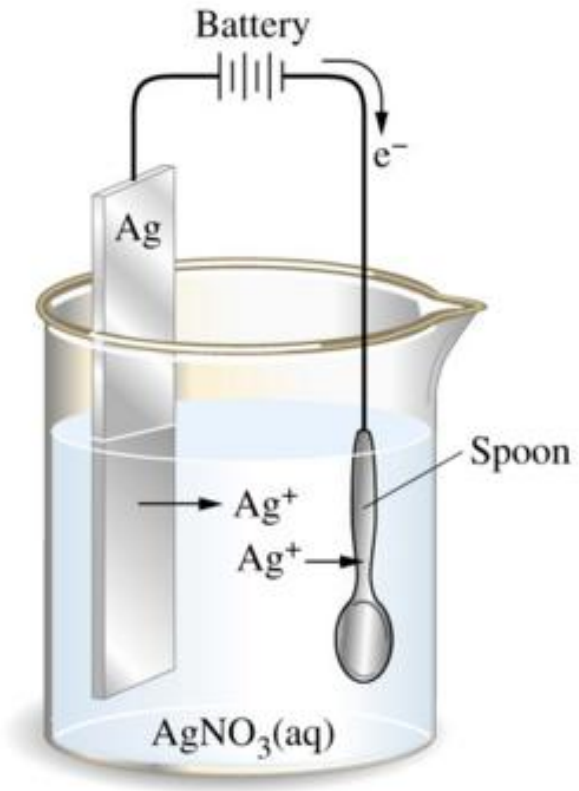
Example 2: Consider the reaction

$$Cu^{2+}(aq) + 2I^{-}(aq) \rightarrow Cu(s) + 2I_2(s)$$

Does the reaction go spontaneously in the direction indicated, under standard conditions?

ELECTROLYTIC CELLS

USING ELECTRICAL ENERGY TO DRIVE NONSPONTANEOUS REACTIONS



http://chemwiki.ucdavis.edu/Analytical_Chemistry/Electrochemistry/Electrolytic_Cells/Electroplating

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Outline

Electrolytic cell

Construction and Operation of an electrolytic Cell

Predicting the Products of Electrolysis

- Electrolysis of Pure Molten Salts
- Electrolysis of Aqueous Salt Solutions

Electroplating

ELECTROLYTIC CELLS

USING ELECTRICAL ENERGY TO DRIVE NONSPONTANEOUS REACTIONS

An **electrolytic cell** is an electrochemical cell in which an electric current drives an otherwise nonspontaneous reaction.

The process of producing a chemical change in an electrolytic cell is called **electrolysis**

To understand these changes, keep in mind the cause of the electron flow:

- In a voltaic cell, electrons are generated at the anode, so it is negative, and electrons are consumed at the cathode, so it is positive.

- In an electrolytic cell, the electrons come from the external power source, which supplies them to the cathode, so it is negative, and removes them from the anode, so it is positive.

