

Ch. 19 Electrochemistry and its Applications

- electron flow = electricity
 - electrochemistry = the study of electron transfer
 - “reduction” and “oxidation” (“redox”) chemistry is central
1. Product-favored redox reactions run batteries
 2. Voltmeters quantify electrochemistry
 - measure reactivity of redox reactions
 3. Reactant-favored redox reactions can be pushed to product side by external electricity
 - “Electrolysis”
 - Electrolysis is the source of many pure metals and other not found in nature (“Electroplating”)

$$\text{Cr}^{3+} + 3\text{e}^- \rightarrow \text{Cr} \quad (\text{chrome-plating})$$
 4. One can also force oxidation reactions under the appropriate conditions

$$2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^- \quad (\text{for disinfecting water})$$
 5. “Corrosion”, “rusting” are redox processes that are undesirable and that we need to prevent

Assigning Oxidation Numbers (See Section 5.4)

This is a more complete set of rules than your textbook. It always works.

Use these rules in order.

The sum of all oxidation numbers of all elements = charge on substance.

		Oxidation Number:	Examples:
1.	Atoms in their elemental state	= 0	Fe, H ₂ , O ₂
2.	Monatomic ions	= charge	F ¹⁻ , Na ¹⁺ , Fe ³⁺

IN COMPOUNDS

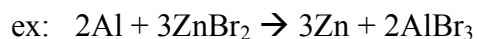
3.	Group 1A	= +1	NaCl, KNO ₃
4.	Group 2A	= +2	MgO
5.	Fluorine	= -1	HF, ClF
6.	Hydrogen	= +1	H ₂ O
7.	Oxygen	= -2	SO ₂ , HClO ₄
8.	Group 7A (Halogen family)	= -1	HCl
9.	Group 6A (Oxygen family)	= -2	PbS ₂

The sum of all oxidation numbers of all elements = charge on substance.

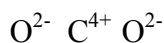
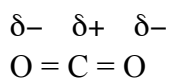
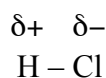
Key: For anything else, (or for a group 7A or group 6A in the presence of higher priority atoms), set its oxidation number = “x”, and solve for “x” such that the ox. #'s = actual charge.

Find Ox #'s for1. H₂OC C:2. PCl₃ P:3. HSO₄⁻ S:4. KMnO₄ Mn:5. Mg₃(PO₄)₂ P:6. HClO₂ Cl:

19.1 Redox Reactions (Review: 5.3)

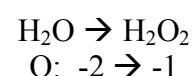
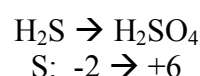
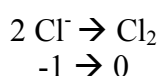
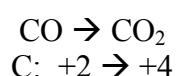
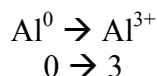
Recognizing Redox Reactions:

- Any reaction in which an elemental substance is involved is always a redox reaction
 - The element can be on either reactant or product side, or both
- Any reaction involving a Change in "oxidation number" is a redox reaction (review 5.4)
 - Oxidation numbers count charges in molecular as well as ionic compounds
 - In a polar covalent bond, a more electronegative atom is given negative charge (credited with bonding electrons), and a less electronegative atom is given positive charge (as if it wasn't seeing the bonding electrons at all)

Notes, Terms

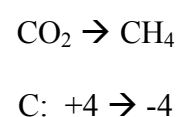
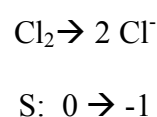
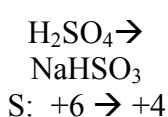
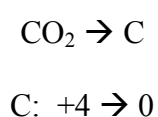
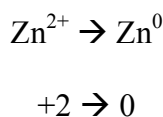
1. Oxidation: loss of e's

- Ox # increases (more positive or less negative)

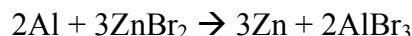


2. Reduction: gain of e's

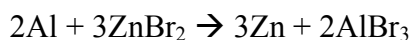
- Ox # is "reduced" (less positive or more negative)



- All redox reactions require both an electron giver (the thing that is oxidized) and an electron taker (the thing that is reduced)
 - Essentially a redox reaction involves a competition for a limited supply of electrons
 - In the example shown, there aren't enough electrons for both Al and Zn to be in their reduced zero-charge form. One or the other must be in its electron-deficient oxidized form



