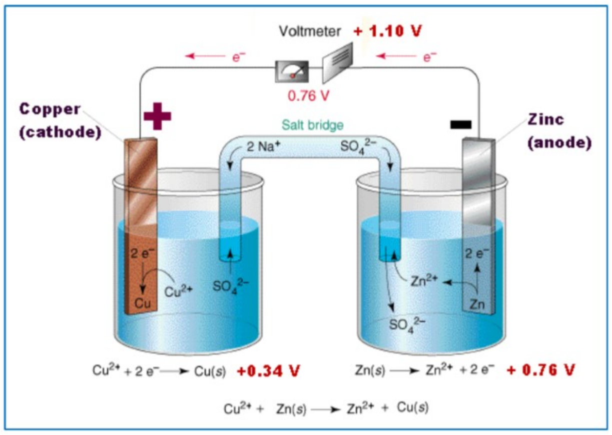
UNIT 10: Electrochemistry (Redox)

Vocabulary:

Anode
Cathode
Electrochemical Cell
Electrode
Electrolytic Cell
Redox
Reduction Half Reaction
Oxidation Half Reaction
Reducing Agent
Oxidizing Agent
Oxidation Number
Half reaction
Galvanic or Voltaic Cell
Salt bridge

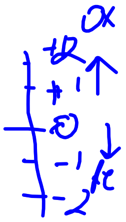


Unit Objectives:

- Define and identify oxidation reactions
- Define and identify reduction reactions
- Assign oxidation numbers to elements in a compound
- Write and balance half reactions
- Identify oxidizing agents and reducing agents
- Distinguish between voltaic and electrolytic cells
- Identify the components of an electrochemical cell
- Indicate the direction of electrons and ions through an electrochemical cell
- Determine, using Table J, whether a reaction if spontaneous or not

REDuction – OXidation Reactions (AKA Redox): rxns that involve the TRANSFER OF ELECTRONS; both reduction and oxidation *must* happen SIMULTANEOUSLY!

Reduction = GAIN OF ELECTRONS by an atom or ion; OXIDATION NUMBER goes DOWN/REDUCES



Oxidation = LOSS OF ELECTRONS by an atom or ion; OXIDATION NUMBER goes UP/INCREASES

A way to remember →

L E O the lion goes **G E R**

Lose e- oxidation gain e- reduction

*Oxidation and reduction happen because of the DESIRE for electrons in a chemical reaction. Species prefer to either LOSE or GAIN electrons in a chemical reaction.

AND

**Oxidation and reduction are MUTUAL or SIMULTANEOUS reactions and one cannot happen without the other. If one atom LOSES electrons, there must be another atom that will GAIN electrons.

Al was oxidized LeO
Cu was reduced GER

Example: $2\ \overset{0}{Al} + 3\ \overset{+2\ -1}{CuCl_2} \rightarrow 2\ \overset{+3\ -1}{AlCl_3} + 3\ \overset{0}{Cu}$

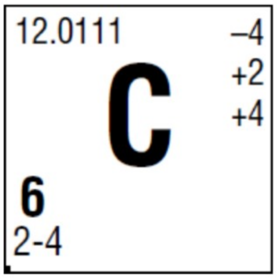
Aluminum is above Cu on Table J so it will replace it! Notice how Al is all by itself (on left of arrow) with a zero charge and then bonded (on right of arrow) where it takes on a charge

IDENTIFYING REDOX REACTIONS

One way that we can begin to **identify a redox reaction** is to inspect the OXIDATION NUMBERS from reactant to product side (for every element involved in the reaction). Oxidation numbers are used to track the MOVEMENT OF ELECTRONS (electron transfer) from reactant to product side of rxn

Oxidation Number (State) = POSITIVE, NEGATIVE, OR NEUTRAL (ZERO) VALUES that can be assigned to atoms; used to identify how many electrons are being lost or gained by an atom/ion when they FORM BONDS

*top listed # to the upper right is the most common oxidation number for that element



Trick 1: SINGLE REPLACEMENT REACTIONS are always REDOX!