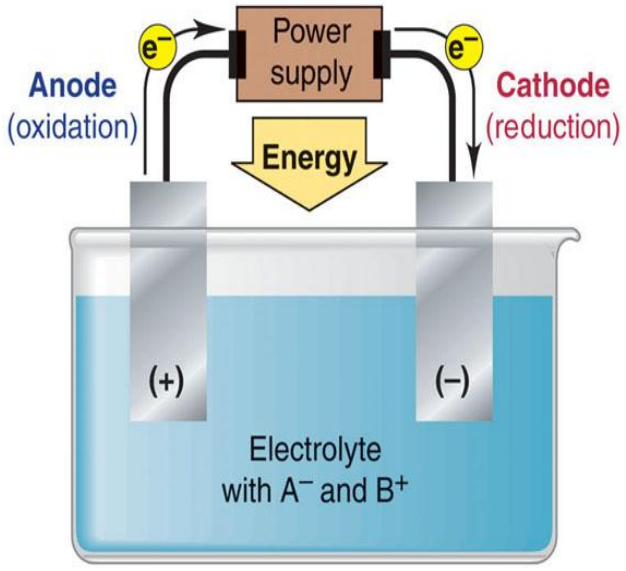


Table 21.3 Comparison of Voltaic and Electrolytic Cells

Cell Type	ΔG	E_{cell}	Electrode		
			Name	Process	Sign
Voltaic	< 0	> 0	Anode	Oxidation	-
Voltaic	< 0	> 0	Cathode	Reduction	+
Electrolytic	> 0	< 0	Anode	Oxidation	+
Electrolytic	> 0	< 0	Cathode	Reduction	-

Predicting the Products of Electrolysis

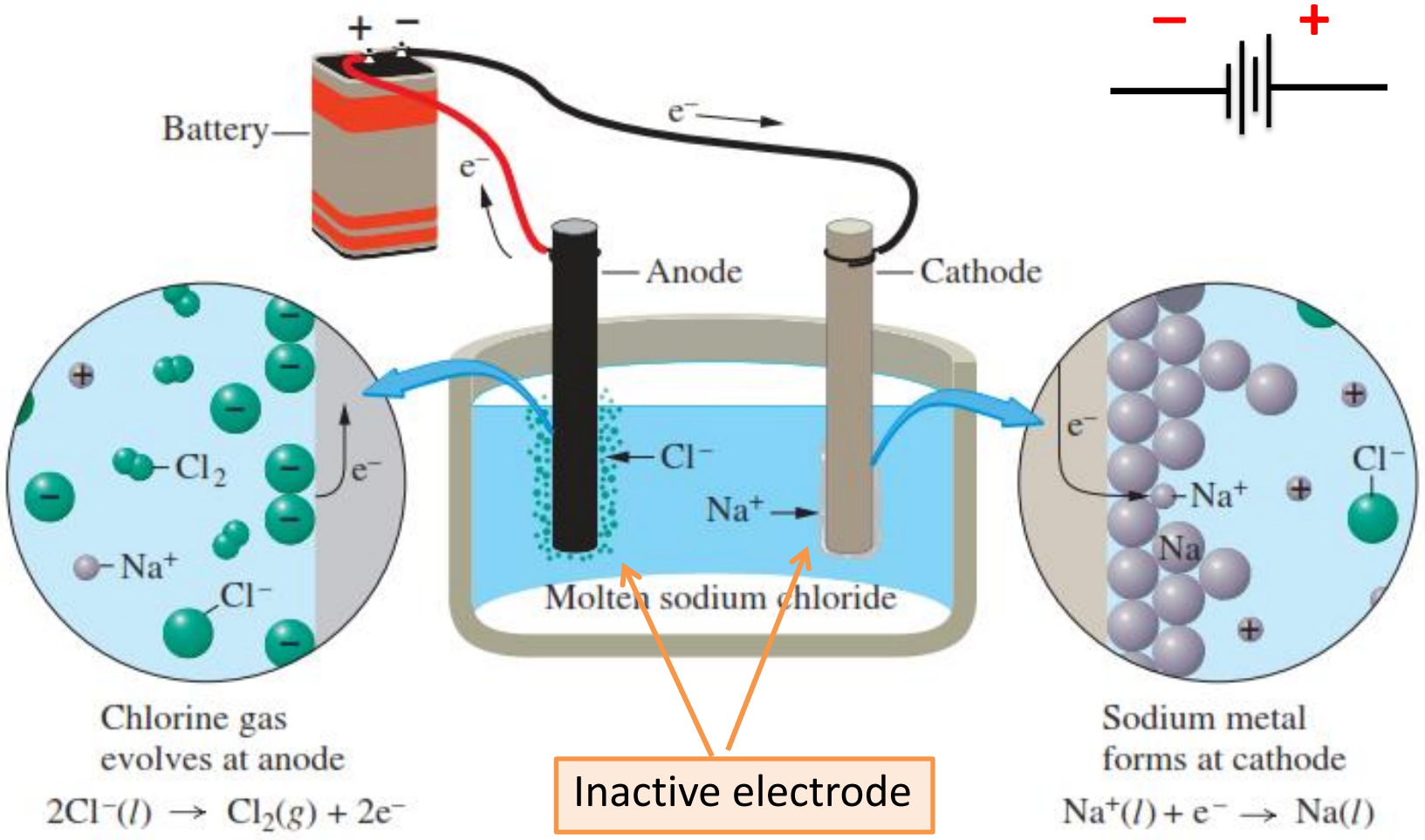
Electrolysis, the splitting (lysing) of a substance by the input of electrical energy, is often used to decompose a compound into its elements.