- That Al^{3+} ends up oxidized and Zn^0 ends up reduced suggests that Zn has a higher electron-love than Al
- Competition for limited electrons not unlike acid/base competition for limited H^+ 's

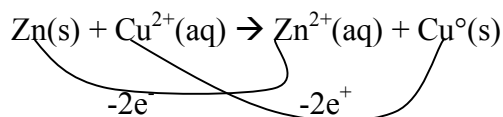


4. "Oxidizing Agent" or "Oxidant": causes something else to be oxidized
 - is itself reduced
 - Zn^{2+} , which is itself reduced, is the "oxidizing agent" because it causes Al to be oxidized
5. "Reducing Agent": causes something else to be reduced
 - is itself oxidized
 - by giving it's electrons to the other guy, it causes the other guy to be reduced, but is oxidized in the process
 - Al, which is itself oxidized, is the "reducing agent" because it causes Zn^{2+} to be reduced
6. "Redox" reduction – oxidation
7. Electrons must balance in a redox reaction: the number given up by the reducing agent must equal the number accepted by the oxidizing agent

Identify the oxidizing and reducing agents and count how many electrons transfer

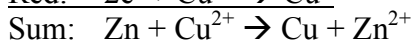
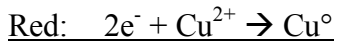
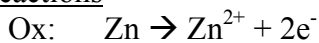
1. $2\text{Na} + 2\text{HCl} \rightarrow 1\text{H}_2 + 2\text{NaCl}$
2. $2\text{KMnO}_4 + 6\text{NaCl} \rightarrow 2\text{MnO}_2 + 3\text{Cl}_2$ (some H_2O , KOH , NaOH also involved)

19.2 Half Reactions, Redox, and Balancing



- both oxidation and reduction must occur
- electrons must balance

Half Reactions



Suppose: Zn^{2+} reacts with Na. Draw the oxidation and reduction half reactions, and balance them for electrons. Combine them to make the sum redox reaction:

Reduction

Oxidation

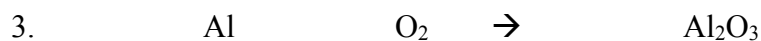
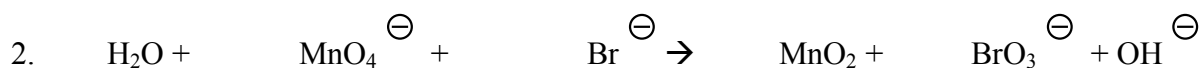
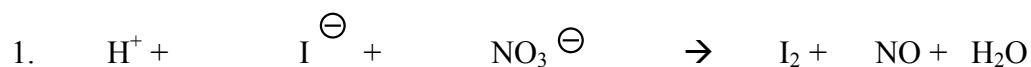
Net Sum

Balancing Redox

1. Identify oxidation numbers for redox actors
2. Set coefficients for them so that the **#e's released = #e's accepted**
 - focus completely on the atoms whose oxidation numbers change
3. Then balance any redox spectators
4. Check at the end to make sure:
 - Charges balance
 - Atoms balance

Note: Test problems will give you all of the species involved. Some OWL problems will be harder and will not include all of the chemicals

Balance (Test Level)



Some Harder OWL-Level problems:

- Sometimes H_2O , OH^- , H^+ are omitted, and need to be added in order to balance oxygens and hydrogens
- In knowing how to do this, it is helpful to distinguish acid versus base conditions
- Under acid conditions, it's appropriate to have H^+ but not OH^-
- Under base conditions, it's appropriate to have OH^- but not H^+

Acid Conditions

- Identify oxidation numbers for redox actors
- Balance the redox actors
- Add H_2O 's to balance oxygen
- Add H^+ 's to balance hydrogens and charge

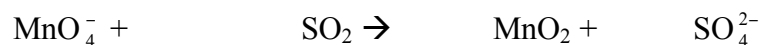
Base Conditions

- Identify oxidation numbers for redox actors
- Balance the redox actors
- Add OH^- 's to balance charge
- Add H_2O 's to balance hydrogens

- 1. Acid conditions:



- Base conditions: balance, adding OH^- (to balance charge) and H_2O (to balance hydrogens)
 - once you've balanced the redox actors, put in as many hydroxides as needed to balance the charges
 - then put in as many H_2O 's as needed to balance hydrogens



