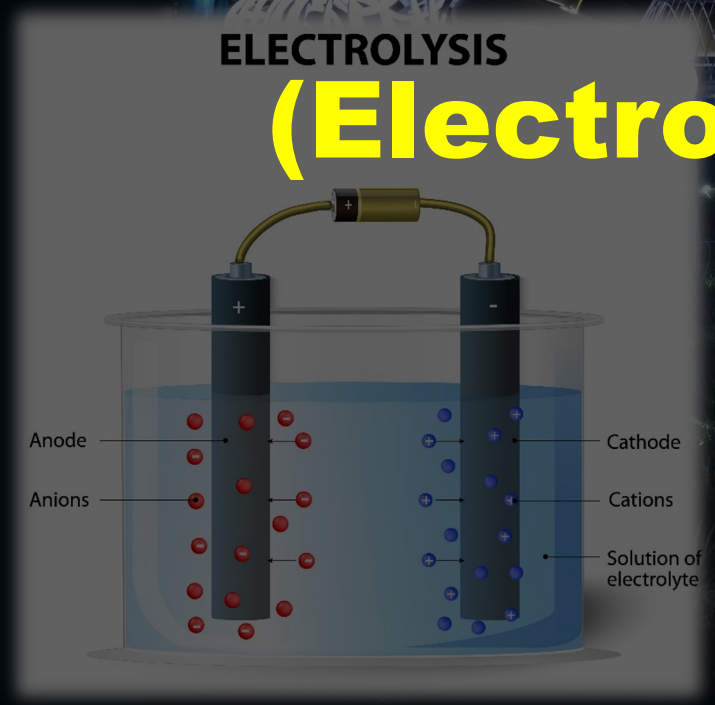
Electrochemistry & Oxidation-Reduction Reactions

(Electrochemical Fundamentals)



Michael Faraday

Reduction-Oxidation (Redox) Reactions

Reduction-oxidation (redox) reactions are reactions in which electrons are transferred from one substance to another. Two easy mnemonics for this subject are:

Losing
Electrons is
Oxidation

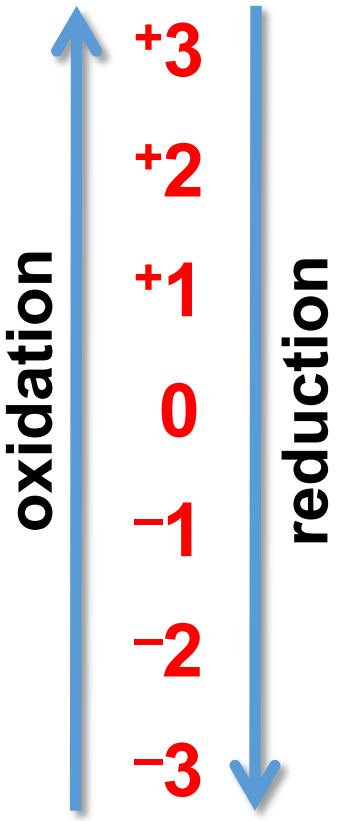
Oxidation
Is
Losing

Gaining
Electrons
Reduction

Reduction
Is
Gaining

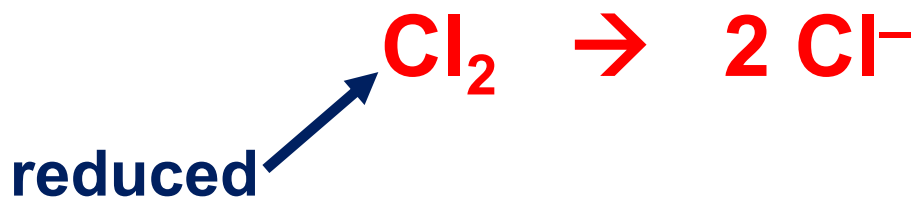
Reduction-Oxidation (Redox) Reactions

Another way to remember this is that when an atom's charge *goes down*, that atom has been reduced. If the atom's charge *goes up*, then it has been oxidized.

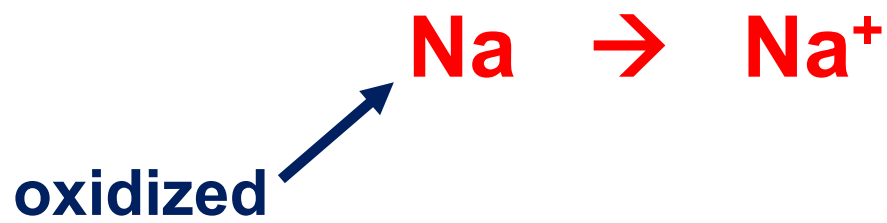


Reduction-Oxidation (Redox) Reactions

In the following transformation, going from left-to-right, has chlorine been oxidized or reduced?



In the following transformation, going from left-to-right, has sodium (Na) been oxidized or reduced?



Reduction-Oxidation (Redox) Reactions

In ***redox reactions***, the element or reactant that *gives up* its electrons (get oxidized) is called the ***reducing agent*** or ***reductant***.

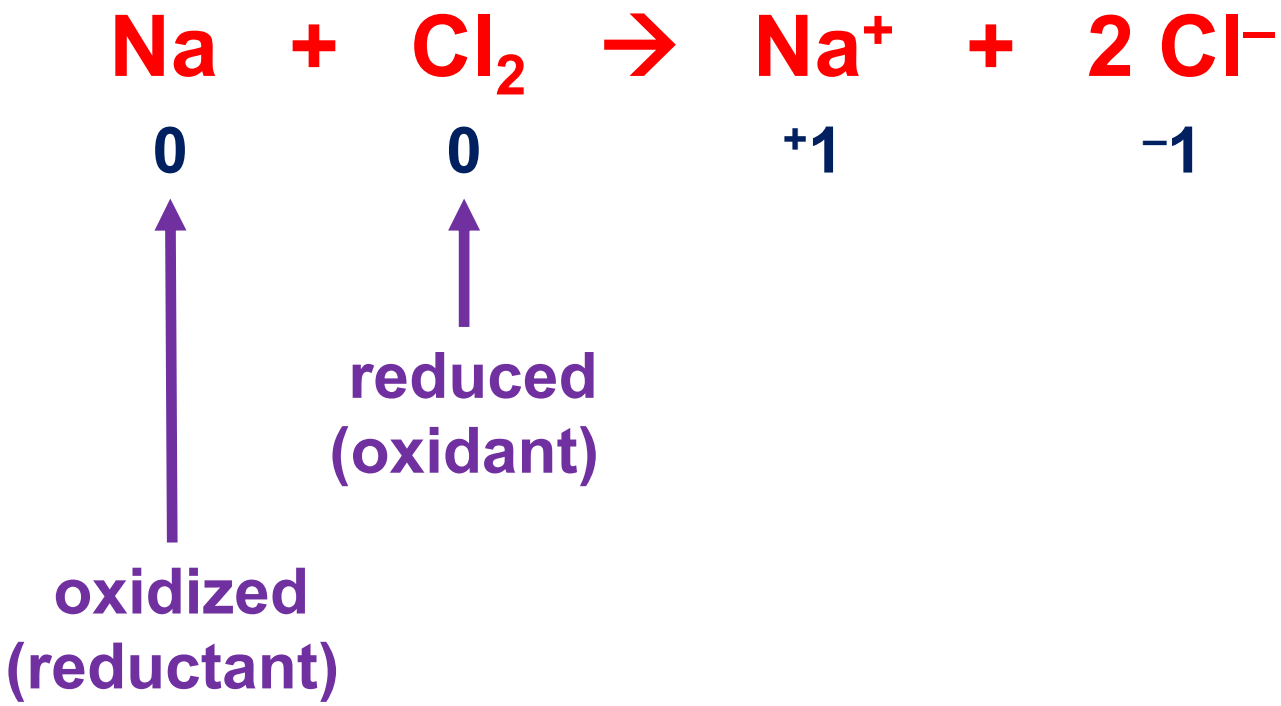
- This can be confusing. Just remember: if you add the word "agent," then it means the opposite. The ***reductant*** (***reducing agent***) is the reactant that *gets oxidized*.
- Why? Because the ***reductant*** is the thing that *reduces* the other reactant. It does that by giving electrons to the other reactant and thereby getting oxidized itself.

In contrast, the element or reactant that *receives* electrons (gets reduced) is called the ***oxidizing agent*** (or ***oxidant***).

- By analogy, the ***oxidant*** (***oxidizing agent***) is the reactant that *gets reduced*.
- Why? Because the ***oxidant*** is the thing that *oxidizes* the other reactant. It does that by accepting electrons from the *other* reactant and thereby getting reduced itself.

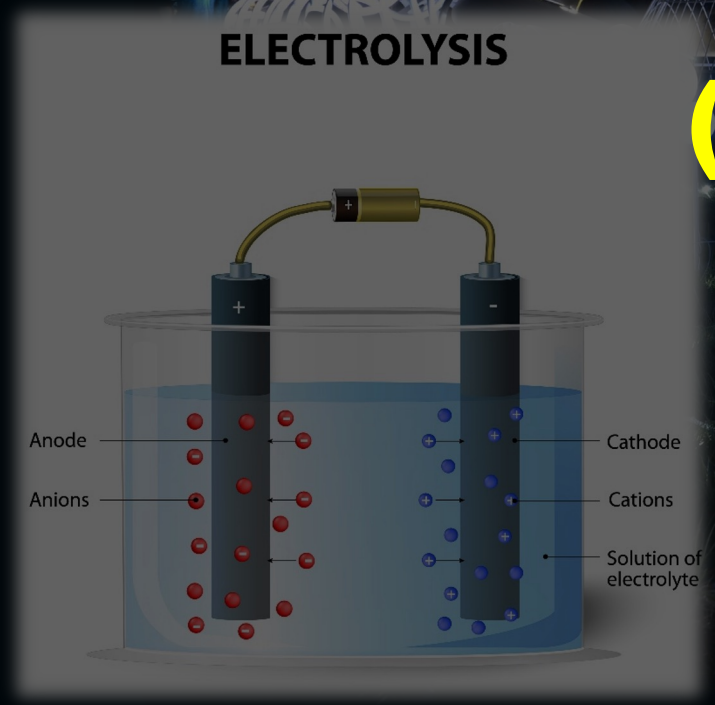
Reduction-Oxidation (Redox) Reactions

In the following reaction, which substance (Na or Cl) is the reductant, and which one is the oxidant?



Electrochemistry & Oxidation-Reduction Reactions

(Oxidation States)



Michael Faraday

Oxidation Numbers (an Intro)

In our prior video, I taught you that ***reduction-oxidation (redox) reactions*** are reactions in which electrons are transferred from one substance to another.

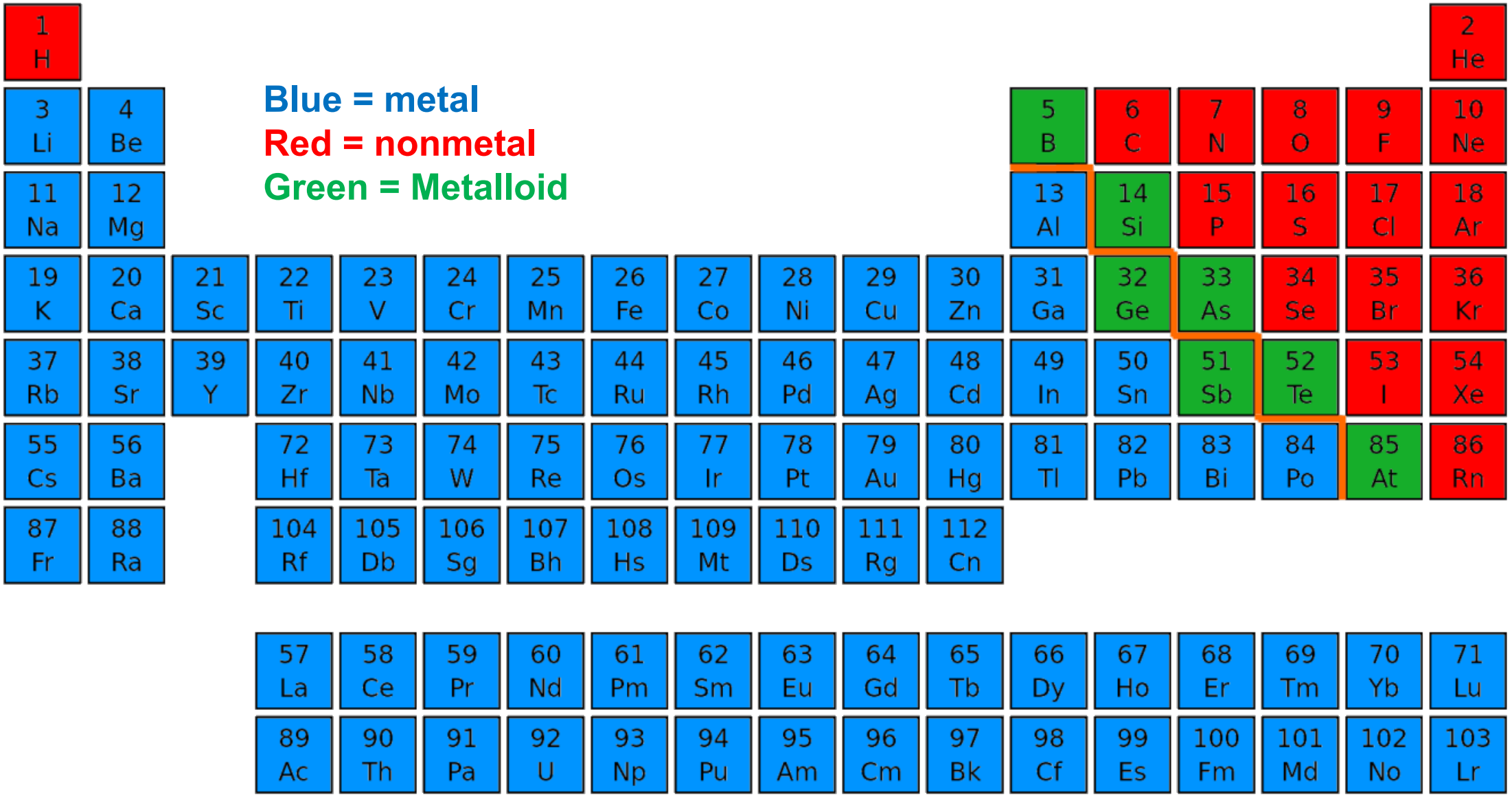
I also taught you that the substance that *gives electrons away* gets ***oxidized*** and is called the ***reductant*** (***reducing agent***). In contrast, the substance that *accepts* electrons gets ***reduced*** and is called the ***oxidant*** (***oxidizing agent***). We can remember this by memorizing the mnemonics ***OIL RIG*** or ***LEO*** the lion says ***GER***.

To be able to better track and identify ***reductants*** and ***oxidants***, chemists created something called ***oxidation numbers***. These are used primarily as a simple way of identifying which atoms get oxidized and which ones get reduced. ***Oxidation numbers*** are not an *absolutely true* reflection of actual atoms' true charges. It's just a system that helps us identify ***reductants*** and ***oxidants***.

Type of element:	Oxidation number:
Uncharged atoms all by themselves or only bonded to other atoms of the same element (like H_2, Na, Cl_2, Al, etc.)	Zero
monatomic ions (K^+, S^{2-}, Mg^{2+}, Al^{3+}, etc.)	the ion's charge
Nonmetals	• Usually negative. • Fluorine is always –1. Other halogens are usually –1, but *can* be positive if bonded to oxygen. • Oxygen is usually $^-2$, except in peroxides (like H_2O_2), where it's –1. • Hydrogen is +1 when bonded to nonmetals and –1 when bonded to metals.

