

Unit 4: Exam Review

ELECTROCHEMISTRY

PS: PLEASE DO MY ECIS REVIEW. I LIKE TO READ THE COMMENTS. THEY'RE FUNNY

Exam Four Learning Outcomes

Identify an oxidation – reduction (redox) reaction based on changes in oxidation numbers across the chemical change.

Identify oxidizing/reducing agents in chemical reaction.

Completely balance a redox reaction in acidic or basic solution.

Recognize degrees of reactivity based on an activity series or a standard potential table.

Apply standard potential data to determine the relative strength of oxidizing and reducing agents.

Construct an electrochemical cell diagram or drawing which includes the identification of the anode, cathode, and salt bridge from either a redox reaction or from the short hand cell notation.

Show the direction of electron flow, the sign of the electrodes, the direction of ion flow in the salt bridge, on a given cell diagram or drawing.

Describe the standard hydrogen electrode (SHE) and state its function.

Apply standard potential data to calculate the standard cell potential for an electrochemical cell and from the sign of the potential predict if the cell is voltaic or electrolytic.

Calculate the cell potential for a nonstandard cell.

Describe fully the relationship between the standard free energy and the standard cell potential

Describe fully the relationship between standard cell potential and the equilibrium constant

Explain thermodynamically the operation of a concentration cell, and be able to predict the concentration in the cell based on the measured cell potential.

Understand the relationship between the quantity of charge delivered or produced (coulombs) and the amount of reactant used or product formed (moles) for both voltaic and electrolytic cells.

Describe the basic principles of battery design and function.

Identify the differences and similarities of the three fundamental types of batteries: primary cells, secondary cells, and fuel cells.

Know the details of the chemical reactions used in a lead-acid battery.

Note that this does not include photovoltaics, specifics of PEM, knowing the half-reaction of the different cells, etc.

Batteries

- 1. Primary Cell:** a voltaic cell capable only of discharging. Primary cells are one-time use batteries.
 - The common primary cells in our lives are alkaline cells (D, C, AA, AAA, etc.)
 - These all involve the same reaction, meaning they have the same standard potential.
 - They differ in size; therefore, they differ in current. A large surface area (D-batteries) will have a greater current (less internal resistance)
- 2. Secondary Cell:** a battery that can act like a voltaic cell when discharging, but can also act like an electrolytic cell when recharged (examples: cell phone battery, lead-acid car battery, Lithium-Ion). Secondary cells can be used numerous times (or continuously) until eventually the battery degrades.
 - **Lead-Acid Car Battery:** a specific type of secondary cell that involves lead in three solid oxidation states. **A car battery relies on the fact that an alternator can physically generate the electricity necessary to recharge the battery** *omitted on Dr. McCord's exam

Corrosion Definitions

- 1. Active Metal:** a metal that is easily oxidized
- 2. Sacrificial Anode:** a more reactive metal (an active metal) that is placed in close proximity to a metal surface to prevent the corrosion (oxidation, especially rusting of iron and steel) of the metal surface.
 - In a sense, you are forcing one metal to undergo corrosion so that the metal you need to preserve is protected (hence the name, “sacrificial anode”)
 - **Remember, this will only work in a situation where your sacrificial anode is more likely to undergo oxidation than your metal surface.**

Unit 4 Equations

1. Electrochemical Cell Potential

$$\mathcal{E}^{\circ}_{cell} = \mathcal{E}^{\circ}_{cathode} - \mathcal{E}^{\circ}_{anode}$$