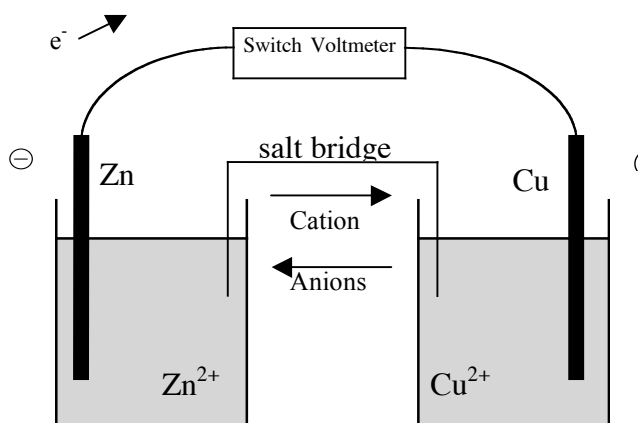
19.3 Electrochemical Cells



- when redox partners are in direct contact (in the same beaker, in the same solution) direct electron transfer occurs: no measurable or useful electron flow

Electrochemical (“Voltaic”) Cell: redox reactants are separated, so electron flow is forced to go through external circuit \Rightarrow measurable, useful electricity

Setup (fig 19.5 Moore, Brown 20.5)



2 Solid metals = “electrodes”

- electrodes can be metal, plates or wires, or graphite or some other materials: (must be conductive)
- “Anode” = electrode Oxidized (vowels) $\text{Zn} \rightarrow \text{Zn}^{2+}$
 - electron source
 - dissolving
 - negative sign on a battery
- “Cathode” = electrode reduced (consonant) $\text{Cu}^{2+} \rightarrow \text{Cu}$
 - e- receiver
 - physically electrode grows (Cu^0 forming)
 - positive sign on battery

Two “Half Cells” and “Half Reactions”

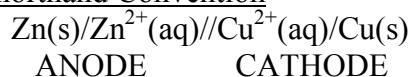
- “Anode” side = Where the oxidation half reaction occurs ($\text{Zn} \rightarrow \text{Zn}^{2+}$ beaker)
- “Cathode” side = Where the reduction half reaction occurs ($\text{Cu}^{2+} \rightarrow \text{Cu}$ beaker)

Salt Bridge Connector

- In an electrochemical cell, cations are being produced in the anode half ($\text{Zn} \rightarrow \text{Zn}^{2+}$), and cations are being removed in the reduction side ($\text{Cu}^{2+} \rightarrow \text{Cu}$)
- Solutions need to maintain charge balance, so the anode side needs to either gain anions or lose excess cations, and the cathode side needs to either gain cations or lose anions in order to charge-balance.
- This is accomplished via either a “salt bridge” or “semipermeable membrane” (“porous barrier”): something that allows ions to pass

Direction of Ion flow:

- Cations move from anode (being produced) to cathode (to replace cations reduced)
- Anions move from cathode to anode, to balance forming cations

Cell Shorthand Convention

// = barrier between half cells

/ = distinction between electrodes and ions

Many variations on electrochemical cell engineering

- Special cells when H₂ gas is produced (Brown 20.8)
- Many types with conductive graphite electrodes on which surface other redox half-reactions occur
- “Dry cells” involving thick paste mixtures rather than any solvent (many batteries)

19.4 Electrochemical Cells and Voltage

- Voltage depends on redox reactivity, the chemical force for electron transfer

E_{cell} = cell potential in volts ($V = J/C$ $C = \text{coulomb of electricity}$)

E°_{cell} = **standard** potential

Standard Conditions

- 1.0 M concentration
- 25°C
- gases (if any) at 1.0 atm

Since a cell consists of 2 half cells:

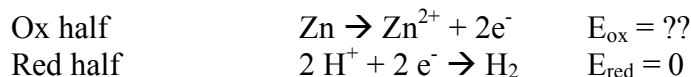
$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{oxidation}} + E^{\circ}_{\text{reduction}}$ <p style="text-align: center;">Anode Cathode</p>

Each half reaction has an E° , relative to self-defined **reference half reaction**



Show Table 19.1, OWL Handout

Example: $\text{Zn} + 2\text{HCl} \rightarrow \text{H}_2 + \text{ZnCl}_2$ $E_{\text{cell}}^{\circ} = +0.76$



$$E^{\circ}_{\text{cell}} = +.76 = E_{\text{ox}} + E_{\text{red}} = E_{\text{ox}} + 0 \quad \text{so } \boxed{E^{\circ}_{\text{ox}} = +0.76 \text{ V}}$$

The same approach can be used to find the potentials for any other half reaction.