Zn oxidized leo

H reduced ger

Ex: ___ $\overset{0}{Zn}_{(s)}$ + ___ $\overset{+1\ -1}{HCl}_{(aq)}$ → ___ $\overset{+2\ -1}{ZnCl}$ + ___ $\overset{0}{H_2}_{(g)}$

*Zn/ H are by themselves on one side and bonded on the opposite side

Trick 2: DOUBLE REPLACEMENT REACTIONS are NOT REDOX! (Never)

Ex: ___ $\overset{+1\ \ -1}{Na(OH)}$ + ___ $\overset{+1\ -1}{HCl}$ → ___ $\overset{+1\ \ -1}{NaCl}$ + ___ $\overset{+1\ \ -1}{H(OH)}$

*charges stay the same for all elements in the rxn

Rules for assigning OXIDATION STATES (numbers):

1) UNCOMBINED ELEMENTS (elements not bonded to another element) have an oxidation number of ZERO.
This includes any formula that has *only* one chemical symbol in it (single elements & diatomic elements).

Examples: $Al(s)^0$ $Na(s)^0$ $Cl_2(g)^0$ $H_2(g)^0$

2) In COMPOUNDS, the sum of the CHARGES for all elements must ADD UP TO ZERO.

Ex: NaCl
Na: 1(+1) = +1
Cl: 1(-1) = -1
0!

Ex: Mg_3N_2
Mg: 3(+2) = 6
N: 2(-3) = -6
0!

Ex: HNO_3
H: 1(+1) = +1
N: 1(+5) = +5
O: 3(-2) = -6
0!

* The OXIDATION NUMBER is the number INSIDE the PARENTHESES. It is the charge on ONE atom of that element!
** Remember that we almost always write the (+) ELEMENT FIRST and the (-) ELEMENT LAST in a compound formula.
*** Trick: You can keep polyatomic ions together and use the charge from Table E to determine the oxidation numbers for those elements.

EXAMPLE: $\overset{+1}{H}\overset{-1}{Cl}$

EXCEPTION to this rule: NH_3

3) GROUP 1 METALS always have a +1 oxidation number when in a compound (bonded to another species).
GROUP 2 METALS always have a +2 oxidation number when located within a compound.

Ox #:
Ex: $\overset{+1}{Li}\overset{-1}{Cl}$ $\overset{+2}{Mg}\overset{-1}{Cl_2}$

4) FLUORINE is always a -1 in compounds. The other HALOGENS (ex: Cl, Br, I) are also -1 as long as they are the most electronegative element in the compound.

Ox #:
Ex: $\overset{+1}{H}\overset{-1}{F}$ $\overset{+2}{Ca}\overset{-1}{Cl_2}$ $\overset{+1}{Na}\overset{-1}{Br}$

5) HYDROGEN is a +1 in compounds unless it is combined with GROUP 1 or GROUP 2 METAL, in which case it is -1.

Ox #:
Ex: $\overset{+1}{H}\overset{-1}{Cl}$ $\overset{+1}{Li}\overset{-1}{H}$

6) OXYGEN is USUALLY -2 in compounds.

Ox #:
Ex: $\overset{+1}{H_2}\overset{-2}{O}$

When combined with Fluorine (F), which is more electronegative, OXYGEN IS +2.

Ox #:
Ex: $\overset{+2}{O}\overset{-1}{F_2}$

When in a PEROXIDE OXYGEN IS -1. A peroxide is a compound that has a formula of X_2O_2.

Ox #:
Ex: $\overset{+1}{Na_2}\overset{-1}{O_2}$ $\overset{+1}{H_2}\overset{-1}{O_2}$

7) The sum of the oxidation numbers in polyatomic ions must equal the CHARGE ON THE ION (SEE TABLE E).