2. Faraday's Law, plating a metal

$$\frac{I \cdot t}{n \cdot F} = \text{moles created}$$

3. Convert between electrical potential (\mathcal{E}) and free energy (ΔG)

$$\Delta G = -nF\mathcal{E}$$

$$\Delta G^{\circ} = -nF\mathcal{E}^{\circ}$$

4. Convert between electrical potential (\mathcal{E}) and the equilibrium constant (K)

$$\mathcal{E}^{\circ} = \frac{RT}{nF} \ln K$$

$$\mathcal{E}^{\circ} = \frac{0.05916}{n} \log K$$

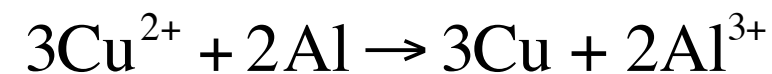
5. Non-standard Cell Potential

$$\mathcal{E} = \mathcal{E}^{\circ} - \frac{RT}{nF} \ln Q$$

$$\mathcal{E} = \mathcal{E}^{\circ} - \frac{0.05916}{n} \log Q$$

Electrochemistry Definitions

- 1. Redox Reaction:** a chemical reaction that involves the transfer of electrons from one species to another, resulting in a change in oxidation state. A redox reaction involves one species undergoing reduction and another undergoing oxidation.
- 2. Oxidation State:** a number assigned to an element based on the number of electrons gained or lost by that element in a compound or solution
- 3. Reduction:** a species gains electrons, resulting in a lower oxidation state
- 4. Oxidation:** a species loses electrons, resulting in a higher oxidation state
- 5. Oxidizing Agent:** the species that drives the oxidation of another species in a redox reaction ; the oxidizing agent is always the species undergoing reduction
- 6. Reducing Agent:** the species that drives the reduction of another species in a redox reaction ; the reducing agent is always the species undergoing oxidation



LEO says GER
OIL RIG

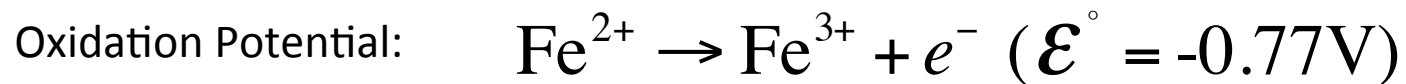
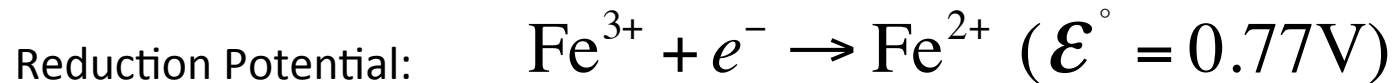
Electrochemical Potential

- **Electrical Cell Potential ($\mathcal{E}^\circ_{\text{cell}}$):** the voltage associated with the redox reaction occurring in an electrochemical cell

$$\mathcal{E}^\circ_{\text{cell}} = \mathcal{E}^\circ_{\text{cathode}} - \mathcal{E}^\circ_{\text{anode}}$$

in this equation, both \mathcal{E}° values are reduction potentials read from a table

- Keep in mind that we can still express an oxidation potential on the exam in the following way:



Electrochemical Cell Definitions

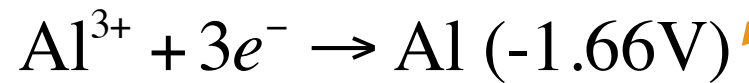
1. **Cathode**: the site of reduction (Red Cat) ; takes in electrons from the wire
2. **Anode**: the site of oxidation (An Ox) ; gives electrons to the wire
3. **Voltaic Cell (Galvanic Cell)**: an electrochemical cell with a positive standard cell potential ; the redox reaction of the cell occurs without an external power source (spontaneous)
4. **Electrolytic Cell**: an electrochemical cell with a negative standard cell potential ; the redox reaction of the cell relies on an external power source (non-spontaneous)
5. Shorthand Notation:

anode | anodic solution || cathodic solution | cathode

inert metal | anode reactant | anode product || cathode reactant | cathode product | inert metal

The Electrochemical Cell

Using the following half-reactions, show the voltaic and electrolytic cells that can be created:



Reduction potentials from your coversheet

Checklist:

- Label anode, cathode
- Charges on anode, cathode
- Direction of electrons
- Conductive Wire
- Salt Bridge
- Voltmeter or Power Source

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

Galvanic Voltage: **2.43V** = (0.77V) - (-1.66V) ; **Al | Al³⁺ || Fe³⁺, Fe²⁺ | Pt**

Electrolytic Voltage: **-2.43V** = (-1.66V) - (0.77V) ; **Pt | Fe²⁺, Fe³⁺ || Al³⁺ | Al**

The Electrochemical Cell Summary

	voltaic cells	electrolytic cells
free energy, ΔG	negative (-)	positive (+)
potential, E	positive (+)	negative (-)
push/pull of electrons	from the chemical reactions of the two half-reactions	from an external electrical power source
anode	negative (-)	positive (+)
cathode	positive (+)	negative (-)

In all electrochemical cells, the electrons travel from the site of oxidation (anode) to the site of reduction (cathode). The main difference is that voltaic cells are spontaneous cells, **where the redox reaction drives the current**. In an electrolytic cell, the redox reaction is non-spontaneous. **Therefore, the push/pull of current is driven by an external power source.**

Faraday's Law

Last week we said that electrolytic cells can be very important to create a metal from its ions.