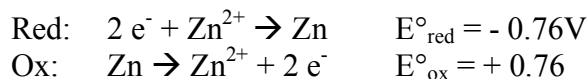
19.5 Using E°_{cell} and known Half Potentials

$$E^\circ_{\text{cell}} = E^\circ_{\text{ox}} + E^\circ_{\text{red}}$$

1. Tables list reduction halves E°_{red}

$\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$	+0.77V
$\text{Cu}^{2+} \rightarrow \text{Cu}$	+0.34V
$2 \text{H}^+ \rightarrow \text{H}_2$	0.00
$\text{Pb}^{2+} \rightarrow \text{Pb}$	-0.13
$\text{Ni}^{2+} \rightarrow \text{Ni}$	-0.25
$\text{Cr}^{3+} \rightarrow \text{Cr}^{2+}$	-0.74

2. When a half is reversed, sign reverses



$$E^\circ_{\text{ox}} = -E^\circ_{\text{red}}$$

Q: What is the oxidation potential for $\text{Cu} \rightarrow \text{Cu}^{2+}$?

3. Key skill: Given known halves, deduce E°_{cell} .



4. Stoichiometry coefficients don't matter to E° 's

- In previous example, the reduction potential for Fe^{3+} was still +0.77 V, even though the balanced reaction had 2 Fe^{3+} ions being reduced.

5. Key skill: Given an overall E°_{cell} and one known or knowable half potential, calculate the half potentials for the other half.



Find E°_{red} for: $\text{Sn}^{2+} \rightarrow \text{Sn}$

Find E°_{ox} for: $\text{Sn} \rightarrow \text{Sn}^{2+}$

6. All redox half-reaction potentials are relative to H^+ reduction ($E^\circ_{\text{red}}=0$) or H_2 oxidation ($E^\circ_{\text{ox}}=0$)

$\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$	+0.77V
$\text{Cu}^{2+} \rightarrow \text{Cu}$	+0.34V
$2 \text{H}^+ \rightarrow \text{H}_2$	0.00
$\text{Pb}^{2+} \rightarrow \text{Pb}$	-0.13
$\text{Ni}^{2+} \rightarrow \text{Ni}$	-0.25
$\text{Cr}^{3+} \rightarrow \text{Cr}^{2+}$	-0.74

7. For a product-favored reaction, $E^\circ_{\text{cell}} = \text{positive}$
- more positive the better

Q: Which of the following are favorable redox reactions?

- a. $\text{Cu} + \text{Sn}^{2+} \rightarrow \text{Sn} + \text{Cu}^{2+}$ $E^\circ_{\text{cell}} = -0.48\text{V}$
- b. $\text{Cu} + 2\text{Fe}^{3+} \rightarrow \text{Cu}^{2+} + 2\text{Fe}^{2+}$ $E^\circ_{\text{cell}} =$
- c. $\text{Cu}^{2+} + \text{Ni} \rightarrow \text{Ni}^{2+} + \text{Cu}$ $E^\circ_{\text{cell}} =$

Logic:

8. For half reactions, the more positive the more favorable

<u>Reductions</u>			<u>Oxidations</u>		
$\text{F}_2 \rightarrow 2 \text{F}^-$	+2.87	great	$2 \text{F}^- \rightarrow \text{F}_2$	-2.87	terrible
$\text{Cu}^{2+} \rightarrow \text{Cu}$	+0.34	good	$\text{Cu} \rightarrow \text{Cu}^{2+}$	-0.34	bad
$\text{Ni}^{2+} \rightarrow \text{Ni}$	-0.25	bad	$\text{Ni} \rightarrow \text{Ni}^{2+}$	+0.25	good
$\text{Li}^+ \rightarrow \text{Li}$	-3.0	terrible	$\text{Li} \rightarrow \text{Li}^+$	+3.0	great