Electrolysis of Pure Molten Salts (without water)

Electrolysis of Aqueous Salt Solutions (with water)

Electrolysis of Pure Molten Salts

The electrolyte is the molten salt itself, and the ions move through the cell because they are attracted by the oppositely charged electrodes.



Standard Electrode (Half-Cell) Potentials*

Half-Reaction	$E°$ (V)
$Au^{3+}(aq) + 3e^- \rightleftharpoons Au(s)$	+1.50
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$	+1.36
$O_2(g) + 2H_2O(l) + 4e^- \rightleftharpoons 4OH^-(aq)$	+0.40
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0.00
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	−2.71
$Ca^{2+}(aq) + 2e^- \rightleftharpoons Ca(s)$	−2.87
$Sr^{2+}(aq) + 2e^- \rightleftharpoons Sr(s)$	−2.89
$Ba^{2+}(aq) + 2e^- \rightleftharpoons Ba(s)$	−2.90
$K^+(aq) + e^- \rightleftharpoons K(s)$	−2.93
$Li^+(aq) + e^- \rightleftharpoons Li(s)$	−3.05

Electrolysis of Pure Molten Salts

Cathode

anode

$$Na^+(l) + e^- \longrightarrow Na(l) \qquad E^o = -2.71$$

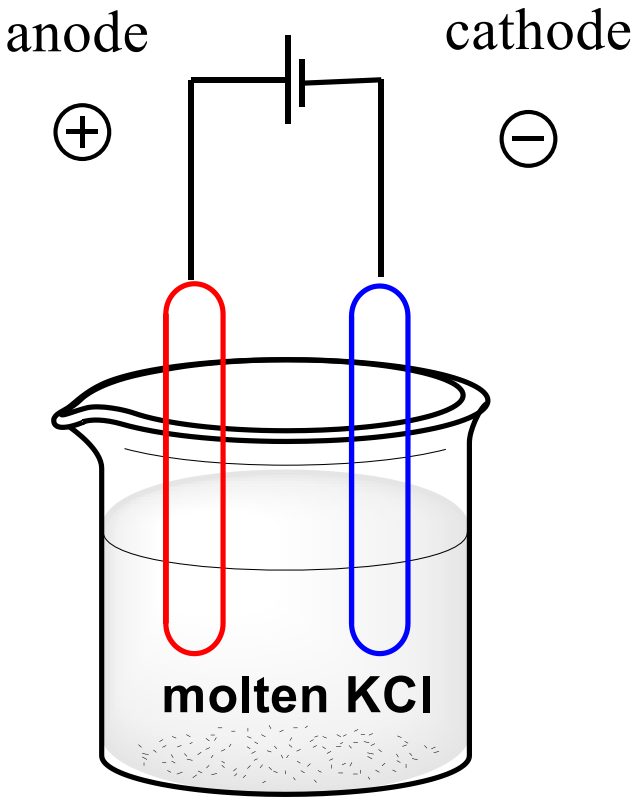
$$Cl^-(l) \longrightarrow \tfrac{1}{2}Cl_2(g) + e^- \qquad E^o = +1.36$$

$$Na^+(l) + Cl^-(l) \longrightarrow Na(l) + \tfrac{1}{2}Cl_2(g)$$

Cl_2 will produced at anode
Na will produced at cathode

E^o_{cell} = -2.71 – 1.36
= -4.07 V

Example 1: Write the half-reactions for the electrolysis of the following molten; KCl,