- We can run an electrolytic cell by inputting voltage with a power source
- In an experimental setting, it's more reasonable to calculate the amount of moles using current, time, and a little bit of information about the overall reaction (number of moles, Faraday's constant):

$$\frac{I \cdot t}{n \cdot F} = \text{moles created}$$

- You should recognize that electrolysis, metal plating, and any plain electrolytic cells with a given current use Faraday's Law

Free Energy and Electrical Work

1. There is a simple relationship between free energy and electrical potential:

$$\Delta G = -nF\mathcal{E}$$

2. This equation can be applied to tell us about the capacity for an electrochemical system to do work:

$$w = -q \cdot \mathcal{E}$$

3. These values are ideal, meaning we are calculating the maximum electrical work, **or the maximum reversible non-expansion work.**
4. This relationship provides an effective way of determining the capacity for a chemical system to do work when we do not have a change in gas moles (no change in volume)

Electrical Potential and Equilibrium

Now that we know the relationship between electrical potential and free energy:

$$\Delta G^\circ = -nF\mathcal{E}^\circ \qquad \Delta G^\circ = -RT \ln K$$

We can very clearly connect the dots between free energy and the equilibrium constant, K :

$$\mathcal{E}^\circ = \frac{RT}{nF} \ln K$$

$$\mathcal{E}^\circ = \frac{0.05916}{n} \log K$$

Non-Standard Cells Electrical Potential

You can use Q to determine the non-standard potential with the Nernst Equation:


$$\mathcal{E} = \mathcal{E}^\circ - \frac{RT}{nF} \ln Q \quad \text{OR:} \quad \mathcal{E} = \mathcal{E}^\circ - \frac{0.05916}{n} \log Q$$

Remember how Q works (and remember that Q depends only on aqueous and gaseous species!):

- Q is the given concentrations (or pressures) of the products raised to the power of their coefficients divided by the reactants raised to the power of their coefficients.
- If you add product, your voltage drops
- If you add reactant, your voltage increases

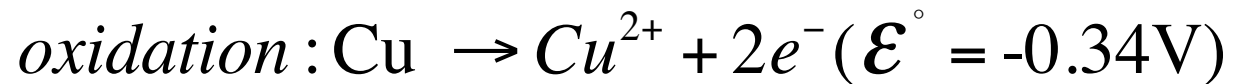
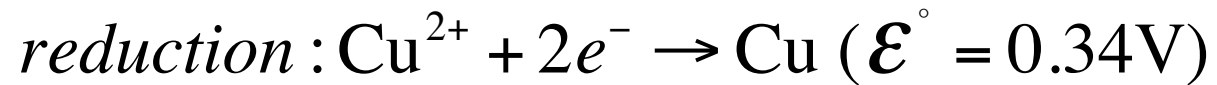
Conceptual Summary: Standard Cells

Electrical Potential ϵ°	Free Energy ΔG°	Equilibrium Constant K	Spontaneous?
Positive	Negative	Greater than 1	Yes
Negative	Positive	Less than 1	No
Zero	Zero	Equal to 1	At Equilibrium


Concentration Cell

The Concentration Cell

A concentration cell is simply a cell that has identical half-reactions and achieves a positive cell potential by having a favorable Q-value in the Nernst Equation.



$$\mathcal{E}^{\circ}_{\text{cell}} = \mathcal{E}^{\circ}_{\text{reduction}} + \mathcal{E}^{\circ}_{\text{oxidation}}$$
$$\mathcal{E}^{\circ}_{\text{cell}} = 0\text{V}$$

$$\mathcal{E} = \cancel{\mathcal{E}^{\circ}}_{=0\text{V}} - \frac{0.05916}{n} \log Q$$

You can maximize \mathcal{E} by minimizing Q:

1. Increasing the concentration of Cu^{2+} in the cathode compartment
2. Decreasing the concentration of Cu^{2+} in the anode compartment

☰ back to Tables Listing (index.php)

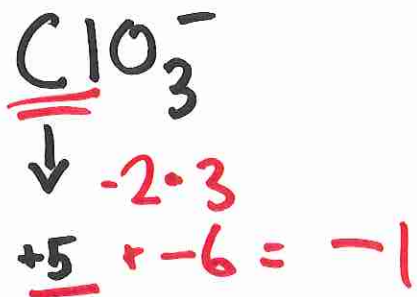
Standard Potentials at 25°C

Half Reaction	Potential
$F_2 + 2e^- \rightleftharpoons 2F^-$	<u>+2.87 V</u>
$Pb^{4+} + 2e^- \rightleftharpoons Pb^{2+}$	<u>+1.67 V</u>
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36 V
$Ag^+ + e^- \rightleftharpoons Ag$	+0.80 V
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.77 V
$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0.34 V
$2H^+ + 2e^- \rightleftharpoons H_2$	0.000 V
$Fe^{3+} + 3e^- \rightleftharpoons Fe$	-0.04 V
$Pb^{2+} + 2e^- \rightleftharpoons Pb$	-0.13 V
$Fe^{2+} + 2e^- \rightleftharpoons Fe$	-0.44 V
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	-0.76 V
$Al^{3+} + 3e^- \rightleftharpoons Al$	-1.66 V
$Mg^{2+} + 2e^- \rightleftharpoons Mg$	-2.36 V
$Li^+ + e^- \rightleftharpoons Li$	<u>-3.05 V</u>