Also, the combined oxidation numbers of all atoms in your compound should add up to your compound's total charge.

Where are metals, non-metals, and metalloids?



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Also, the combined oxidation numbers of all atoms in your compound should add up to your compound's total charge.

Oxidation Numbers

Other tips:

- Unless they are uncharged atoms all by themselves, Group 1 metals are +1, and Group 2 metals are +2. For example, in NaCl, Na's oxidation state is +1. In $BaCl_2$, Ba's oxidation state is +2.
- Except when existing as uncharged atoms all by themselves, Al is +3, Zn is +2, Cd is +2, and Ag is +1.
- Transition elements' (d-block metals') oxidation numbers must be determined from the other elements in the compound.
- The most electronegative atoms get their typical oxidation state.
- When assigning oxidation numbers, the last element assigned gets whatever number balances the charge for the entire compound.

Polyatomic Ions

This is a great time to remind you that you need to memorize certain ***polyatomic ions***' names, formulas, and charges. These are the ones that I personally make my university students memorize for freshman chemistry.

Cations

Ammonium **NH_4^+**

Anions

acetate CH_3COO^-

Cyanide CN^-

Nitrate NO_3^-

Phosphate PO_4^{3-}

sulfate SO_4^{2-}

carbonate CO_3^{2-}

hydroxide HO^-

permanganate MnO_4^-

Polyatomic Ions

This is a great time to remind you that you need to memorize certain ***polyatomic ions***' names, formulas, and charges. These are the ones that I personally make my university students memorize for freshman chemistry.

However, the EXAM requires you to **memorize** a lot more!

+1 CHARGE		-1 CHARGE		-2 CHARGE		-3 CHARGE	
ion	**name**	**ion**	**name**	**ion**	**name**	**ion**	**name**
NH_4^+	ammonium	$H_2PO_3^-$	dihydrogen phosphite	HPO_3^{2-}	hydrogen phosphite	PO_4^{3-}	phosphate
H_3O^+	hydronium	$H_2PO_4^-$	dihydrogen phosphate	HPO_4^{2-}	hydrogen phosphate	AsO_3^{3-}	arsenite
Hg_2^{2+}	mercury(I)	HCO_3^-	hydrogen carbonate	CO_3^{2-}	carbonate	AsO_4^{3-}	arsenate
		HSO_3^-	hydrogen sulfite	SO_3^{2-}	sulfite	N^{3-}	nitride
		HSO_4^-	hydrogen sulfate	SO_4^{2-}	sulfate		
		NO_2^-	nitrite	$S_2O_3^{2-}$	thiosulfate		
		NO_3^-	nitrate	$C_2O_4^{2-}$	oxalate		
		OH^-	hydroxide	CrO_4^{2-}	chromate		
		CH_3COO^-	acetate	$Cr_2O_7^{2-}$	dichromate		
		CrO_2^-	chromite	O_2^{2-}	peroxide		
		CN^-	cyanide	S_2^{2-}	disulfide		
		CNO^-	cyanate	O^{2-}	Oxide		
		CNS^-	thiocyanate	S^{2-}	Sulfide		
		MnO_4^-	permanganate				
		ClO^-	hypochlorite				
		ClO_2^-	chlorite				
		ClO_3^-	chlorate				
		ClO_4^-	perchlorate				
		BrO^-	hypobromite				
		BrO_2^-	bromite				
		BrO_3^-	bromate				
		BrO_4^-	perbromate				
		IO^-	hypoiodite				
		IO_2^-	iodite				
		IO_3^-	iodate				
		IO_4^-	periodate				
		N_3^-	azide				

Examples

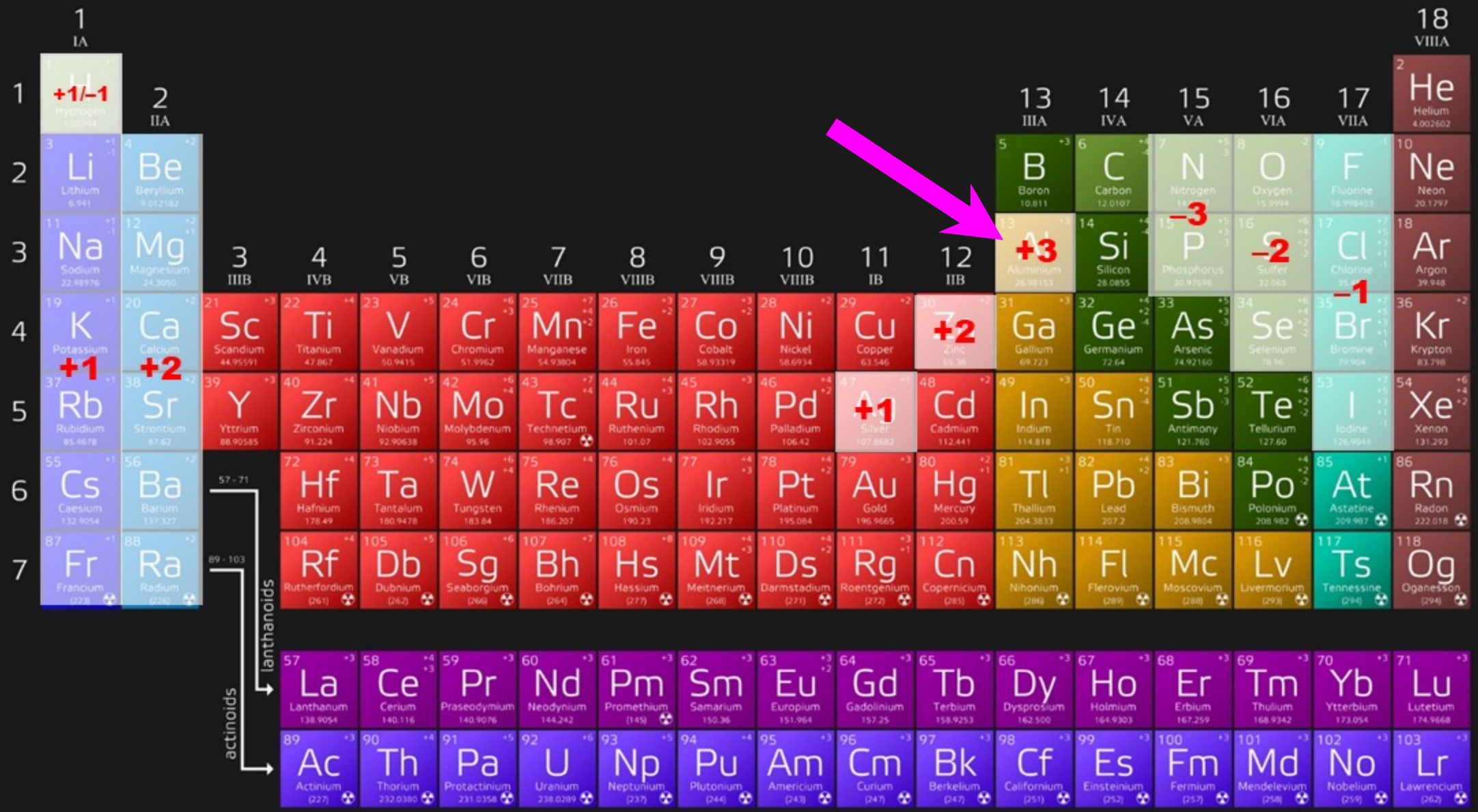
Assign oxidation states for all of the atoms to the following:

- Al_2O_3
- Na_2SO_3
- H_2O_2
- $C_2H_3O_2^{1-}$

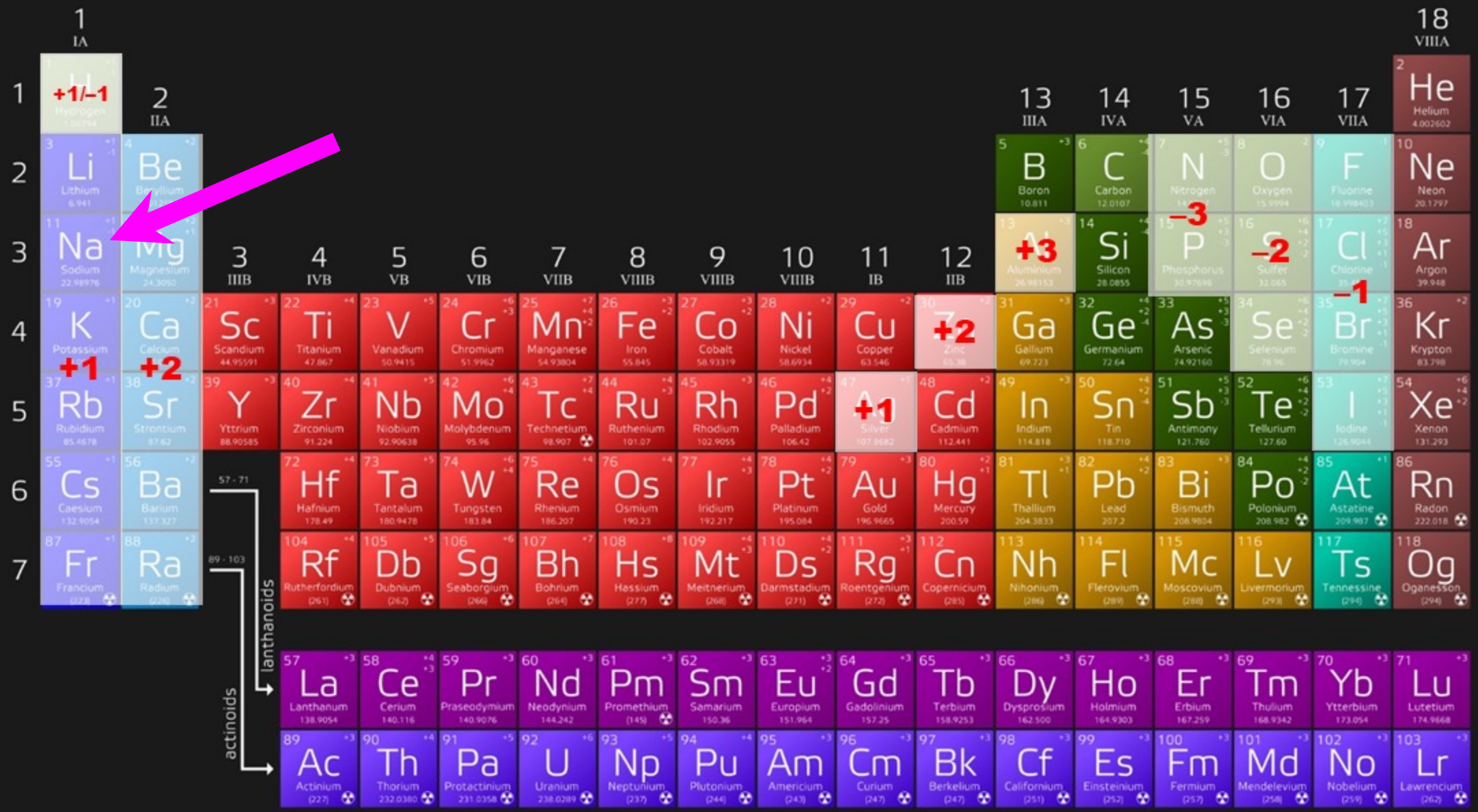
Type of element:	Oxidation number:
Uncharged atoms all by themselves or only bonded to other atoms of the same element (like H_2, Na, Cl_2, Al, etc.)	Zero
monatomic ions (K^+, S^{2-}, Mg^{2+}, Al^{3+}, etc.)	the ion's charge
Nonmetals	• Usually negative. • Fluorine is always –1. Other halogens are usually –1, but *can* be positive if bonded to oxygen. • Oxygen is usually $^-2$, except in peroxides (like H_2O_2), where it's –1. • Hydrogen is +1 when bonded to nonmetals and –1 when bonded to metals.

Also, the combined oxidation numbers of all atoms in your compound should add up to your compound's total charge.

Predicting An Ion's Charge



Predicting An Ion's Charge



Examples

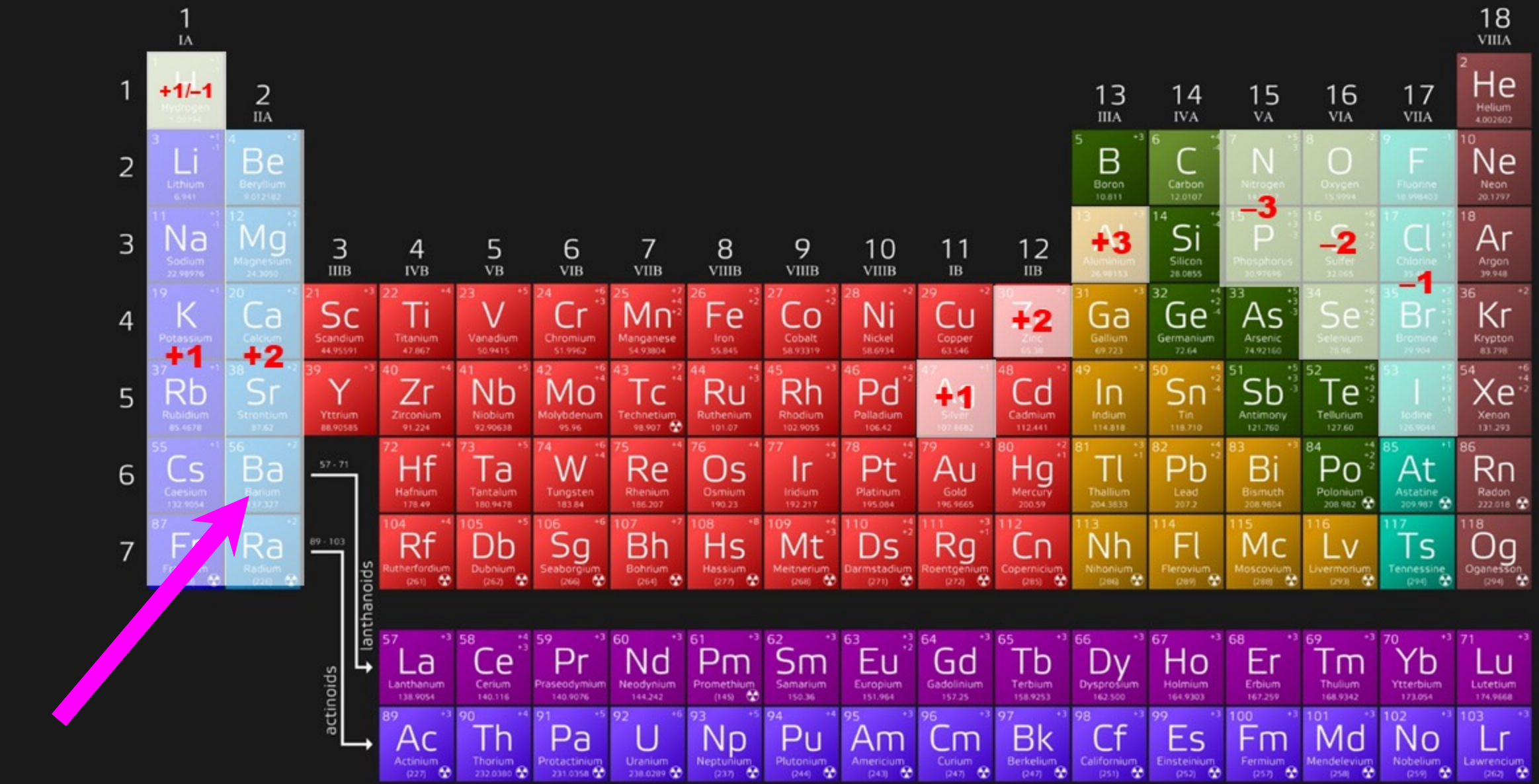
For the following chemical reaction:

$$Ba_{(s)} + Cl_{2\,(g)} \rightarrow BaCl_{2\,(s)}$$

. . . Please assign the oxidation state for each element on both sides of the equation. Then answer the following questions:

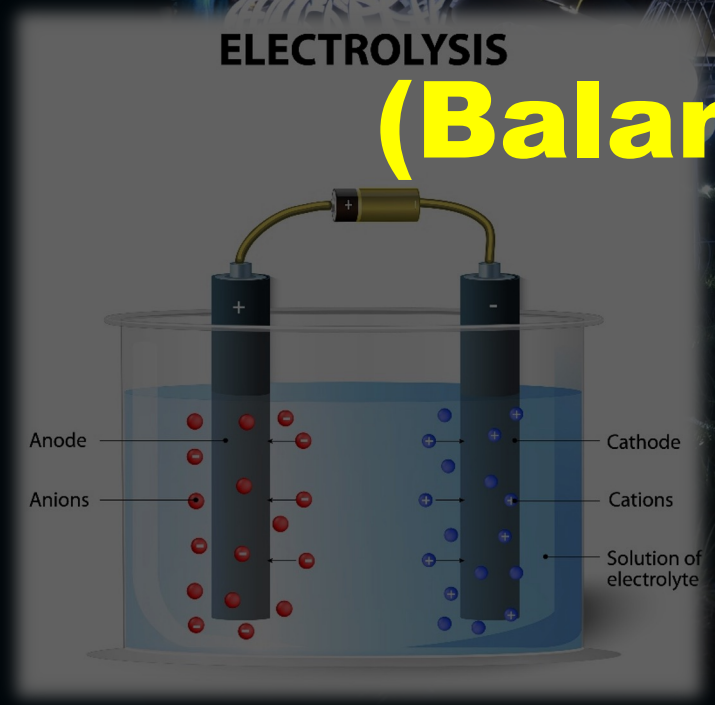
- Which reactant gets oxidized?
- Which reactant gets reduced?
- What is the reducing agent?
- What is the oxidizing agent?

Predicting An Ion's Charge



Electrochemistry & Oxidation-Reduction Reactions

(Balancing Redox Reactions)



Michael Faraday

Balancing Redox Reactions

In order to get a clearer and more mathematically-accurate picture of what's going on in any particular ***redox*** reaction, electrochemists sometimes go through the process of *balancing* that ***redox reaction***.

This process essentially involves taking the *overall* reaction and separating its oxidation and reduction components into two individual equations called ***half-reactions***.

We then do some other stuff to those ***half-reactions***, which enables us (once again) to obtain a clearer and more mathematically-accurate picture of what's going on.

Balancing Redox Reactions

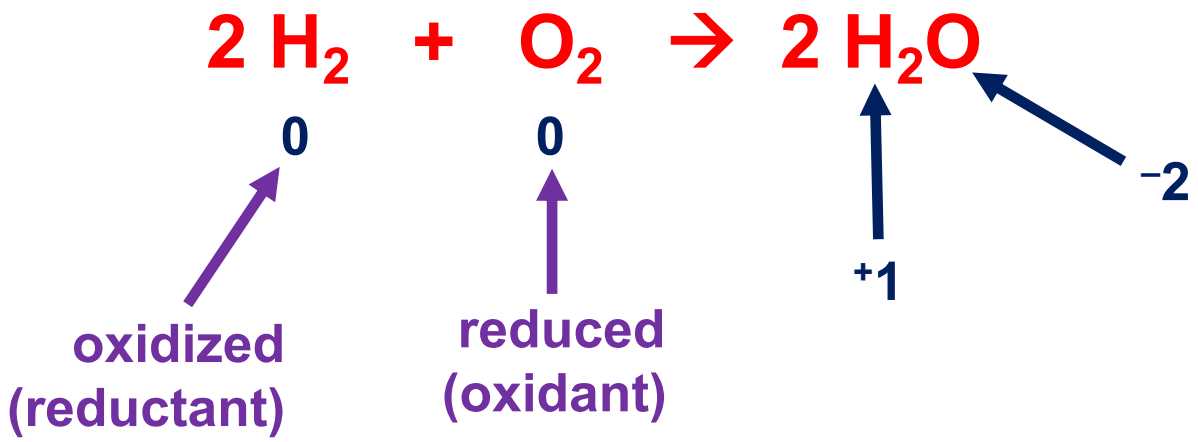
For example, let's examine following redox reaction:

$$2\,H_2 + O_2 \rightarrow 2\,H_2O$$

Type of element:	Oxidation number:
Uncharged atoms all by themselves or only bonded to other atoms of the same element (like H_2, Na, Cl_2, Al, etc.)	Zero
single-atom ions (K^+, S^{2-}, Mg^{2+}, Al^{3+}, etc.)	the ion's charge
Nonmetals	• Usually negative. • Fluorine is always –1. Other halogens are usually –1, but *can* be positive if bonded to oxygen. • Oxygen is usually –2, except in peroxides (like H_2O_2), where it's –1. • Hydrogen is +1 when bonded to nonmetals and –1 when bonded to metals.

Balancing Redox Reactions

For example, let's examine following redox reaction:



As you can see, in this reaction, H_2 gets oxidized, while O_2 gets reduced. If we wanted, then, we could separate the oxidation and reduction processes into two separate equations (or ***half-reactions***) . . .

Balancing Redox Reactions

$$2\,H_2 + O_2 \rightarrow 2\,H_2O$$

. . . Like this:

- **Oxidation**

$$2\,H_2 \rightarrow 4\,H^+ + 4\,e^-$$

- **Reduction**

$$4\,e^- + O_2 \rightarrow 2\,O^{2-}$$

How to Balance Redox Reactions

(Acidic Conditions)

- **Step 1:** Identify what is getting oxidized and what is getting reduced.
- **Step 2:** Separate the oxidation reaction from the reduction reaction. (These two reactions you've now written are called ***half-reactions***.)
- **Step 3:** Balance all the atoms that are NOT oxygen or hydrogen.
- **Step 4:** Balance oxygen atoms by adding $\mathbf{H_2O}$ to whichever side is needed.
- **Step 5:** Balance hydrogen atoms by adding $\mathbf{H^+}$ to whichever side is needed.
- **Step 6:** Add $\mathbf{e^-}$ wherever necessary, to balance the charge on each side of the equation.
- **Step 7:** As needed, add integers to your ***half-reactions*** to make the number of moles of $\mathbf{e^-}$ equal in each of your ***half-reactions***. This final, balanced number of $\mathbf{e^-}$ is the number of overall electrons-per-mole that get transferred in this particular ***redox reaction***.

How to Balance Redox Reactions

(Basic Conditions)

- **Steps 1-5:** The same as for acidic conditions.
- **Step 6:** For each H^+ you added to your ***half-reactions***, now add the same number of OH^-'s to both sides of the equation. Now, wherever an H^+ and an OH^- appear on the same side an equation, combine them to form H_2O's.
- **Step 7:** Add e^- wherever necessary, to balance the charge on each side of the equation.

  Step 8: As needed, add integers to your ***half-reactions*** to make the number of moles of e^- equal in each of your ***half-reactions***. This final, balanced number of e^- is the number of overall electrons-per-mole that get transferred in this particular ***redox reaction***.

Examples

The following reaction:

$$Cr(C_2H_3O_2)_3 + Zn_{(s)} \rightarrow Cr_{(s)} + ZnSO_4$$

. . . is a _____-electron process.

Type of element:	Oxidation number:
Uncharged atoms all by themselves or only bonded to other atoms of the same element (like H_2, Na, Cl_2, Al, etc.)	Zero
monatomic ions (K^+, S^{2-}, Mg^{2+}, Al^{3+}, etc.)	the ion's charge
Nonmetals	• Usually negative. • Fluorine is always –1. Other halogens are usually –1, but *can* be positive if bonded to oxygen. • Oxygen is usually $^-2$, except in peroxides (like H_2O_2), where it's –1. • Hydrogen is +1 when bonded to nonmetals and –1 when bonded to metals.

Also, the combined oxidation numbers of all atoms in your compound should add up to your compound's total charge.

Examples

Please balance the following ***redox*** reaction under acidic conditions:

$$MnO_4^{1-}{}_{(aq)} + Cl^-{}_{(aq)} \rightarrow MnO_{2\,(aq)} + Cl_{2\,(l)}$$

- This redox reaction is a _____-electron process.

Examples

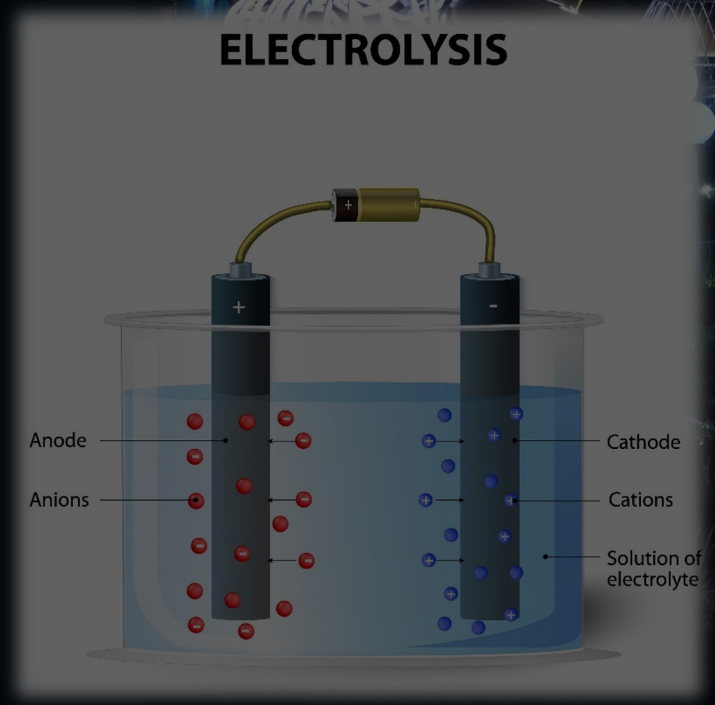
Please balance the following ***redox*** reaction under basic conditions:

$$MnO_4^{1-}{}_{(aq)} + Cl^-{}_{(aq)} \rightarrow MnO_2{}_{(aq)} + Cl_2{}_{(l)}$$

- This redox reaction is a _____-electron process.

Electrochemistry & Oxidation-Reduction Reactions

(Voltaic Cells)

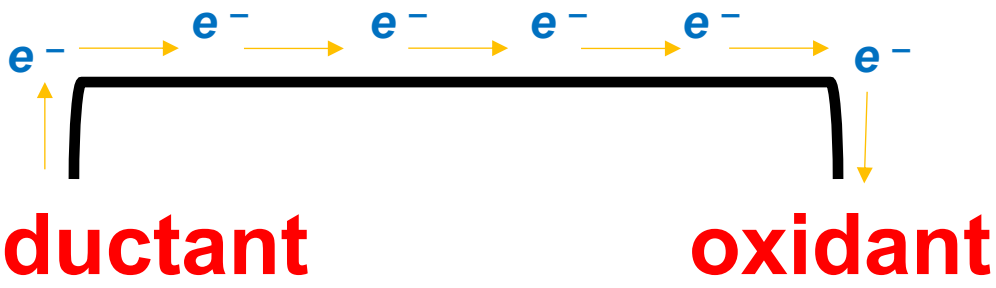


Michael Faraday

Galvanic (Voltaic) Cells

As we've already learned in this chapter, in ***redox reactions***, one substance (called the ***reductant***) passes electrons to another substance (called the ***oxidant***).

What do you think would happen if you separated the ***reductant*** from the ***oxidant*** and then placed a wire between them? If you did that, then the electrons would flow through the wire, from the ***reductant*** to the ***oxidant***, as the ***redox*** reaction proceeded.



Galvanic (Voltaic) Cells

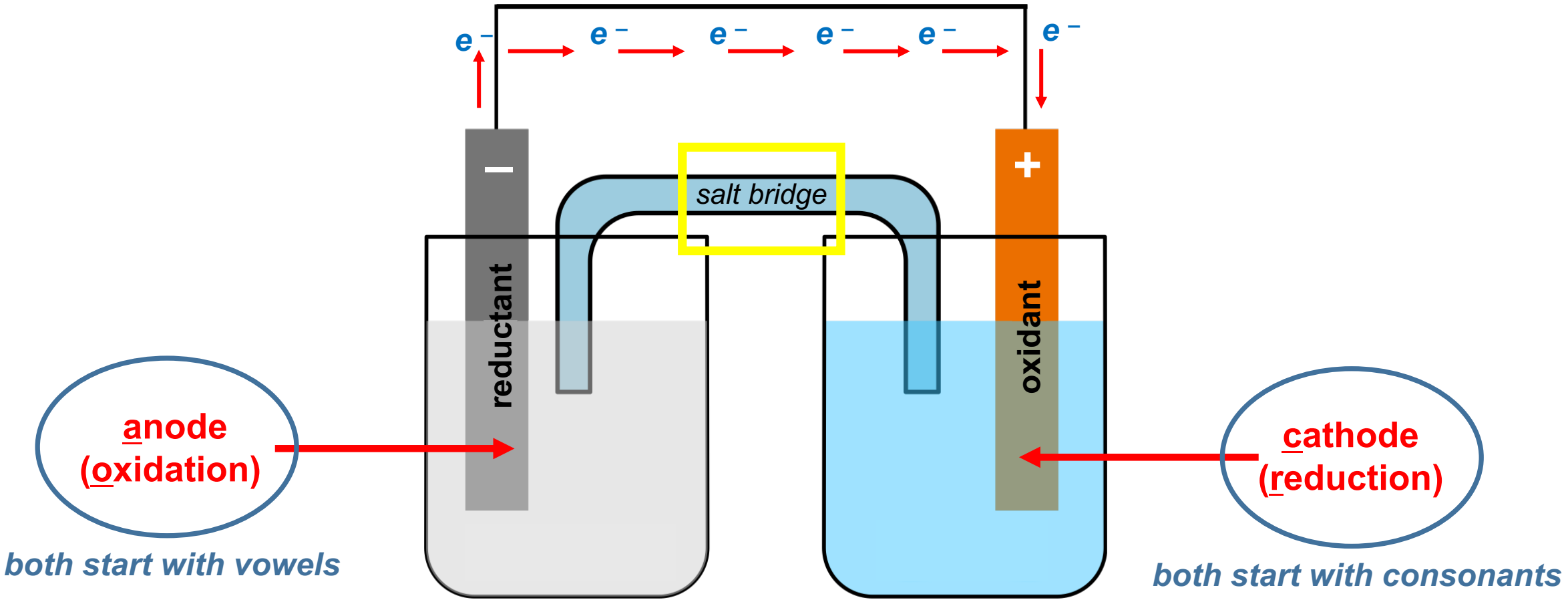
This kind of setup is called a ***battery***. Okay, technically, it's actually called a ***galvanic cell*** or a ***voltaic cell***. Strictly speaking, ***batteries*** can either be single ***galvanic*** or ***voltaic cells***, or multiple cells placed together.