Reaction at cathode

_____

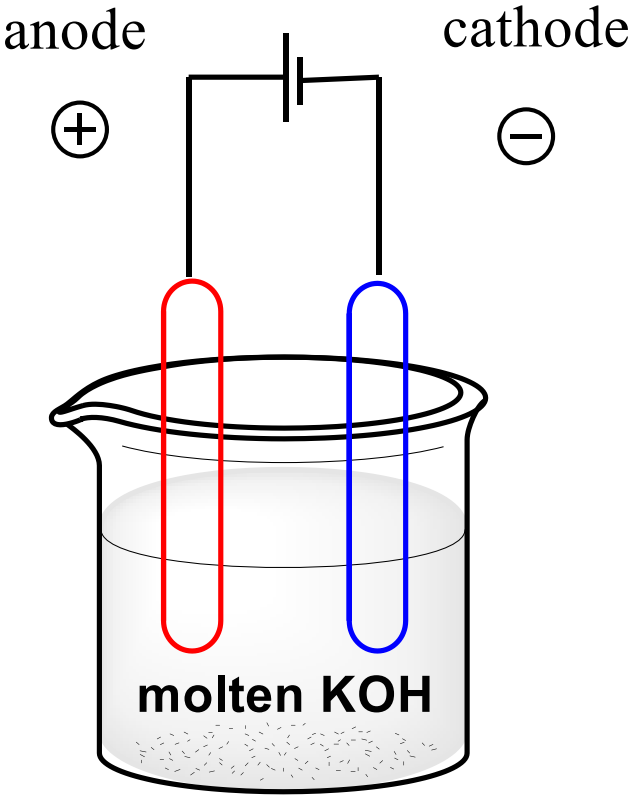
Reaction at anode

_____

Products that are obtained from this electrolysis are

E^{o}_{cell}

Example 2: Write the half-reactions for the electrolysis of the following molten; KOH,



Reaction at cathode

_____

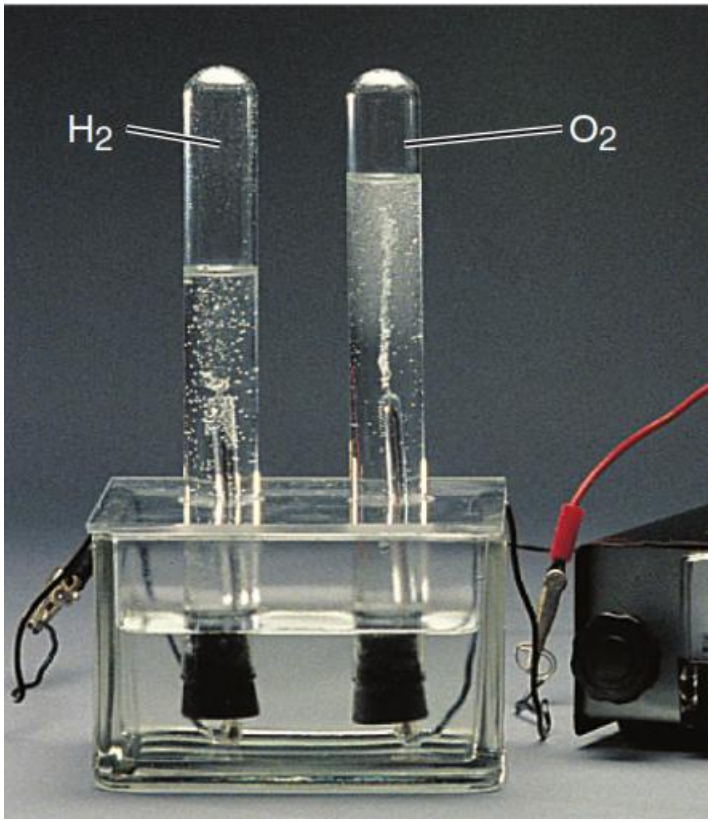
Reaction at anode

_____

Products that are obtained from this electrolysis are_____

E^{o}_{cell}

Electrolysis of Water



Anode (oxidation)