Ex: $Cr_2O_7^{2-}$

Cr: 2(+6) = 12
O: 7(-2) = -14

= -2 (charge on ion)

A reaction is REDOX if…OXIDATION NUMBERS CHANGE FOR 2 ELEMENTS WITHIN A REACTION

Reduction (GER) = GAIN OF ELECTRONS by an atom or ion; OXIDATION NUMBER goes DOWN/REDUCES

Oxidation (LEO) = LOSS OF ELECTRONS by an atom or ion; OXIDATION NUMBER goes UP/ OXIDIZES

Assign oxidation numbers for all elements and complete the tables:

Example 1: $\overset{0}{C} + \overset{+1}{H_2}\overset{-2}{O} \rightarrow \overset{+2}{C}\overset{-2}{O} + \overset{0}{H_2}$

	Charge: Increases/Decreases	e⁻: Lost/Gained	Oxidized/Reduced
C^0	Increase	lose e^-	Oxidized
H^{+1}	Decrease	gain e^-	Reduced

Example 2: $\overset{+4}{Mn}\overset{-2}{O_2} + 4\overset{+1}{H}\overset{-1}{Cl} \rightarrow \overset{+2}{Mn}\overset{-1}{Cl_2} + \overset{0}{Cl_2} + 2\overset{+1}{H_2}\overset{-2}{O}$

	Charge: Increases/Decreases	e⁻: Lost/Gained	Oxidized/Reduced
Cl^{-1}	increase	lost e^-	Oxidized
Mn^{+4}	decrease	gained e^-	reduced

Oxidizing Agent (OA) = SPECIES that is REDUCED; species that DOES THE OXIDIZING

Reducing Agent (RA) = SPECIES that is OXIDIZED; species that DOES THE REDUCING

*NOTE: OA & RA are ALWAYS located on the REACTANT SIDE!

Assign oxidation numbers for all elements and identify the OA and RA:

Example: $\overset{0}{C} + \overset{+1}{H_2}\overset{-2}{O} \rightarrow \overset{+2}{C}\overset{-2}{O} + \overset{0}{H_2}$

OA = H^{+1} (Ger)

RA = C^{0} (Leo)

HALF REACTIONS

Half reactions allow us to show the EXCHANGE OF ELECTRONS in a redox rxn.
For each redox reaction, we can illustrate two HALF REACTIONS.
One half-reaction shows OXIDATION and other shows REDUCTION.

Example of a Reduction Half Reaction:

$$Fe^{3+} + \mathbf{3e-} \rightarrow Fe^{0}$$

*Electrons on left hand side, GAINED in the rxn (GER).
Notice also how the charge for Fe goes down from left to right, REDUCTION (GER). Charge goes down because Fe GAINED e^-.

Example of an Oxidation Half Reaction:

$$Fe^{0} \rightarrow Fe^{3+} + \mathbf{3e-}$$

*Electrons on left hand side, LOST in the rxn (LEO).
Notice also how the charge for Fe goes up from left to right, OXIDATION (LEO). Charge goes up because Fe LOST e^-.

NOTICE: Always ADD ELECTRONS to the side of rxn that has a HIGHER TOTAL CHARGE (remember: electrons are NEGATIVE!)

FOLLOWING THE LAW OF CONSERVATION:

- ✓ Half reactions follow the LAW OF CONSERVATION OF MASS. This means that there must be the SAME NUMBER OF ATOMS on both sides of the reaction arrow.
- ✓ There must also be a CONSERVATION OF CHARGE. In half reactions, the NET CHARGE MUST BE THE SAME ON BOTH SIDES of the equation, although it doesn't necessarily need to equal zero.