But the chemistry is the same. Batteries work by running a ***redox reaction*** in which the ***reductant*** and ***oxidant*** are in separate chambers, with some kind of wire connecting the two. As electrons flow from the ***reductant*** to the ***oxidant*** (their flow, by the way, is called ***current***), the energy of that flow can be used to power devices.

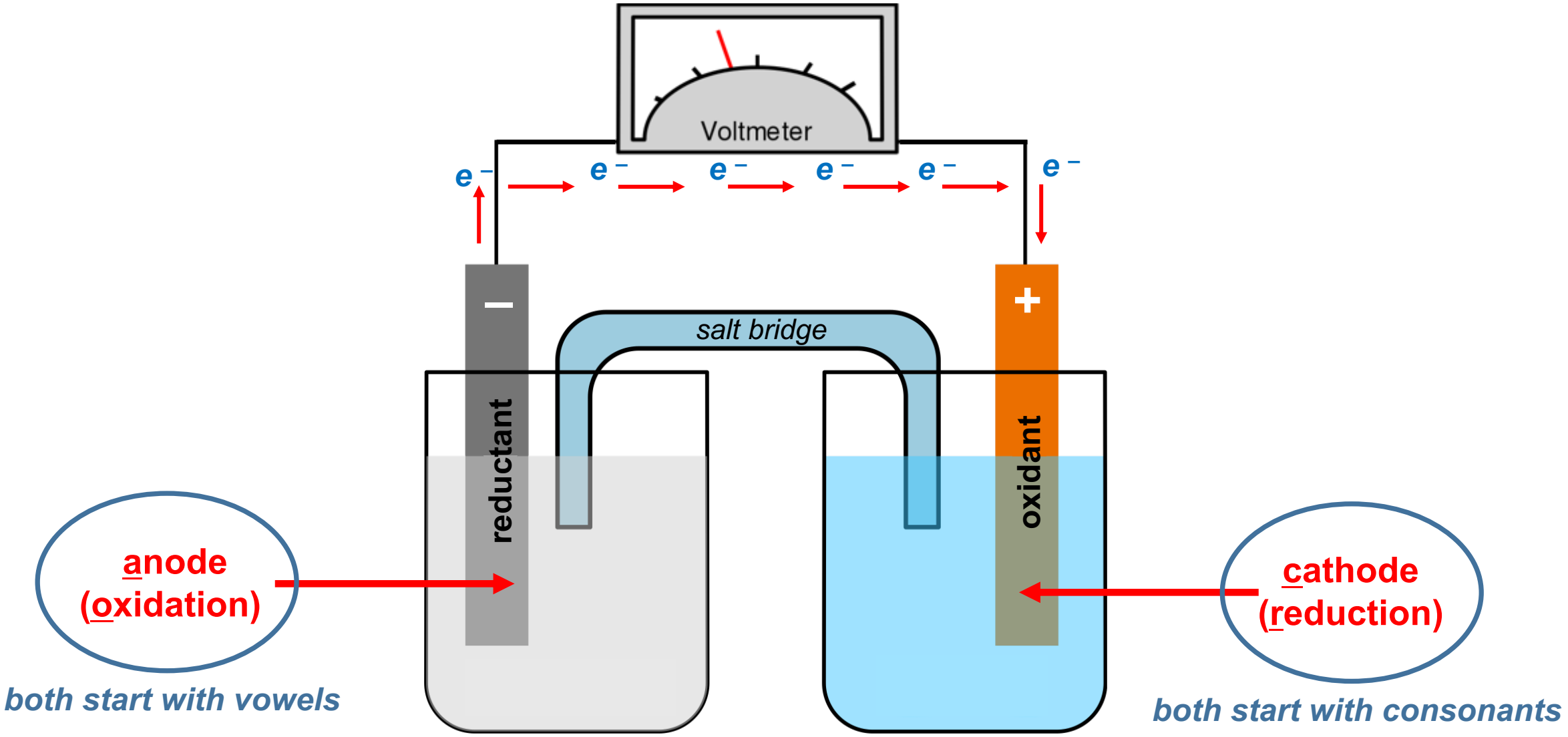
Galvanic (Voltaic) Cells

Remember:

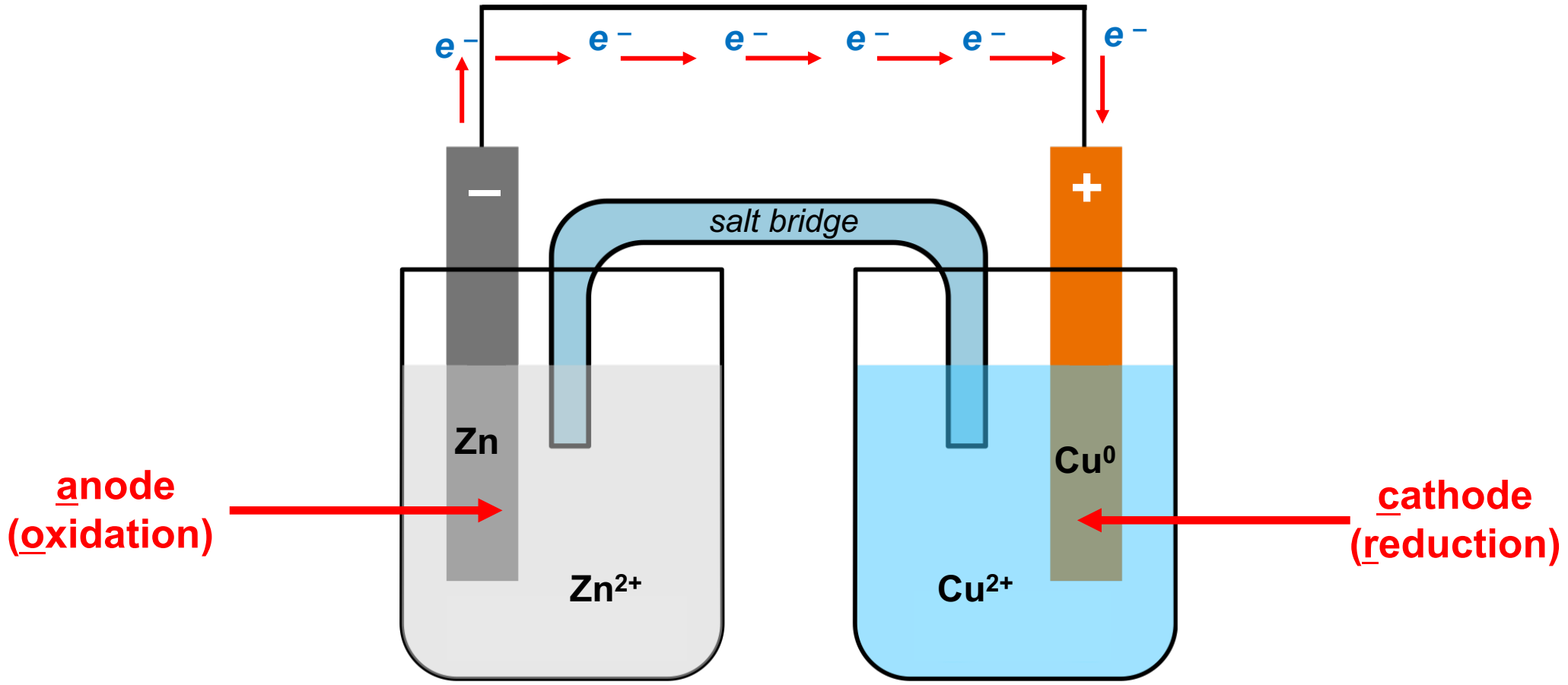
- In a ***voltaic cell***, electrons *always* flow **from anode to cathode**.
- The **anode is negative** and the **cathode is positive** in ***galvanic cells***.



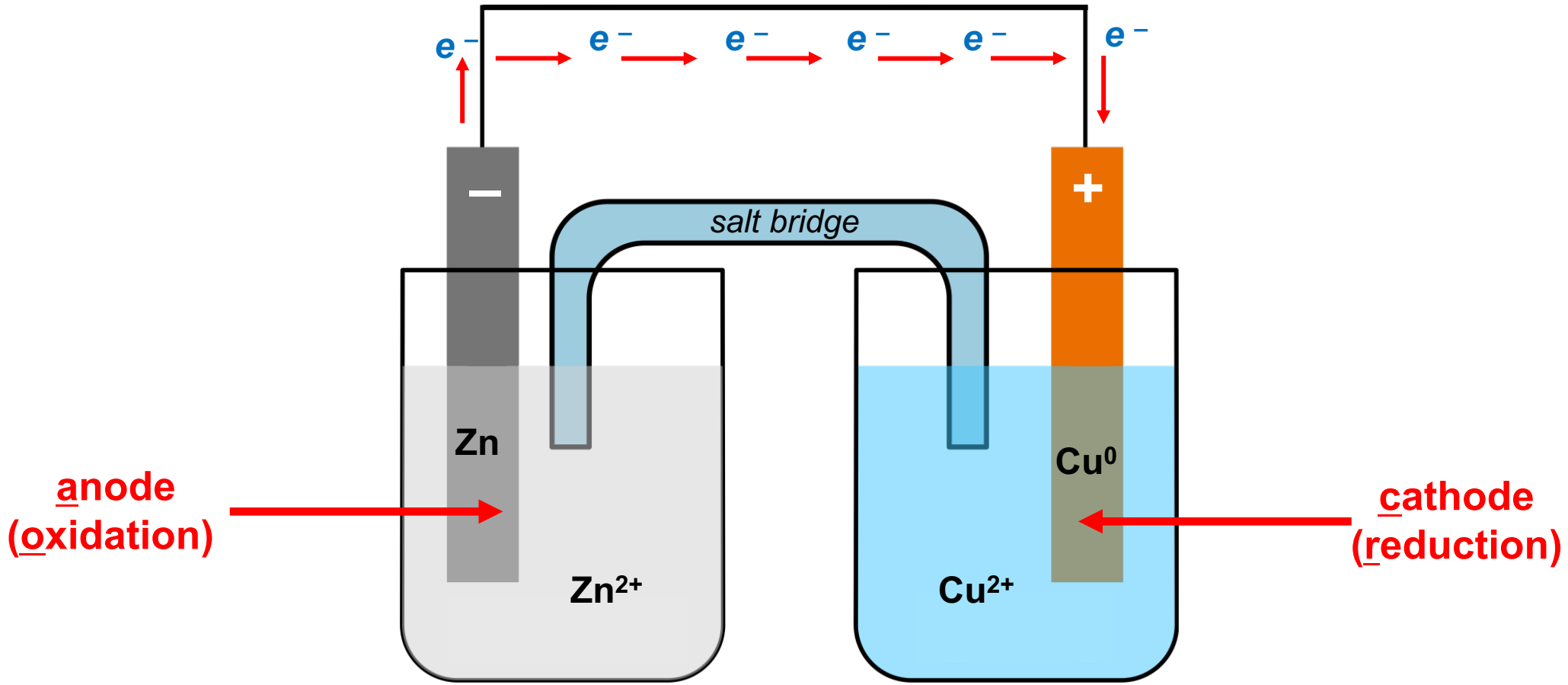
Galvanic (Voltaic) Cells



Galvanic (Voltaic) Cells



The ***salt bridge*** serves as a source of unreactive cations and ions (for example, like NaCl: Na^+ and Cl^-), which flow back-and-forth into the anode and cathode chambers, as needed, to counterbalance charges as they build up. Otherwise, batteries would be deadly explosive.



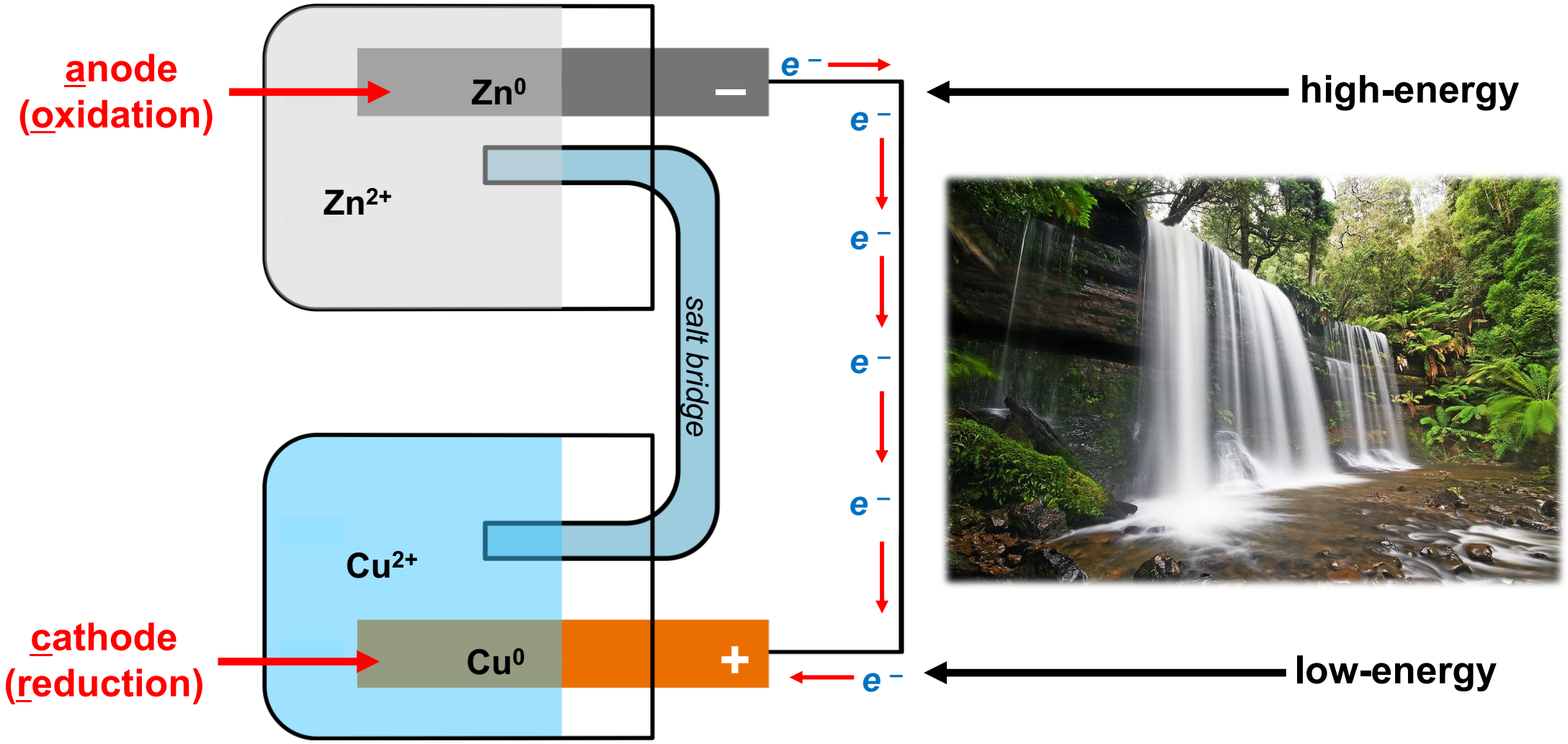
Galvanic (Voltaic) Cells

Electricity, then, is really just a flow of electrons, which we can capture to power things. In ***galvanic*** (***voltaic***) ***cells*** or batteries, those electrons flow –like water down a waterfall—from high-energy to low-energy. Because this flow is ***spontaneous*** (in a thermodynamic sense), ***ΔG*** for a ***galvanic cell*** is negative.

high-energy

low-energy

Galvanic (Voltaic) Cells



EMF and Electrode Potential

A ***voltaic cell's*** ability to provide energy is called its ***electromotive force*** (***emf***), also called its ***electrode potential*** (***E_{cell}***).