$2H_2O(l) \rightarrow \mathbf{O_2}(g) + 4H^+(aq) + 4e^-$ E = 1.23 V

Cathode (reduction)

$2H_2O(l) + 2e \rightarrow \mathbf{H_2}(g) + 2OH^-(aq)$ E = -0.83 V

Overall reaction

$2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$

$E_{cell} = -0.83 - 1.23 = -2.06$ V

Oxidation half-reaction

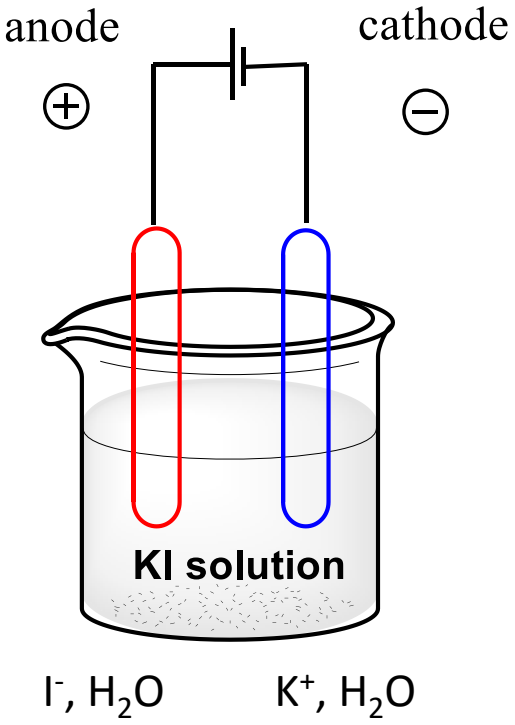
$2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-$

Reduction half-reaction

$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$

Electrolysis of Aqueous Salt Solutions

Aqueous salt solutions are mixtures of ions and water, so we have to compare the various electrode potentials to predict the electrode products



Cathode (reduction)

$K^+(aq) + e^- \longrightarrow K(s)$ $\quad E^o = -2.93$ V

$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$ $\quad E^o = -0.83$ V

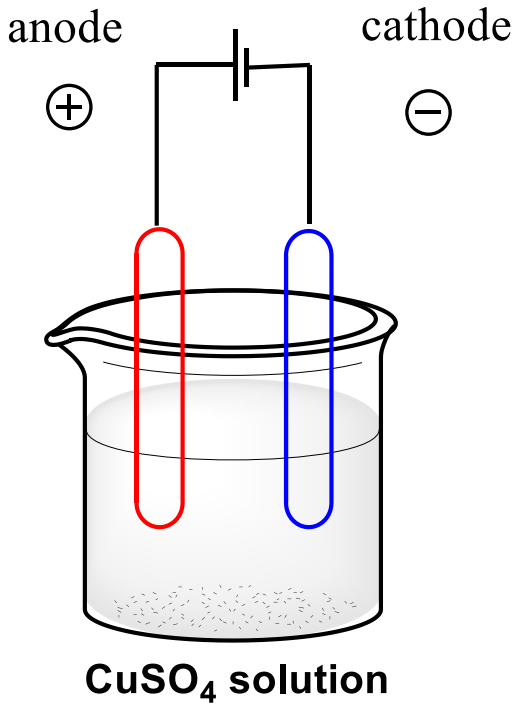
Anode (oxidation)

$2I^-(aq) \longrightarrow I_2(s) + 2e^-$ $\quad E^o = 0.53$ V

$2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-$ $\quad E^o = 1.23$ V

So, I_2 form at anode
H_2 and OH^- form at cathode

Example1: What do you expect to be the half-reactions in the electrolysis of aqueous copper(II) sulfate [$CuSO_4$]?