RULES FOR SETTING UP HALF REACTIONS

1) Assign oxidation numbers to all elements in reaction
2) Draw brackets and identify oxidation & reduction
3) Begin to set up half reactions. Pull out brackets bringing element symbol and assigned charge with you. Set up as a reaction with arrow connecting two sides that have different oxidation numbers assigned. Only trick: diatomics must be pulled out as a pair. This is the only time you ever "bring subscripts with you" in creating half reactions!
4) FOR REACTIONS INVOLVING DIATOMIC ELEMENTS ONLY: Balance mass 1st (make sure there are the same number of elements on each side of each half reaction)
5) Lastly, balance charge in each half reaction by inserting appropriate amount of electrons into each half reaction to attain conservation of charge. Always add electrons to the side that has a more positive charge. REMEMBER, electrons are negative in nature! Net charges on each side of rxn should be equal after adding electrons.

Assign oxidation numbers to all elements or polyatomic ions. Label the brackets for reduction (red) or oxidation (ox).

Ex. 1:

Red

$$\overset{0}{Mg} + \overset{+2}{Zn}\overset{-1}{Cl_2} \rightarrow \overset{+2}{Mg}\overset{-1}{Cl_2} + \overset{0}{Zn}$$

ox

OXIDATION Half Reaction:

$Mg^0 \rightarrow \underline{Mg^{+2}} + \underline{2e^-}$

REDUCTION Half Reaction:

$Zn^{+2} + \underline{2e^-} \rightarrow \underline{Zn^0}$

Ex. 2 (balance masses):

Ox

$$2\overset{0}{Hg} + \overset{0}{I_2} \rightarrow 2\overset{+1\,-1}{HgI}$$

Red

<u>OXIDATION</u> Half Reaction (make sure to ***<u>balance the masses</u>***):

$2Hg^{0} \rightarrow 2Hg^{+1} + 2e^{-}$

<u>REDUCTION</u> Half Reaction:

$I_2^{0} + 2e^{-} \rightarrow 2I^{-1}$

Ex. 3 (balance charges):

Red

$$\overset{0}{Cu} + 2\overset{+1}{Ag}\underset{-1}{(NO_3)} \rightarrow \overset{+2}{Cu}\underset{-2}{(NO_3)_2} + 2\overset{0}{Ag}$$

Ox

<u>OXIDATION</u> Half Reaction:

$Cu^{0} \rightarrow Cu^{+2} + 2e^{-}$

<u>REDUCTION</u> Half Reaction:

$2Ag^{+1} + 2e^{-} \rightarrow 2Ag^{0}$

Now, we need to ***<u>balance the charges</u>***:

$2 \times (Ag^{+1} + 1e^{-} \rightarrow Ag^{0}) = 2\,Ag^{+1} + 2\,e^{-} \rightarrow 2\,Ag^{0}$

Table J and Spontaneous Reactions

Table J
Activity Series**

Most	Metals	Nonmetals	Most
	Li	F_2	
	Rb	Cl_2	
	K	Br_2	
	Cs	I_2	
	Ba		
	Sr		
	Ca		
	Na		
	Mg		
	Al		
	Ti		
	Mn		
	Zn		
	Cr		
	Fe		
	Co		
	Ni		
	Sn		
	Pb		
	**H_2		
	Cu		
	Ag		
Least	Au		Least

**Activity Series based on hydrogen standard

Note: H_2 is *not* a metal

General Rule: elements higher on Table J are more reactive than the elements below them

Spontaneous rxn = rxn occurs w/out adding energy to system

- If the "single" element is more active than the "combined" element, the reaction will be spontaneous.

Non-spontaneous rxn = rxn will not occur unless energy is added to system

- If the "single" element is less active than the "combined" element, the reaction will NOT be spontaneous.