The purists in the room might argue that technically speaking, these two terms (***emf*** and ***E_{cell}***) have slightly different definitions. They would be correct. However, I don't care. As far as the DAT is concerned, these terms are more-or-less interchangeable. After all, I'm trying to keep things simple and not bog you down with lots of unnecessary details.

As I already mentioned, in ***voltaic cells***, because the flow of electrons is ***spontaneous*** from anode to cathode, ***ΔG*** for voltaic cells is negative. But what about ***E_{cell}?*** Well, when ***ΔG*** is negative, ***E_{cell}*** is positive. Thus:

spontaneous = negative ***ΔG*** = positive ***E_{cell}***

nonspontaneous = positive ***ΔG*** = negative ***E_{cell}***

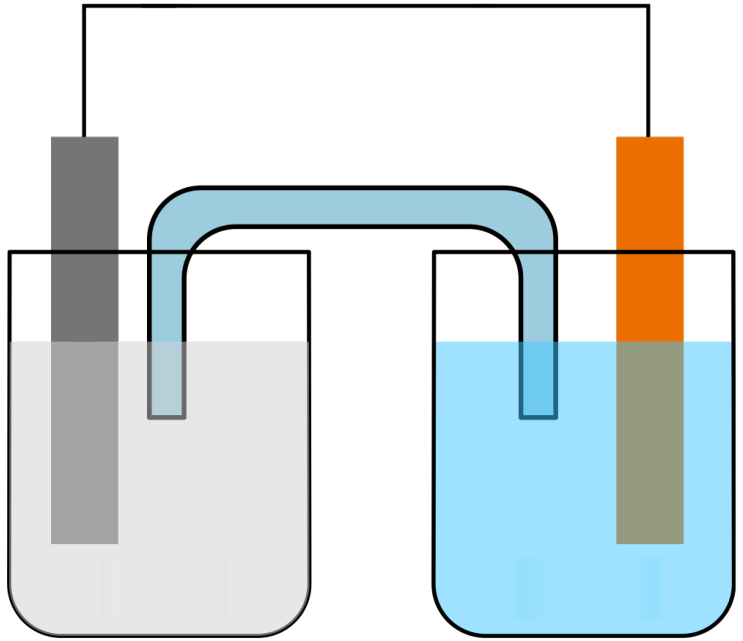
EMF and Electrode Potential

If you think about it, this should make sense. In ***galvanic cells***, electrons flow from the negatively-charged ***anode*** to the positively-charged ***cathode***.

Because electrons are negatively-charged, it should make sense that they would "want" to go *away* from the negatively-charged ***anode*** and *toward* the positively-charged ***cathode***, because when it comes to charges, opposites attract.

Question

Using the diagram to the right for the following reaction in a galvanic cell:



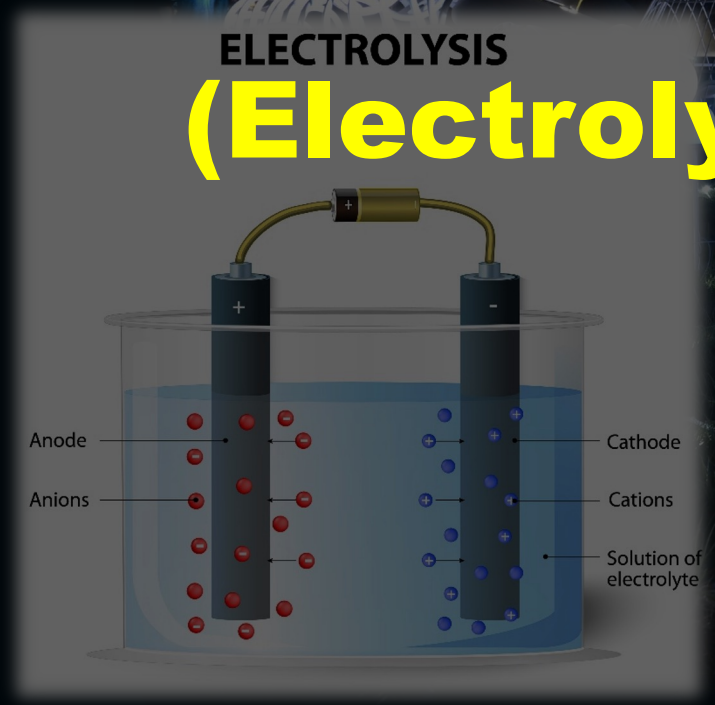
$$Zn + CuSO_4 \rightarrow Cu + ZnSO_4$$

. . . Please indicate or answer each of the following:

- Identify the elements being oxidized and reduced.
- What flows through the wire?
- What flows through the salt bridge?
- Label the flow of electrons in the correct direction.
- What is each metal made of at the anode and cathode? What is each solution made of?
- What is the purpose of the counterion?
- What is a salt bridge?

Electrochemistry & Oxidation-Reduction Reactions

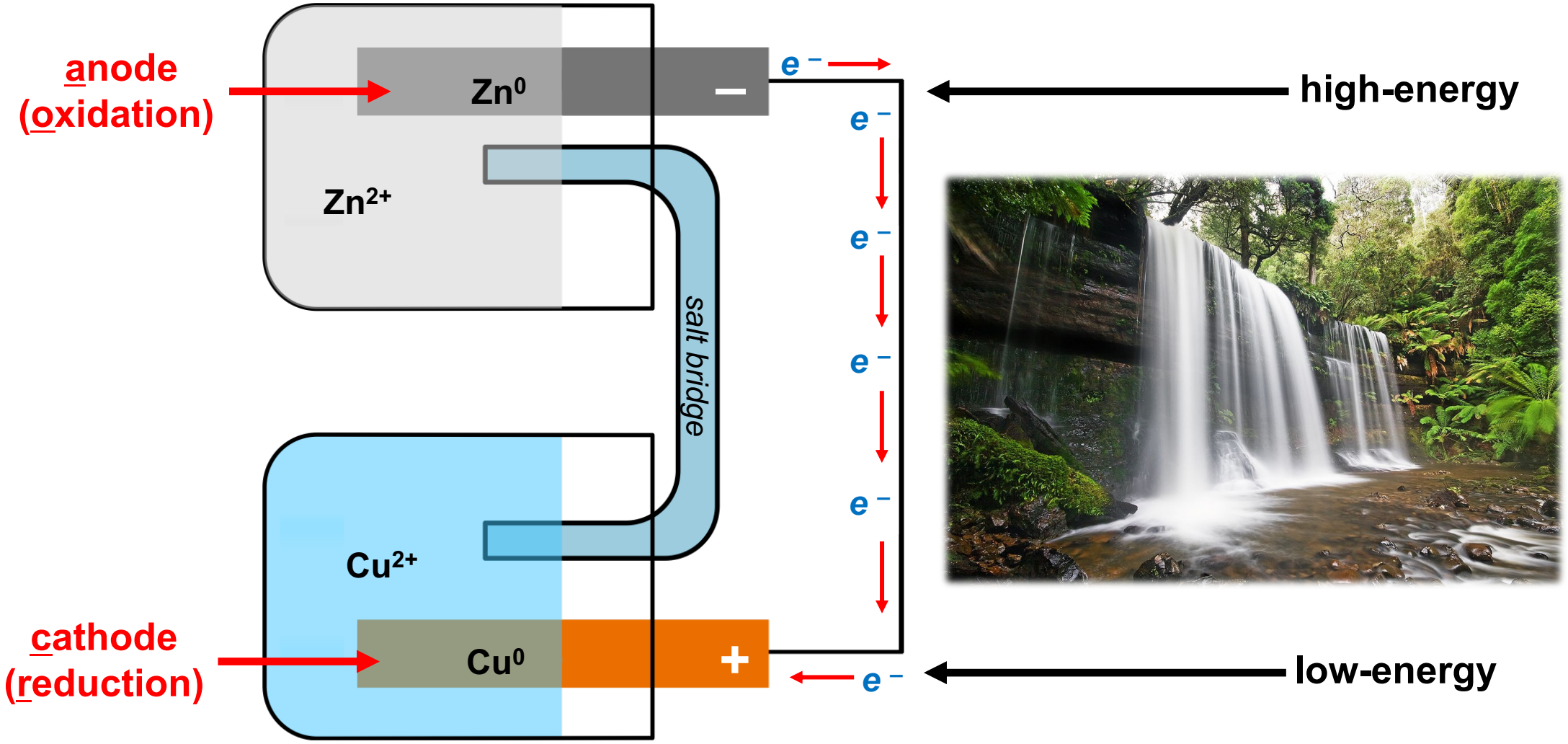
(Electrolytic Cells and Electrolysis)



Michael Faraday

To Review . . .

In a prior video, I taught you . . .



In This Video . . .

In this video I'll teach you about ***electrolytic cells***, which are more-or-less the same, except that they push electrons energetically *uphill*, from oxidant to reductant, in the *opposite* direction from which they would normally go.

So in essence, in an ***electrolytic cell***, we provide an *external* electric current that pushes electrons *uphill, from the former oxidant to the former reductant.* Because ***electrolytic cells*** push electrons in an energetically *uphill* direction, their electron flow is NOT spontaneous.

In This Video . . .

This means that for ***electrolytic cells***, ***ΔG*** is positive, and E_{cell} (the cell's ***electrode potential***) is negative, because they are ***nonspontaneous***:

spontaneous = negative ***ΔG*** = positive E_{cell}

nonspontaneous = positive ***ΔG*** = negative E_{cell}

This process of pushing electrons energetically uphill is called ***electrolysis***.

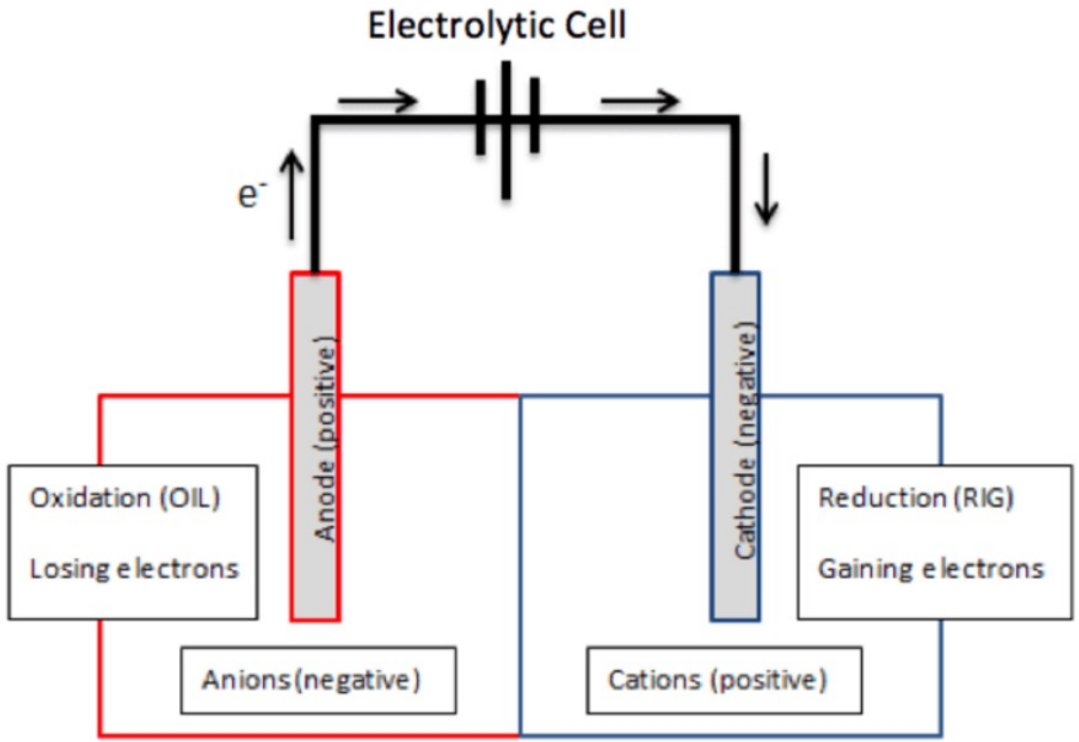
Why?

At this point you might wonder, “Why in the world would we ever want to push electrons energetically *uphill?”* In other words, why would we ever want to perform ***electrolysis?***

There are many situations in which pushing electrons energetically *uphill* might be useful. The most common I can think of is when you want to *recharge* a battery. You plug it into your outlet, and your outlet provides electrical energy that pushes the electrons in your dead battery *uphill* from its previous ***cathode*** to its previous ***anode***, thereby restoring the battery to its original state.

By definition, the ***anode*** is always the site of oxidation, and the ***cathode***, of reduction. This is true for both ***galvanic/voltaic*** cells, and ***electrolytic*** cells.

The major difference between these two types of cells is that in an ***electrolytic cell***, the ***anode*** is positive and ***cathode*** is negative, while in a ***galvanic/voltaic*** cell, the ***anode*** is negative and the ***cathode*** is positive.



Why?

By definition, the ***anode*** is always the site of oxidation, and the ***cathode***, of reduction. This is true for both ***galvanic/voltaic*** cells, and ***electrolytic*** cells.

The major difference between these two types of cells is that in an ***electrolytic cell***, the ***anode*** is positive and ***cathode*** is negative, while in a ***galvanic/voltaic*** cell, the ***anode*** is negative and the ***cathode*** is positive.

In both, the flow of the electrons is the same, from ***anode*** to ***cathode***. Now, because the ***anode*** is positive and ***cathode*** is negative in electrolytic cells, the reaction is nonspontaneous in electrolytic cells. Thus, a power source is required to make electrolytic reactions occur.

In ***galvanic/voltaic*** cells, the ***anode*** is negative, the ***cathode*** is positive, the reaction is spontaneous. Thus, ***galvanic/voltaic*** cells can act as a batteries.

Why?

At this point you might wonder, “Why in the world would we ever want to push electrons energetically *uphill?”* In other words, why would we ever want to perform ***electrolysis?***

There are many situations in which pushing electrons energetically *uphill* might be useful. The most common I can think of is when you want to *recharge* a battery. You plug it into your outlet, and your outlet provides electrical energy that pushes the electrons in your dead battery *uphill* from its previous ***cathode*** to its previous ***anode***, thereby restoring the battery to its original state.

But there are others, as well. Take, for example, the following reaction:

$$H_2O \rightarrow H_2 + O_2$$

Why?

$$H_2O \rightarrow H_2 + O_2$$

For reasons that I'll cover in a later video, this reaction is ***nonspontaneous***, as written. In other words, the ***redox*** reaction of converting H_2O into H_2 and O_2 requires an *input* of energy, achieved through ***electrolysis***.

So again I ask, "Why would you want to do ***electrolysis?"*** Well, in this example, you would do ***electrolysis*** if you wanted to obtain H_2 or O_2 gas.

Why?

$$H_2O \rightarrow H_2 + O_2$$

This is how hydrogen-powered cars work. By passing electricity through water, their fuel cells perform ***electrolysis*** on H_2O, which reduces and converts the hydrogen in H_2O into H_2 gas, which is flammable and can be used as a combustible fuel in their engines.