9. Chemical Logic: Redox patterns depend on electron love (predictable periodic trends)
- Higher love for electrons \rightarrow more favorable to be reduced (gain electrons)
 - Higher love for electrons \rightarrow more unfavorable to be oxidized (lose electrons)
 - Fluorine is the most electronegative of the four elements, lithium the least
 - Fluorine loves to be reduced (gain electrons), so has best reduction potential
 - Fluoride hates to be oxidized (lose electrons), so has the worst oxidation potential
 - Lithium has low electron love, so is easily oxidized
 - Because it is so unattractive towards electrons, lithium cation has lousy oxidation potential

Q1: Based on table, rank the electron affinities for Cu, H₂, Ni, and Pb

Q2: Which would be a stronger oxidizing agent (stealer of e's), Cu²⁺ or Ni²⁺ ?

Q3: Which would be a stronger reducing agent (giver of e's), Cu or Ni ?

Redox conjugates: Oxidizing vs. Reducing Agents, Oxidized versus Reduced Forms

Love For Electrons	Strength as Oxidizing Agents		Strength as Reducing Agents	Love For Electrons
		$\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$ $\text{Cu}^{2+} \rightarrow \text{Cu}$ $2 \text{H}^+ \rightarrow \text{H}_2$ $\text{Pb}^{2+} \rightarrow \text{Pb}$ $\text{Ni}^{2+} \rightarrow \text{Ni}$ $\text{Cr}^{3+} \rightarrow \text{Cr}^{2+}$	+0.77V +0.34V 0.00 -0.13 -0.25 -0.74	

On table:

Left Side

- 1 **Oxidized form** (less electrons)
- 2 **Oxidizing Agents** (may wish to grab electrons from something else and so oxidize the other thing)
- 3 Higher up = stronger oxidizing agent
- 4 Higher up = greater love for electrons
- 5 Higher E°_{red} \Rightarrow
 - a. more easily reduced
 - b. stronger love for e's
 - c. stronger oxidizing agent

Right Side

- Reduced Form** (more electrons)
Reducing Agents (able to give electrons to something else and so reduce the other thing)
Lower down = stronger reducing agent
Lower down = lesser love for electrons

- Often things aren't charted like this. But for two things in their oxidized forms, the one with the higher E°_{red} \Rightarrow
 - a. more easily reduced
 - b. stronger love for e's
 - c. stronger oxidizing agent

If charting reduction potentials:

- upper left = strongest oxidizing agent = max electron love = most easily reduced
- bottom right = strongest reducing agent = minimum electron love = most easily oxidized.

Some Representative Problem Types

- a. Rank the oxidizing agents by strength
- b. Rank the reducing agents by strength
- c. Which will react with Cu^{2+} ?
- d. Which will react with Cu^0 ?

Brown Fig. 20.10

Love For Electrons	Strength as Oxidizing Agents		Strength as Reducing Agents	Love For Electrons
		$\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$	+0.77V	
		$\text{Cu}^{2+} \rightarrow \text{Cu}$	+0.34V	
		$2 \text{H}^+ \rightarrow \text{H}_2$	0.00	
		$\text{Pb}^{2+} \rightarrow \text{Pb}$	-0.13	
		$\text{Ni}^{2+} \rightarrow \text{Ni}$	-0.25	
		$\text{Cr}^{3+} \rightarrow \text{Cr}^{2+}$	-0.74	

- Strongest Oxidizing agent: top left (max e- love)
- Strongest Reducing agent: bottom right (min e- love)

Odds and Ends

- An oxidizing agent on table will react (product-favored) with any reducing agent lower
 - Will not react with any reducing agent higher (reactant favored)
 - A reducing agent will only react with an oxidizing agent higher on the chart
 - What species would react with Pb^{2+} ?
 - What species would react with Pb?
- For two species to react, one must be in reduced form (reducing agent), and the other in oxidized form (oxidizing agent)
 - What of the following species could react with Cu^{2+} ?

$2 \text{H}^+ \quad \text{H}_2 \quad \quad \quad \text{Pb}^{2+} \quad \text{Pb} \quad \quad \quad \text{Ni} \quad \text{Ni}^{2+} \quad \quad \quad \text{Cr}^{2+} \quad \text{Cr}^{3+}$
 - What of the following species could react with Cr^{2+} ?