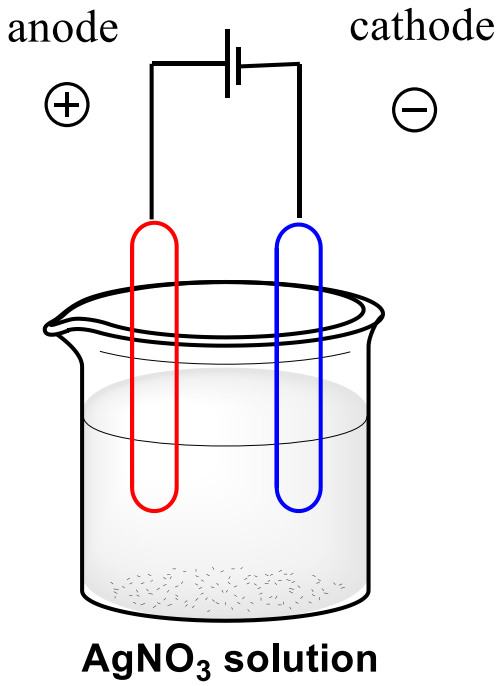
$Cu^{2+} + 2e \rightarrow Cu(s)$ E = +0.34 V

$2H_2O(l) + 2e \rightarrow H_2(g) + 2OH^-(aq)$ E = -0.83 V

$S_2O_8^{2-} + e \rightarrow SO_4^{2-}$ E = 2.01 V

$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$ E = 1.23 V

Example 2: Give the half-reactions that occur when aqueous silver nitrate ($AgNO_3$) is electrolyzed. Nitrate ion is not oxidized during the electrolysis.



$Ag^+ + e \rightarrow Ag(s)$ E = +0.88 V

$2H_2O(l) + 2e \rightarrow H_2(g) + 2OH^-(aq)$ E = -0.83 V

$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$ E = 1.23 V

Example 3: Use half-reactions to show which product forms at each electrode during the electrolysis of aqueous solutions of the following salts:

(a) KBr
(b) $AgNO_3$
(c) $MgSO_4$

$Mg^{2+} + 2e \rightarrow Mg(s)$ E = -2.37 V
$2H_2O(l) + 2e \rightarrow H_2(g) + 2OH^-(aq)$ E = -0.83 V

$S_2O_8^{2-} + e \rightarrow SO_4^{2-}$ E = 2.01 V
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$ E = 1.23 V

$K^+(aq) + e^- \longrightarrow K(s)$ $E^o = -2.93$ V

$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$ $E^o = -0.83$ V

$2Br^-(aq) \longrightarrow Br_2(s) + 2e^-$ $E^o = 1.07$ V

$2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-$ $E^o = 1.23$ V

Electroplating of Metal

depositing a layer of metal on another substance

Electroplating

The process of depositing a layer of metal on another substance using electrolysis is called **electroplating**.

What are the uses of the electroplating?