There are also *other* useful applications of ***electrolysis***, some of which I'll discuss later on in this video. In the end, the purpose of ***electrolysis*** is usually to convert compounds like H_2O, $NaCl$, or $FeSO_4$ into their parent elements, such as H_2, O_2, Cl_2, Fe, and elemental S.

Two Types of Electrolysis

To perform an ***electrolysis***, your setup needs to contain ions that are flowing freely.

There are two ways of accomplishing this free flow of ions: (1) You can melt your reactants; and (2) You can dissolve the ions in solution.

Thus, there are two kinds of electrolysis: ***molten electrolysis*** and ***aqueous electrolysis***.

I'll talk about ***molten electrolysis*** first.

Molten Electrolysis

Lets imagine that you want to perform the following ***redox*** reaction:

$$\underset{+1\ -1}{2\,KI} \rightarrow \underset{0}{2\,K} + \underset{0}{I_2}$$

Again, this reaction is not spontaneous, from left-to-right, as written in this equation. Thus, it would have to done ***electrolytically***, by pumping energy into the system. This reaction separates into the following two half-reactions:

Oxidation (anode): $2\,I^- \rightarrow I_2 + 2\,e^-$

Reduction (cathode): $2\,e^- + 2\,K^+ \rightarrow 2\,K$

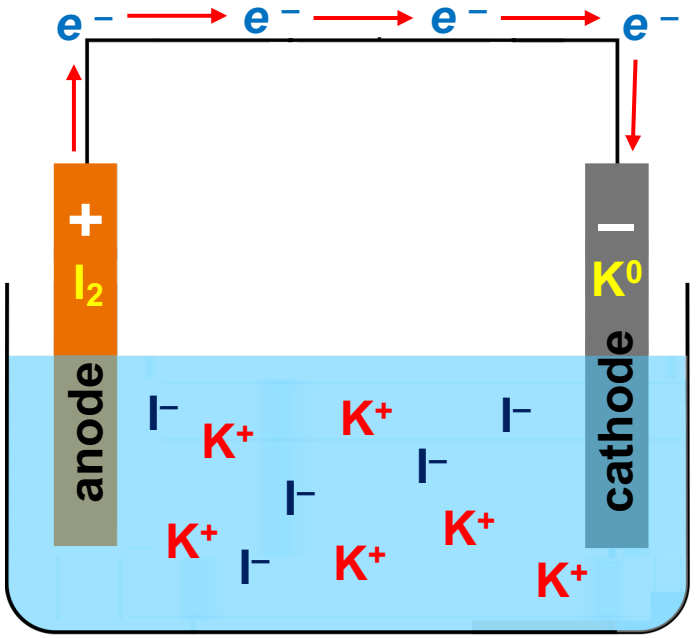
Molten Electrolysis

$$2\,KI \rightarrow 2\,K + I_2$$

Oxidation (anode): $2\,I^- \rightarrow I_2 + 2\,e^-$

Reduction (cathode): $2\,e^- + 2\,K^+ \rightarrow 2\,K$

- Under molten ***electrolysis*** conditions, there is no salt bridge.
- Instead, there is a sea of molten K^+ and I^- ions.
- Electrons still flow from anode to cathode.
- However, unlike ***galvanic cells***, in ***electrolytic cells***, we attach the reaction to a power source. This changes the anode's charge to ***positive*** and the cathode's charge to negative. The power source then drives the electrons towards the cathode, even though they don't want to go in that direction.
- Thus, the K^+ cations flow toward the negatively-charged cathode, where they get reduced to K^0 metal. The I^- anions, in contrast, flow toward the positively-charged anode, where they get oxidized to I_2.
- In an ***electrolytic cells***, then, **cat**ions flow toward the **cath**ode, while **an**ions flow toward the **an**ode.



Aqueous Electrolysis

Under aqueous conditions, we might assume that the same chemical reaction would transpire:

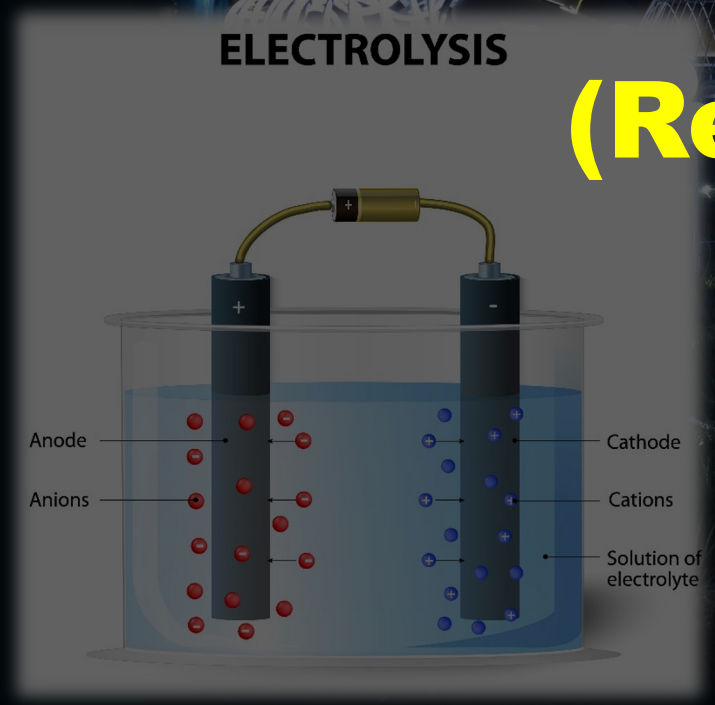
$$2\,KI \rightarrow K + I_2$$

However, the presence of H_2O introduces another potentially competing ***redox*** reaction, which we discussed before:

$$H_2O \rightarrow H_2 + O_2$$

For thermodynamic reasons that I'll talk about in a later video, this mixture ends up reducing H^+ to H_2 while also oxidizing I^- to I_2. So under ***aqueous electrolysis*** conditions, this setup actually forms H_2 and I_2.

Electrochemistry & Oxidation-Reduction Reactions (Reduction Potentials)



Michael Faraday

To Review . . .

In a past video, I taught you that for ***galvanic cells***, ***ΔG*** is negative, and E_{cell} (the cell's ***electrode potential***) is positive, because ***galvanic cells'*** electron flow happens in the ***spontaneous*** direction.

In contrast, ***electrolytic cells*** are the opposite: their electron flow (facilitated by an external power source) happens in the ***nonspontaneous*** direction. Thus, their ***ΔG***'s are positive, and their E_{cell} values are negative. This is summarized as follows:

Galvanic cells: spontaneous = negative ***ΔG*** = positive E_{cell}

Electrolytic cells: nonspontaneous = positive ***ΔG*** = negative E_{cell}

ΔG and E_{cell}

Mathematically, we can relate ΔG and E_{cell} through the following equation:

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

For now, don't worry about this equation.

My only reason for showing it is just so you see that mathematically, ΔG and E_{cell} have opposites signs. That is, when ΔG is negative (spontaneous reaction), E_{cell} is positive, and vice versa.

What is E_{cell}?

At this point you might wonder, "What is E_{cell}, really?" As you might have guessed, there's totally an app for that! By which I mean, there's totally an equation for that!

$$E_{cell} = E_{reduction} + E_{oxidation}$$

In other words, to calculate an electrochemical cell's E_{cell}, you need to look up the E value (called the ***reduction potential***) for the *reduction reaction in your electrochemical cell*. This is the reaction occurring at the ***cathode***.

You then do the same thing for your *electrochemical cell's oxidation reaction*: the reaction occurring at your cell's ***anode***.

What is E_{cell}?

For ***electrolytic cells***, then, we can rewrite this equation:

$$E_{cell} = E_{reduction} + E_{oxidation}$$

. . . As:

$$E_{cell} = E_{cathode} + E_{anode}$$

If E_{cell} is positive, then ΔG is negative, and the process is ***spontaneous***. If E_{cell} is negative, then ΔG is positive, and the process is ***nonspontaneous***.

But where do you find these mythical *"**E**"* (***reduction potential***) values?

Reduction Potentials

Right here!

In all seriously, though, you will be given a table like this on the EXAM, so you don't need to memorize any of this stuff. You do, however, need to know how to use it.

One thing you'll notice is that hydrogen's (H_2's) ***reduction potential*** is 0.00 V.

The reason is that the unit, ***volts*** (***V***), was designed so as to set *this specific reaction* as the 0.00-volt baseline, with all other reactions' ***reduction potentials*** being measured by comparing them to H_2.

Reduction Potentials (*E*)

like to lose electrons

stronger reductants

$K^+ + 1e^- \rightarrow K$	–2.93V
$Na^+ + 1e^- \rightarrow Na$	–2.71V
$Al^{3+} + 3e^- \rightarrow Al$	–1.66V
$Mn^{2+} + 2e^- \rightarrow Mn$	–1.18V
$Zn^{2+} + 2e^- \rightarrow Zn$	–0.76V
$Cr^{3+} + 3e^- \rightarrow Cr$	–0.74V
$Fe^{2+} + 2e^- \rightarrow Fe$	–0.44V
$Ni^{2+} + 2e^- \rightarrow Ni$	–0.25V
$2H^+ + 2e^- \rightarrow H_2$	**0.00V**
$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34V
$I_2 + 2e^- \rightarrow 2I^-$	+0.54V
$Ag^+ + 1e^- \rightarrow Ag$	+0.80V

stronger oxidants

like to steal electrons

Reduction Potentials

The point is, if you want to calculate E_{cell} using this equation:

$$E_{cell} = E_{reduction} + E_{oxidation}$$

. . . Then you just insert the ***reduction potential*** (***E***) values for the cathode and anode reactions into their respective locations in this equation.

positive E_{cell} = negative ΔG = ***spontaneous***

negative E_{cell} = positive ΔG = ***nonspontaneous***

Reduction Potentials

The point is, if you want to calculate E_{cell} using this equation:

$$E_{cell} = E_{reduction} + E_{oxidation}$$

. . . Then you just insert the ***reduction potential*** (***E***) values for the cathode and anode reactions into their respective locations in this equation. You do have to reverse the sign for the $E_{oxidation}$ reaction. After that:

positive E_{cell} = negative ΔG = ***spontaneous***

negative E_{cell} = positive ΔG = ***nonspontaneous***

Answering EXAM Questions

On the EXAM, you may encounter three kinds of ***reduction potential*** questions:

- **What is the strongest oxidizing agent?** To answer this, just find the substance with the highest (most positive) ***reduction potential*** from the table.
- **What is the strongest reducing agent?** To answer this, just find the substance with the lowest (most negative) ***reduction potential*** from the table. For both of these, be careful; the correct answer is the *metal*, not the ion.
- **What are some pairs that will react spontaneously?** For this kind of question, first make sure that a redox reaction can even occur. Sometimes you'll be given two compounds that have already been oxidized, or two that have already been reduced, so a redox reaction is not possible. Then use the equation $E_{cell} = E_{reduction} + E_{oxidation}$. If E_{cell} is **+**, the reaction will occur. If not, then it won't.

Reduction Potentials (*E*)

like to lose electrons

$K^+ + 1e^- \rightarrow K$	–2.93V
$Na^+ + 1e^- \rightarrow Na$	–2.71V
$Al^{3+} + 3e^- \rightarrow Al$	–1.66V
$Mn^{2+} + 2e^- \rightarrow Mn$	–1.18V
$Zn^{2+} + 2e^- \rightarrow Zn$	–0.76V
$Cr^{3+} + 3e^- \rightarrow Cr$	–0.74V
$Fe^{2+} + 2e^- \rightarrow Fe$	–0.44V
$Ni^{2+} + 2e^- \rightarrow Ni$	–0.25V
$2H^+ + 2e^- \rightarrow H_2$	**0.00V**
$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34V
$I_2 + 2e^- \rightarrow 2I^-$	+0.54V
$Ag^+ + 1e^- \rightarrow Ag$	+0.80V

stronger reductants ↑ ↓ **stronger oxidants**

like to steal electrons

Answering EXAM Questions

When doing ***standard reduction potential*** questions, please remember the following:

- Unlike questions that involve ***ΔS***, ***ΔH***, and ***ΔG***, *coefficients can be completely ignored* when using the equation $E_{cell} = E_{reduction} + E_{oxidation}$ *under standard conditions*.

- When using this equation, you DO have to change the sign (+ or –) of the ***standard reduction potential*** in this table, *for your oxidation reaction*.

Reduction Potentials (*E*)

like to lose electrons

$K^+ + 1e^- \rightarrow K$	–2.93V
$Na^+ + 1e^- \rightarrow Na$	–2.71V
$Al^{3+} + 3e^- \rightarrow Al$	–1.66V
$Mn^{2+} + 2e^- \rightarrow Mn$	–1.18V
$Zn^{2+} + 2e^- \rightarrow Zn$	–0.76V
$Cr^{3+} + 3e^- \rightarrow Cr$	–0.74V
$Fe^{2+} + 2e^- \rightarrow Fe$	–0.44V
$Ni^{2+} + 2e^- \rightarrow Ni$	–0.25V
$2H^+ + 2e^- \rightarrow H_2$	**0.00V**
$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34V
$I_2 + 2e^- \rightarrow 2I^-$	+0.54V
$Ag^+ + 1e^- \rightarrow Ag$	+0.80V

stronger reductants ↑

stronger oxidants ↓

like to steal electrons

Questions

When **Mn** and **Zn** metals react in a galvanic cell according to the equation below, will the reaction be spontaneous or nonspontaneous?

Mn + Zn → ???

Also, please indicate what the products of this reaction will be.