$2 \text{H}^+ \quad \text{H}_2 \quad \quad \quad \text{Pb}^{2+} \quad \text{Pb} \quad \quad \quad \text{Ni} \quad \text{Ni}^{2+}$
- Given redox chart, rank electron love and basically predict which reactions are or aren't favorable
- Based on periodic table, predict reactivity **without redox table** (based on general periodic patterns in electron love)
 - General Activity as Reducing Agents (increasing e- love)

$\text{G1} > \text{G2} > \text{Al} > \text{most T-metals} > \text{H}_2 > \text{coinage metals}$
(active metals)

Ex. Li Mg Al Zn, Fe, Cr H₂ Cu, Au

$\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$	+0.77V
$\text{Cu}^{2+} \rightarrow \text{Cu}$	+0.34V
$2 \text{H}^+ \rightarrow \text{H}_2$	0.00
$\text{Pb}^{2+} \rightarrow \text{Pb}$	-0.13
$\text{Ni}^{2+} \rightarrow \text{Ni}$	-0.25
$\text{Cr}^{3+} \rightarrow \text{Cr}^{2+}$	-0.74

5. Given 2 reduction potentials, figure out how a product-favored cell would be constructed and calculate the standard voltage
- Keep the more favorable reduction potential as the reduction half, but reverse the other into its oxidation version
 - Then sum $E^\circ_{\text{red}} + E^\circ_{\text{ox}}$ to get E°_{cell}

Examples

e. Determine what the voltage would be for a cell consisting of Pb^{2+}/Pb and Ni^{2+}/Ni .

f. Determine what the voltage would be for a cell consisting of Pb^{2+}/Pb and Cu^{2+}/Cu .

6. Use observed reactivities to determine:
- relative love for electrons
 - relative strength as reducing agents
 - relative strength as oxidizing agents
 - relative redox table (“activity series”)

Example: $\text{X} + \text{Y}^{2+} \rightarrow \text{Y} + \text{X}^{2+}$ Product-favored redox. Questions: Between X and Y:

- Which element loves electrons more?
- What thing is the strongest reducing agent?
- Which thing is the strongest oxidizing agent?
- Draw a little reduction potential chart, with the strongest oxidizing agent in the upper left corner as usual

A Redox Reaction Always favors “weaker” side

Example: $Q + P^{2+} \leftarrow P + Q^{2+}$ Reactant-favored redox. Between P and Q:

- Which element loves electrons more?
- What thing is the strongest reducing agent?
- Which thing is the strongest oxidizing agent?
- Draw a little reduction potential chart, with the strongest oxidizing agent in the upper left corner as usual

A Redox Reaction Always favors “weaker” side

Miscellaneous Problems

- $Zn + Fe^{2+} \rightarrow Zn^{2+} + Fe$ $E^\circ = 0.32V$
 What is the “reduction potential” for $Fe^{2+} (Fe^{2+} \rightarrow Fe^\circ)$ given the above potential, and given that $Zn^{2+} \rightarrow Zn$ $E^\circ_{red} = -0.76$

- Find E° for product favored reaction involving the following, and balance the reaction

$Fe^{3+} \rightarrow Fe^{2+}$	0.77
$Cu^{2+} \rightarrow Cu$	0.34

 - keep more favorable one as reduction
 - reverse less favorable to make it an oxidation
 - sum E°_{ox} and E°_{red}
 - adjust coefficients to balance e's

- Ditto for

$Br_2 \rightarrow 2 Br^-$	$+1.06$
$Zn^{2+} \rightarrow Zn$	-0.76

	V
$\text{Ag}^+ \rightarrow \text{Ag}$	+0.80
$\text{Cu}^{2+} \rightarrow \text{Cu}$	+0.34
$\text{Zn}^{2+} \rightarrow \text{Zn}$	-0.76
$\text{Al}^{3+} \rightarrow \text{Al}$	-1.66
$\text{Mg}^{2+} \rightarrow \text{Mg}$	-2.36

12. Which species react with Cu^{2+} ?

13. Which species react with Zn° ?

14. Which element loves e's the most? Least?

15. $\text{NiCl}_2 + \text{H}_2 \rightarrow \text{Ni} + 2 \text{HCl}$ $E^{\circ} = -0.28 \text{ V}$

a. Product favored or not?

b. Is reduction potential for Ni^{2+} positive?