Complete the following equations by writing in the products formed or "no rxn"

Ex 1: $Zn + PbCl_2 \rightarrow ZnCl_2 + Pb^{\circ}$

Ex 2: $Zn + BaO \rightarrow$ no rxn

Ex 3: $Ca + CrF_2 \rightarrow CaF_2 + Cr^{\circ}$

Ex 4: $Mn + NiS \rightarrow MnS + Ni^{\circ}$

Ex 5: $Fe + MgI_2 \rightarrow$ No rxn

Ex 6: $Co + PbCl_2 \rightarrow CoCl_2 + Pb^{\circ}$

TWO TYPES of ELECTROCHEMICAL CELLS

1. Voltaic (similar to a battery)
2. Electrolytic (similar to alternator in cars)

SIMILARITIES BETWEEN THE TWO:

- Both involve REDOX reactions; CHEMICAL REACTIONS which involve the flow of ELECTRONS
- Both involve the flow of ELECTRICAL ENERGY, or CURRENT, measured in VOLTS
- Both have 2 ELECTRODES (conductive surfaces where oxidation or reduction occurs); called the ANODE and the CATHODE
- OXIDATION **or** REDUCTION occurs in each half cell

RED CAT	AN OX
Reduction ALWAYS occurs at the cathode (ions gain e-)	Oxidation ALWAYS occurs at the anode (metal loses e-)

- Electrons flow through the WIRE from the ANODE to the CATHODE.

Voltaic Cells

- Cells that SPONTANEOUSLY convert CHEMICAL energy into ELECTRICAL energy or electric CURRENT.
- BATTERIES

CATHODE

- The LESS ACTIVE of the 2 metals (Table J)
- SPONTANEOUSLY ATTRACTS ELECTRONS to it
- the POSITIVE electrode in a VOLTAIC CELL
- electrode where REDUCTION occurs (RED CAT)

ANODE

- The MORE ACTIVE of the 2 metals (Table J)
- SPONTANEOUSLY LOSES ELECTRONS to cathode
- the NEGATIVE electrode in a VOLTAIC CELL
- electrode where OXIDATION occurs (AN OX)

Example 1: Wet Cell

- CAR BATTERIES, are a form of LEAD STORAGE battery

- Consists of LEAD ANODE and LEAD OXIDE CATHODE
- Both electrodes immersed in a SULFURIC ACID solution
- Advantage: process is readily REVERSIBLE (by alternator)
- Disadvantage: very HEAVY, somewhat DANGEROUS

Example 2: Dry Cell

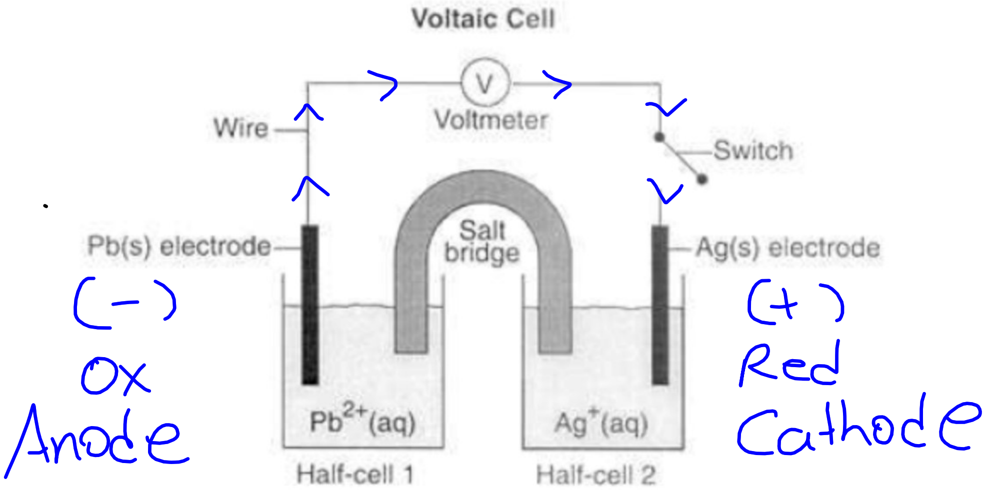
- DRY CELL BATTERIES are the type of batteries in a portable radio, remote control, etc.