Reduction Potentials (*E*)

like to lose electrons

stronger reductants

stronger oxidants

$K^+ + 1e^- \rightarrow K$	–2.93V
$Na^+ + 1e^- \rightarrow Na$	–2.71V
$Al^{3+} + 3e^- \rightarrow Al$	–1.66V
$Mn^{2+} + 2e^- \rightarrow Mn$	–1.18V
$Zn^{2+} + 2e^- \rightarrow Zn$	–0.76V
$Cr^{3+} + 3e^- \rightarrow Cr$	–0.74V
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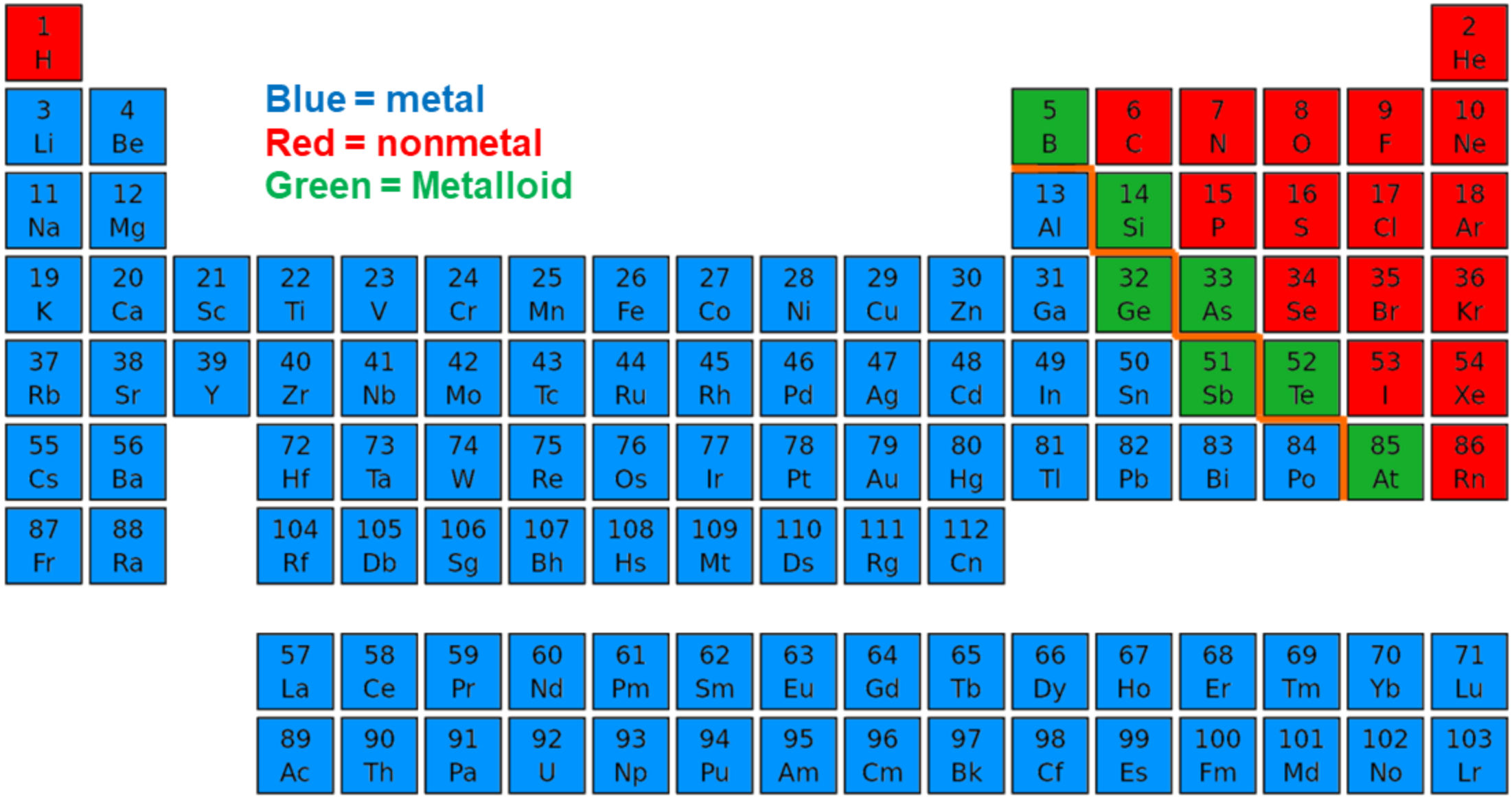
$2H^+ + 2e^- \rightarrow H_2$	**0.00V**
$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34V
$I_2 + 2e^- \rightarrow 2I^-$	+0.54V
$Ag^+ + 1e^- \rightarrow Ag$	+0.80V

like to steal electrons

Where are metals, non-metals, and metalloids?



Questions

When **Na** metal and **Fe^{2+}** cation react in a galvanic cell according to the equation below, will the reaction be spontaneous or nonspontaneous?

Na + Fe^{2+} → ???

Also, please indicate what the products of this reaction will be.

Reduction Potentials (*E*)

like to lose electrons

$K^+ + 1e^- \rightarrow K$	–2.93V
$Na^+ + 1e^- \rightarrow Na$	–2.71V
$Al^{3+} + 3e^- \rightarrow Al$	–1.66V
$Mn^{2+} + 2e^- \rightarrow Mn$	–1.18V
$Zn^{2+} + 2e^- \rightarrow Zn$	–0.76V
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$Ni^{2+} + 2e^- \rightarrow Ni$	–0.25V
$2H^+ + 2e^- \rightarrow H_2$	**0.00V**
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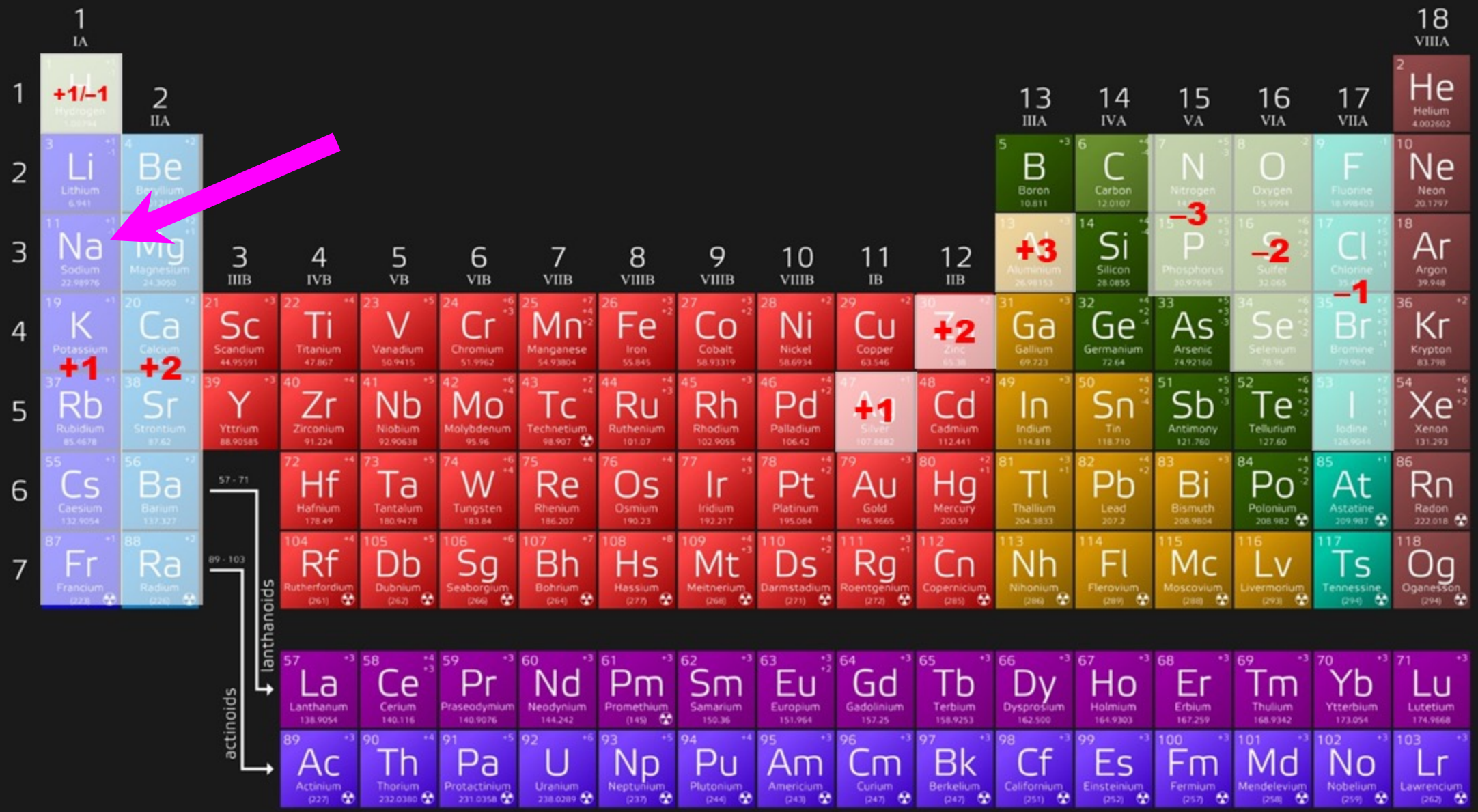
$Ag^+ + 1e^- \rightarrow Ag$	+0.80V

stronger reductants

stronger oxidants

like to steal electrons

Predicting An Ion's Charge



Questions

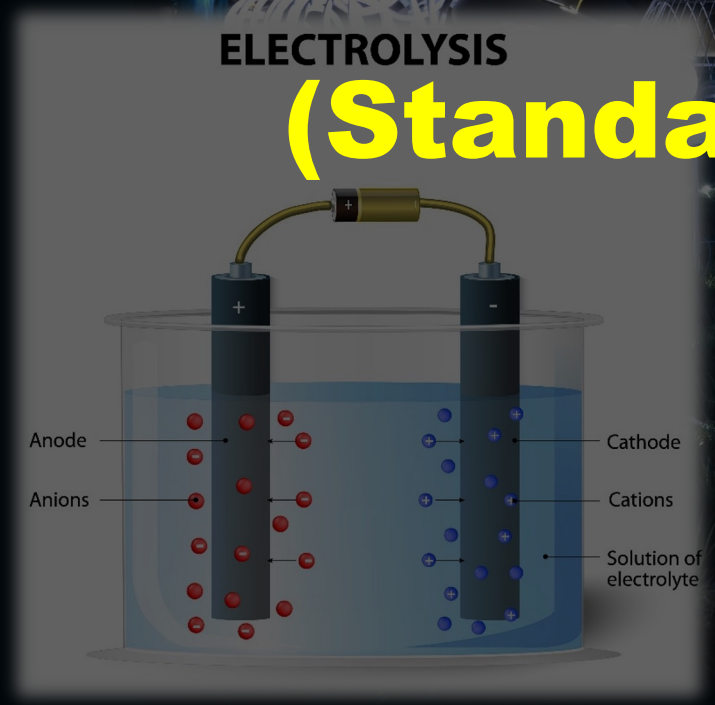
What are the products of the electrolysis of **$KI_{(aq)}$**?

Reduction Potentials (*E*)

$K^+ + 1e^- \rightarrow K$	–2.93V
$I_2 + 2e^- \rightarrow 2I^-$	+0.54V
$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	–0.80V
$O_2 + 4H^+ + 4e^- \rightarrow H_2O$	+1.28V

Electrochemistry & Oxidation-Reduction Reactions

(Standard Reduction Potentials)



Michael Faraday

To Review . . .

You might recall that back in our ***thermodynamics*** chapter, I taught you that there is a difference between ***ΔG*** and ***ΔG°***. To explain, I said that ***ΔG°*** is the ***Gibbs free energy change*** under standard conditions,while ***ΔG*** is the ***Gibbs free energy change*** under nonstandard conditions.

I also taught you that standard conditions are specifically 298 K (25 °C), 1.0 atm, and 1.0 M concentration, which you should not confuse with ***standard temperature pressure*** (***STP***). ***STP*** is 273 K (0 °C), 1.0 atm, and no specific concentration.

By extension, ***ΔS°*** and ***ΔH°*** are the changes in ***entropy*** and ***enthalpy***, respectively, under standard conditions, while ***ΔS*** and ***ΔH*** are the same under nonstandard conditions.

To Review . . .

In an earlier video in *this* chapter, I taught you how to calculate ***electrode potential*** (E_{cell}) by using this equation:

$$E_{cell} = E_{reduction} + E_{oxidation}$$

. . . Which, for a ***galvanic cell***, is the same thing as this:

$$E_{cell} = E_{cathode} + E_{anode}$$

We also did a bunch of example problems. As it turns out, the "***E***" values (***reduction potentials***) I taught you in our prior videos were . . . kind of . . . a lie.

Standard Reduction Potentials

Okay, to be more specific, the ***reduction potentials*** ("***E***") values I taught you were actually ***standard reduction potentials***.
be more technically accurate, they should *actually* be called ***E°*** values.

This slight change, however, does NOT alter *anything* about *how* to use these ***E*** values.

On the EXAM, you will be given a table, like *this* one, and asked questions about E_{cell} or ***E°***. Again, the entire voltage unit scale is based on the reduction of H^+ to H_2, called the ***Standard Hydrogen Electrode*** (***SHE***).

Reduction Potentials (*E*)

like to lose electrons

stronger reductants

$K^+ + 1e^- \rightarrow K$	–2.93V
$Na^+ + 1e^- \rightarrow Na$	–2.71V
$Al^{3+} + 3e^- \rightarrow Al$	–1.66V
$Mn^{2+} + 2e^- \rightarrow Mn$	–1.18V
$Zn^{2+} + 2e^- \rightarrow Zn$	–0.76V
$Cr^{3+} + 3e^- \rightarrow Cr$	–0.74V
$Fe^{2+} + 2e^- \rightarrow Fe$	–0.44V
$Ni^{2+} + 2e^- \rightarrow Ni$	–0.25V
$2H^+ + 2e^- \rightarrow H_2$	**0.00V**
$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34V
$I_2 + 2e^- \rightarrow 2I^-$	+0.54V
$Ag^+ + 1e^- \rightarrow Ag$	+0.80V

stronger oxidants

like to steal electrons

A Reminder . . .

When doing ***standard reduction potential*** questions, please remember the following:

- Unlike questions that involve ***ΔS***, ***ΔH***, and ***ΔG***, *coefficients can be completely ignored* when using the equation $E°_{cell} = E°_{reduction} + E°_{oxidation}$ *under standard conditions*.

- When using this equation, you DO have to change the sign (+ or –) of the ***standard reduction potential*** in this table, *for your oxidation reaction*.

Reduction Potentials (*E*)

like to lose electrons

$K^+ + 1e^- \rightarrow K$	–2.93V
$Na^+ + 1e^- \rightarrow Na$	–2.71V
$Al^{3+} + 3e^- \rightarrow Al$	–1.66V
$Mn^{2+} + 2e^- \rightarrow Mn$	–1.18V
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$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34V
$I_2 + 2e^- \rightarrow 2I^-$	+0.54V
$Ag^+ + 1e^- \rightarrow Ag$	+0.80V

stronger reductants ↑

stronger oxidants ↓

like to steal electrons

Questions

What is the ***standard cell potential***, or ***E°***, for the following reaction?

$Zn + CuSO_4 \rightarrow Cu + ZnSO_4$

Reduction Potentials (*E*)

like to lose electrons

stronger reductants

$K^+ + 1e^- \rightarrow K$	–2.93V
$Na^+ + 1e^- \rightarrow Na$	–2.71V
$Al^{3+} + 3e^- \rightarrow Al$	–1.66V
$Mn^{2+} + 2e^- \rightarrow Mn$	–1.18V
$Zn^{2+} + 2e^- \rightarrow Zn$	–0.76V
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$Fe^{2+} + 2e^- \rightarrow Fe$	–0.44V
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$2H^+ + 2e^- \rightarrow H_2$	**0.00V**
$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34V
$I_2 + 2e^- \rightarrow 2I^-$	+0.54V
$Ag^+ + 1e^- \rightarrow Ag$	+0.80V

stronger oxidants

like to steal electrons

Questions

What is the ***standard cell potential***, or ***E°***, for *this* reaction?

$$Zn^{2+} + Fe \rightarrow Fe^{2+} + Zn$$

Would this reaction be good for a galvanic or electrolytic cell?

Reduction Potentials (*E*)

like to lose electrons

$K^+ + 1e^- \rightarrow K$	–2.93V
$Na^+ + 1e^- \rightarrow Na$	–2.71V
$Al^{3+} + 3e^- \rightarrow Al$	–1.66V
$Mn^{2+} + 2e^- \rightarrow Mn$	–1.18V
$Zn^{2+} + 2e^- \rightarrow Zn$	–0.76V
$Cr^{3+} + 3e^- \rightarrow Cr$	–0.74V
$Fe^{2+} + 2e^- \rightarrow Fe$	–0.44V
$Ni^{2+} + 2e^- \rightarrow Ni$	–0.25V
$2H^+ + 2e^- \rightarrow H_2$	**0.00V**
$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34V
$I_2 + 2e^- \rightarrow 2I^-$	+0.54V
$Ag^+ + 1e^- \rightarrow Ag$	+0.80V

stronger reductants ↑

stronger oxidants ↓

like to steal electrons

Questions

What is the ***standard cell potential***, or ***E°***, for *this* reaction?