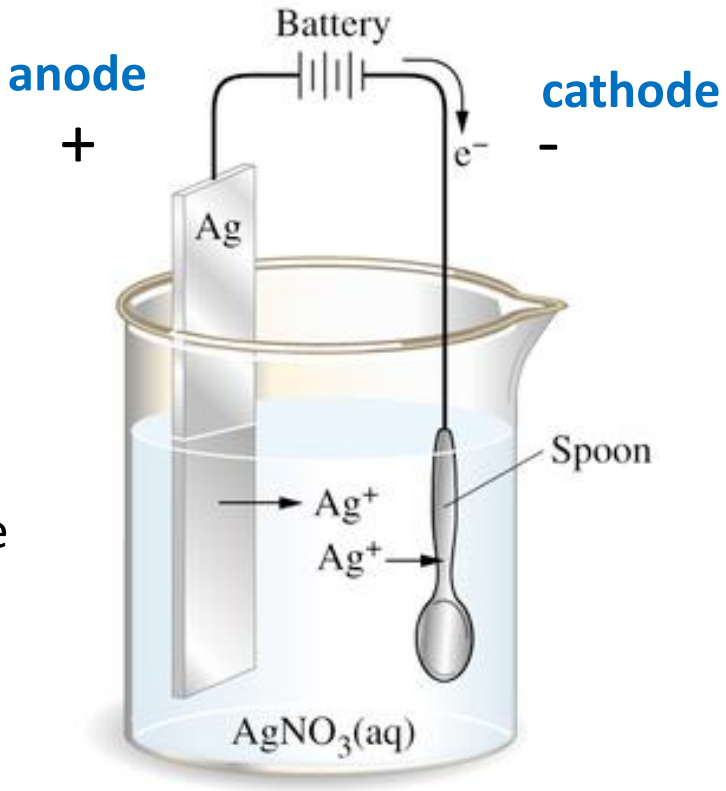
- To give metal objects a better appearance and attraction such as trophies and medals are coated with Gold, silver Brass and rhodium

- To protect metal objects from corrosion or rust e.g. iron plate used in ships which remains in contact with sea water are plated with zinc

Toon, T. Y.; Kwong, C. L.; Sadler, J.; Clare, E. *Chemistry Matters;* Marshall Cavendish Education, 2007.

How are objects electroplated?

- The objective to be plated is made the cathode of the electrolytic cell and anode is the source of the plating metal
- The electrolyte is aqueous solution of a salt of the plating metal.

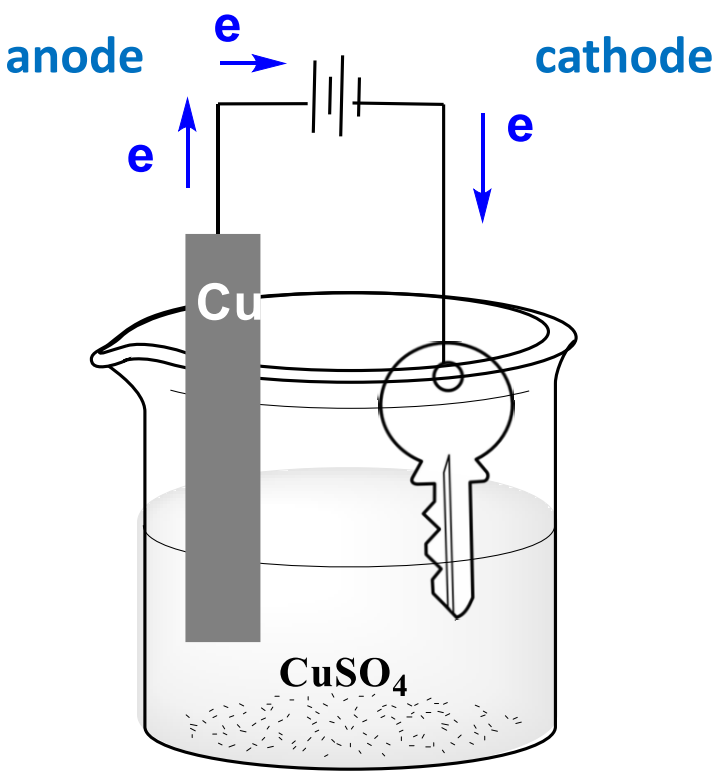


$Ag \rightarrow Ag^+ + e$

$Ag^+ + e \rightarrow Ag$

Toon, T. Y.; Kwong, C. L.; Sadler, J.; Clare, E. *Chemistry Matters;* Marshall Cavendish Education, 2007.

Copper plating



Anode: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$

cathode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Toon, T. Y.; Kwong, C. L.; Sadler, J.; Clare, E. *Chemistry Matters;* Marshall Cavendish Education, 2007.

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3) Zumdahl, S. S. *World of Chemistry; McDougal Littell, 2001.*
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