- CARBON (GRAPHITE) CATHODE surrounded by moist electrolyte paste
- Usually ZINC ANODE

***SALT BRIDGE**

- provides a path for the FLOW OF IONS between the half-cells
- prevents the BUILD-UP OF CHARGE

Voltaic Cells (a.k.a Galvanic Cells)



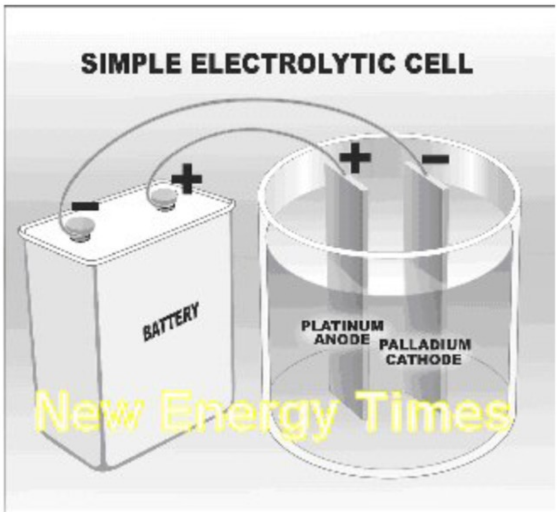
1. Use Table J to predict the direction that electrons will *spontaneously* flow. Draw arrows to indicate the direction on the wire.
2. Based on your answer above, which would be the negative electrode and which would be the positive electrode? Ag = (+) Pb = (−)
3. Explain your answer to #2. Pb is more reactive than Ag, so electrons will flow from Pb to Ag.
4. At which electrode or in which half-cell does reduction occur? Ag
5. At which electrode or in which half-cell does oxidation occur? Pb
6. Which electrode is the cathode? Ag
7. Which electrode is the anode? Pb

Electrons don't flow* **to *the cathode, they flow* **through** *it to the ions in solution. That's why the cathode never becomes negative.*

Electrolytic Cells

- Cells that use ELECTRICAL ENERGY to force a NONSPONTANEOUS CHEMICAL REACTION to occur.
- This process is for ELECTROLYSIS and ELECTROPLATING

Example: ALTERNATOR IN CAR (keeps the car battery replenished with energy)



CATHODE

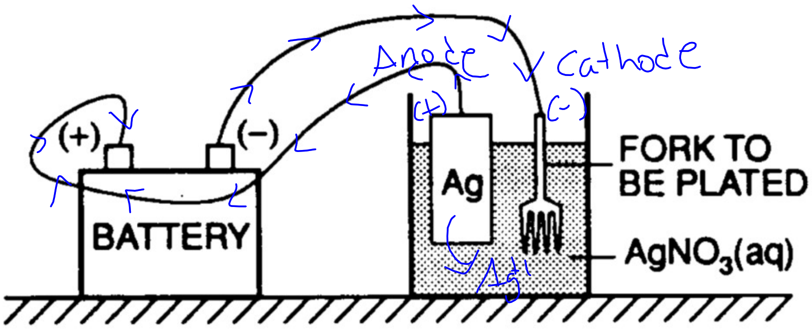
- electrode where ELECTRONS are SENT
- the NEGATIVE electrode (opposite of voltaic cell)
- electrode where REDUCTION occurs (RED CAT)

ANODE

- electrode where ELECTRONS are DRAWN AWAY FROM
- the POSITIVE electrode (opposite of voltaic cell)
- electrode where OXIDATION occurs (AN OX)

NOTICE:

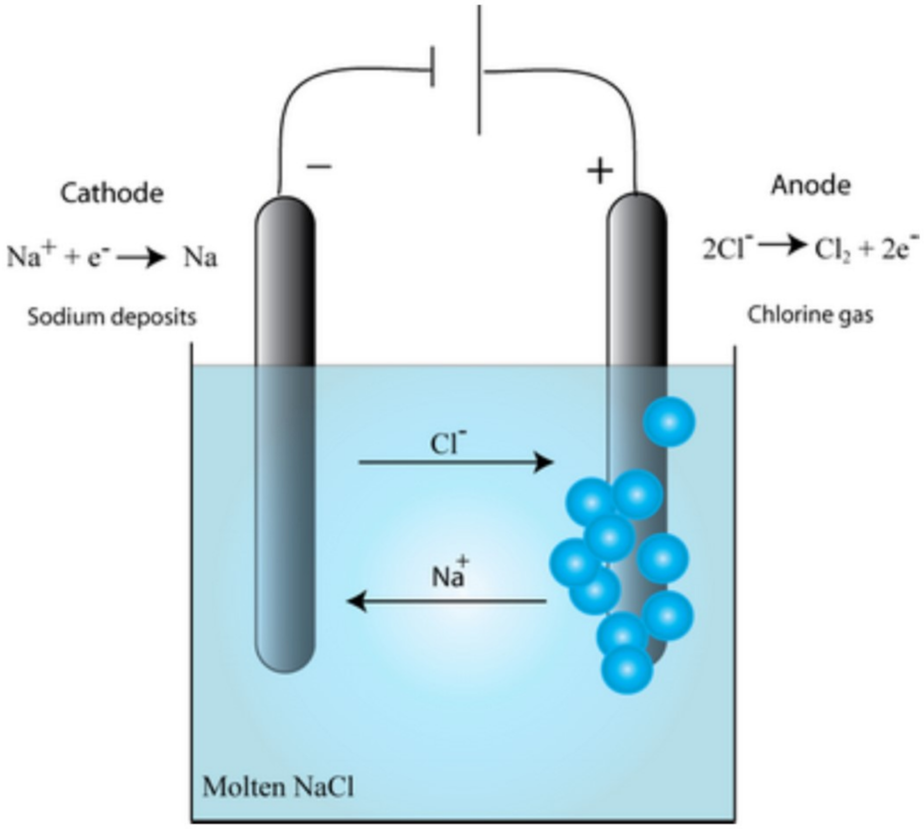
- There is NO SALT BRIDGE. This is a forced chemical reaction.
- You will always see a POWER SOURCE hooked up to an electrolytic cell which drives the FORCED RXN



1. Predict the direction that electrons will flow. Draw arrows to indicate the direction on the wires.
2. Based on your answer above, which would be the negative electrode and which would be the positive electrode? Fork(-) Ag(+)
3. Explain your answer to #2. e^- FORCED onto fork by battery
4. At which electrode does reduction occur? Fork
5. At which electrode does oxidation occur? Ag(s)
6. Which electrode is the cathode? Fork
7. Which electrode is the anode? Ag(s)

Electrolysis of a Fused Salt

- FUSED SALT = MOLTEN SALT = MELTED SALT
- ELECTROLYSIS is used to ISOLATE ACTIVE METALS
  - Metals that are not found alone/uncombined in nature
  - GROUP 1 and GROUP 2 Metals



ex: batteries ex: electroplating electrolysis

Compare and contrast the two types of electrochemical cells:

	GALVANIC/VOLTAIC	ELECTROLYTIC
Flow of e⁻ (spontaneous or forced)	Spontaneous ↓e⁻	Forced ↓e⁻
(+) electrode	Cathode	Anode
(-) electrode	Anode	Chathode
*Direction of e⁻ flow	Anode → Cathode	Anode → Cathode
Reduction ½ cell	Cathode	Cathode
Oxidation ½ cell	Anode	Anode

*Direction of e⁻ flow is either "Anode → Cathode" or "Cathode → Anode"

***<u>Fuel Cells</u>**: galvanic cells for which the reactants are continuously supplied.