$2Cr + 6H^+ \rightarrow 3H_2 + 2Cr^{3+}$

Reduction Potentials (*E*)

like to lose electrons

$K^+ + 1e^- \rightarrow K$	–2.93V
$Na^+ + 1e^- \rightarrow Na$	–2.71V
$Al^{3+} + 3e^- \rightarrow Al$	–1.66V
$Mn^{2+} + 2e^- \rightarrow Mn$	–1.18V
$Zn^{2+} + 2e^- \rightarrow Zn$	–0.76V
$Cr^{3+} + 3e^- \rightarrow Cr$	–0.74V
$Fe^{2+} + 2e^- \rightarrow Fe$	–0.44V
$Ni^{2+} + 2e^- \rightarrow Ni$	–0.25V
$2H^+ + 2e^- \rightarrow H_2$	**0.00V**
$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34V
$I_2 + 2e^- \rightarrow 2I^-$	+0.54V
$Ag^+ + 1e^- \rightarrow Ag$	+0.80V

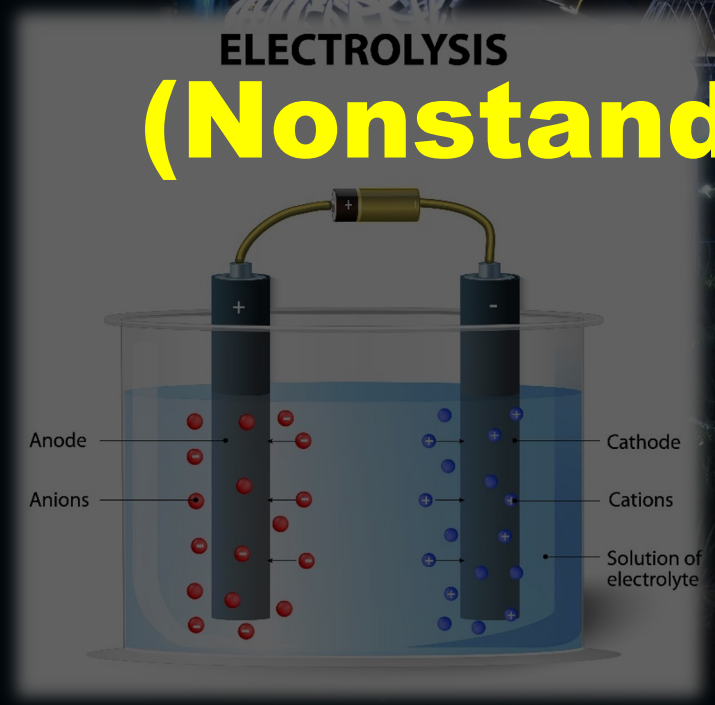
stronger reductants ↑

stronger oxidants ↓

like to steal electrons

Electrochemistry & Oxidation-Reduction Reactions

(Nonstandard Cell Potentials and the Nernst Equation)



Michael Faraday

To Review . . .

Back in our ***thermodynamics*** chapter, I taught you that there is a difference between ***ΔG*** and ***ΔG°***. ***ΔG°*** is the ***Gibbs free energy change*** under standard conditions (298 K / 25 °C, 1.0 atm, and 1.0 M concentration), while ***ΔG*** is the ***Gibbs free energy change*** under nonstandard conditions.

I also taught you that we can mathematically interconvert ***ΔG*** and ***ΔG°*** by using the equation:

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

. . . Which is useful because real-life reactions are almost never run at *standard conditions*, so it's helpful to be able to convert nonstandard results into tabulatable, standard ones.

Nonstandard to Standard

We can do a similar thing to interconvert between ***E*** and ***E°***. This involves the following equation, which is called the ***Nernst equation:***

$$E_{cell} = E°_{cell} - (0.0592 / n) \times \log(Q)$$

. . . Where **n** is the number of moles of electrons transferred in your ***redox*** reaction, and ***Q*** is the reaction quotient: a ratio of products over reactants which is just like the ***equilibrium rate constant K***, except that ***Q*** *may or may not be at equilibrium*, while ***K*** is.

Question

Given the following:

$$Zn + Cu^{2+} \rightarrow Cu + Zn^{2+} \qquad E°_{cell} = +1.10\ V$$

- In which direction will the reaction shift if [Cu^{2+}] is increased to 10 M?
- How will this change in [Cu^{2+}] affect E_{cell}?
- Use the ***Nernst equation*** to solve for E_{cell} under these new conditions.

Questions

- What if we increased the amount of [Cu2+] to 10M?
  Now we're not in standard conditions. According to Le Chatelier, we should shift the reaction to the products (because we increased the concentration of a reactant), which makes this reaction more spontaneous.

- How will this change in [Cu2+] affect Ecell?
  Since it is more spontaneous, that means Ecell increases. **EXAM TIP:** Shift reaction to the right = increases Ecell. Shift reaction to the left = decreases Ecell

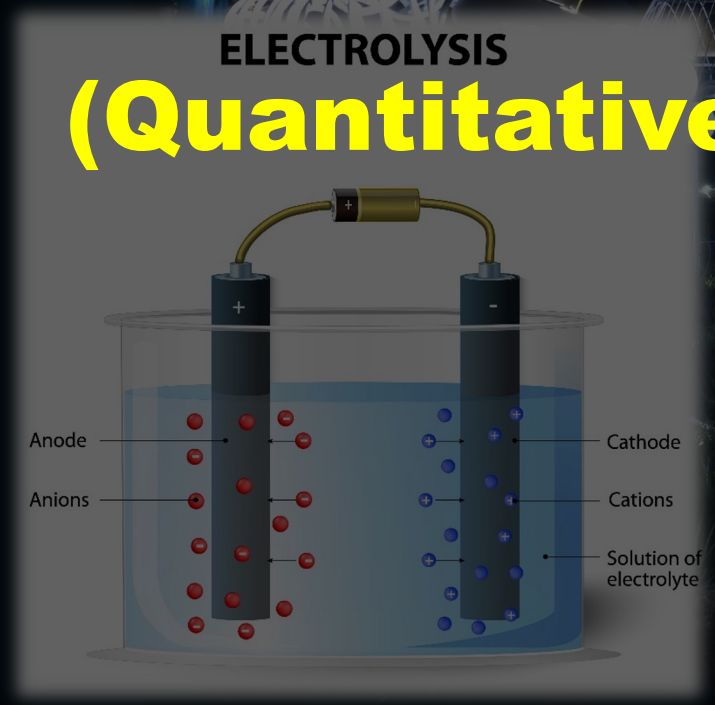
Questions

If you change concentration so as to shift a spontaneous (positive $E°_{cell}$) reaction to the *right*, then it will increase E_{cell}.

If you change concentration so as to shift a spontaneous (positive $E°_{cell}$) reaction to the *left*, then it will decrease E_{cell}.

Electrochemistry & Oxidation-Reduction Reactions

(Quantitative Electrochemical Calculations)

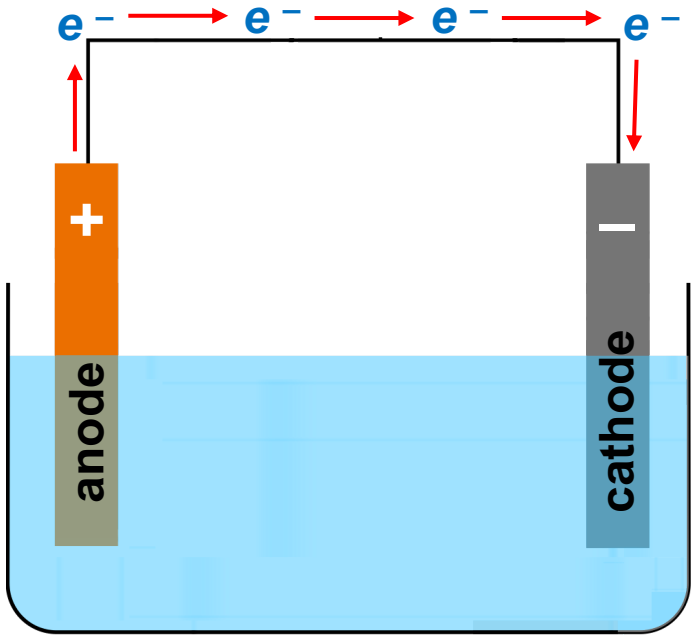


Michael Faraday

Electroplating

In a past video, I taught you that in ***electrolytic cells***, we add an external power source to push our electron current in the *opposite* and energetically-unfavorable (***nonspontaneous***) direction, *toward* the negatively-charged cathode. (In traditional ***galvanic*** or ***voltaic cells***, the *anode* is negatively-charged.

One cool application of this is ***electroplating***. For example,



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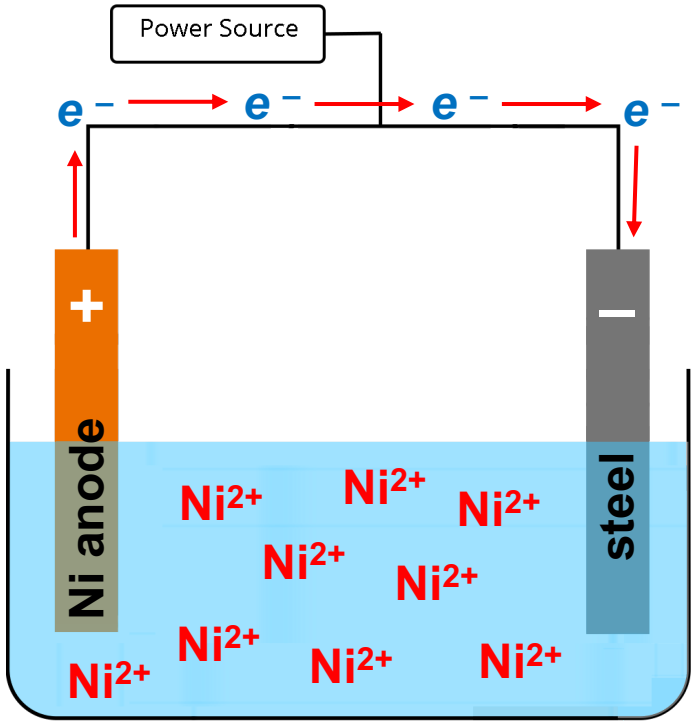
One cool application of this is ***electroplating***. For example, if a steel object is placed into the molten, electrolytic solution, then that object serves as the ***cathode***. If the solution contains a bunch of metallic cations, like Ni^{2+} ions, for example, then as ***electrolysis*** occurs, those ions will be attracted to the negatively-charged steel.



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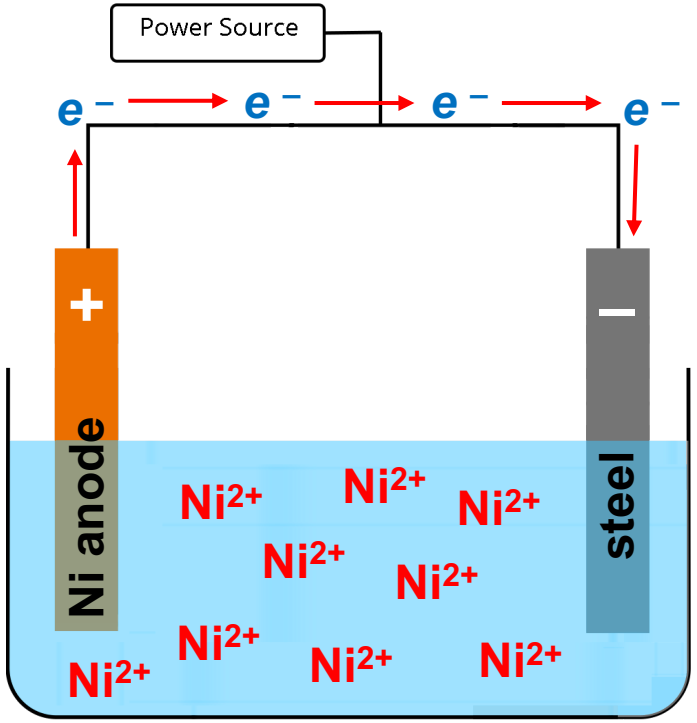
Many of those Ni^{2+} ions then get reduced to Ni^{0} as they cover the surface of the steel, which coats



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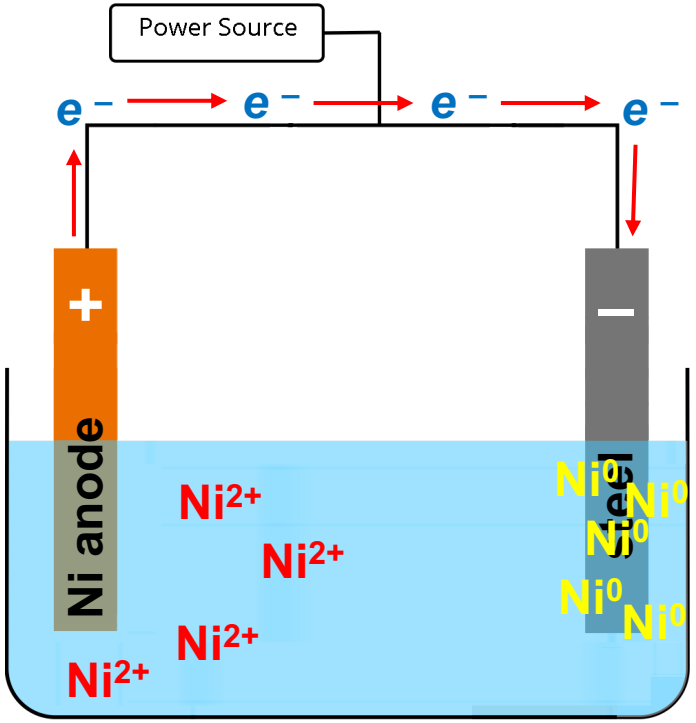
Many of those **Ni^{2+}** ions then get reduced to **Ni^{0}** as they cover the surface of the steel, which coats it with a beautiful nickel finish. This process is called ***electroplating.***

Chromium is another popular metal used in ***electroplating***. This process coats steel and other substances, which makes them shiny and protects them from corrosion.



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Electroplating

When doing ***electroplating***, we might ask, “How much nickel, for *our* example, will eventually end up coating our steel, once we’re all done?”

The answer depends on *the concentration* of your nickel solution, the *amount of current* you apply from your power source, and *how long you run the electrolysis*.

As you might imagine, there absolutely *is* a way to mathematically answer this question . . . That is, to calculate the amount of nickel that will end up plating onto our steel.

The Calculation

To perform these calculations, we have to use the following equation:

$$\text{moles mass of plated product} = \frac{(I)\,(t_s)}{(n)\,(F)}$$

Where:

- I is the current (in **amps**)
- t_s is time (in **seconds**)
- n is number of moles of electrons transferred (per mole of product)
- F is ***Faraday's constant*** (**96,500 C / mol e^-**). For the EXAM $F \approx$ **100,000**.

Just so you know, **1 C** = **1 amp × 1 second**. Also, once you calculate your moles of product, you can easily convert it to grams by multiplying by its molecular weight.

The Calculation

If a 20-amp current passes through molten $BaCl_2$ for 30 minutes, how many grams of Ba are produced?

The Calculation

What amount of time (in seconds) would it take to plate out 0.50 kg of Ag from molten AgCl with a current of 100 amps? (atomic weight of of Ag = 100 g/mol)