Note: all ions are aqueous (aq), many neutral species are solids (s), although some are liquids (l), gases (g), and even aqueous (aq). Use other sources for details on state. They were purposely left off here to save space and keep a cleaner looking table.

Reduction, oxidizing agents
 Oxidation, reducing agents

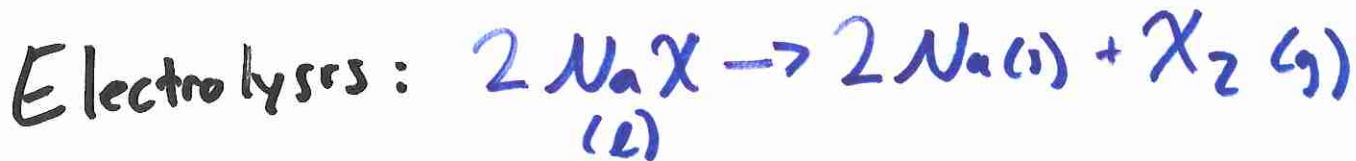
H → +1, O → -2, IA metals → +1
 named metals Iron (III) → 3+



$$\frac{d \cdot t}{n \cdot F} = \text{moles created}$$

n (circled in red) \Downarrow moles e^-
metal mole formed

$+MW \rightarrow g$
 $PV=nRT$ \swarrow @ STP $0^\circ C, 1 \text{ atm}$
 $22.4 \frac{L}{\text{mol}}$
 \searrow V created



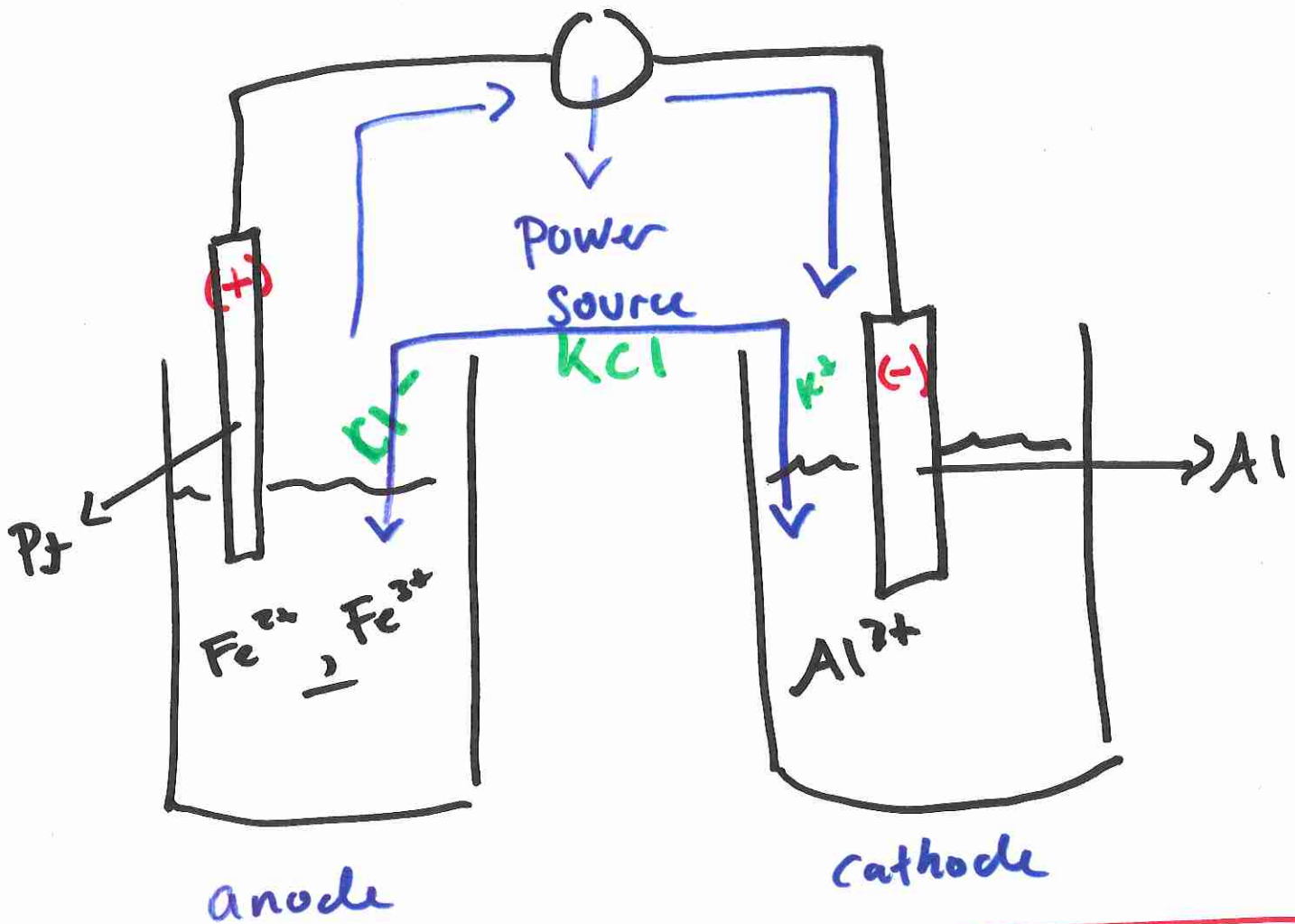
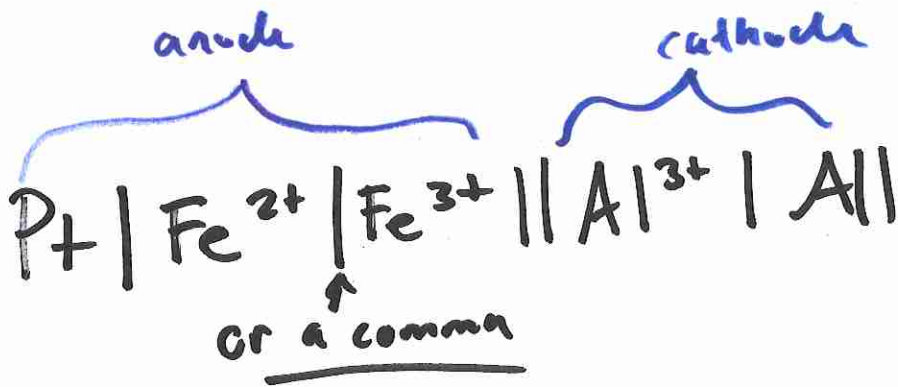
if asked about $\text{Na}(s)$:

$$n=1$$

if asked about $\text{Cl}_2(g)$:

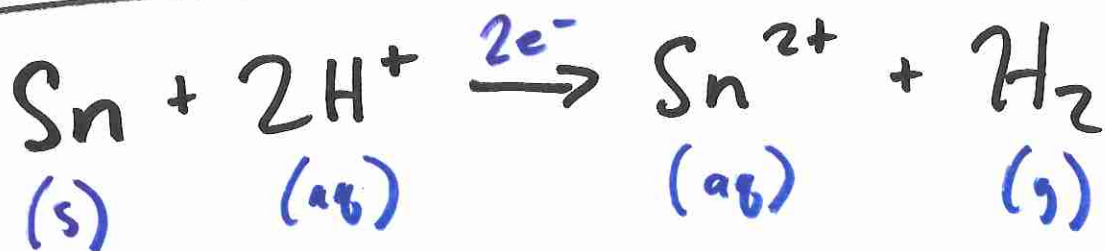
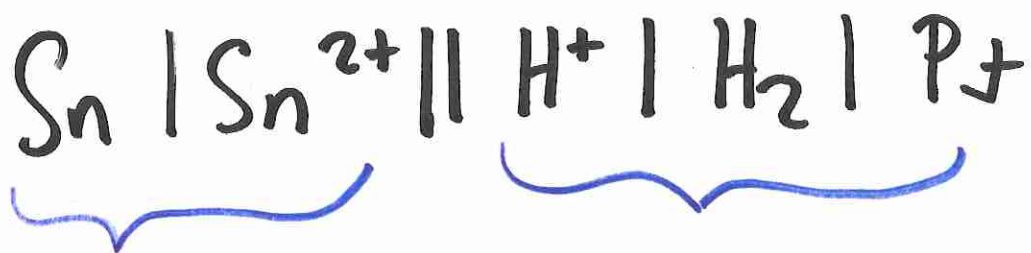
$$n=2$$

\Downarrow metal will always be formed @ cathode



A P E → electrolytic
 ↓ ↓
 anode positive

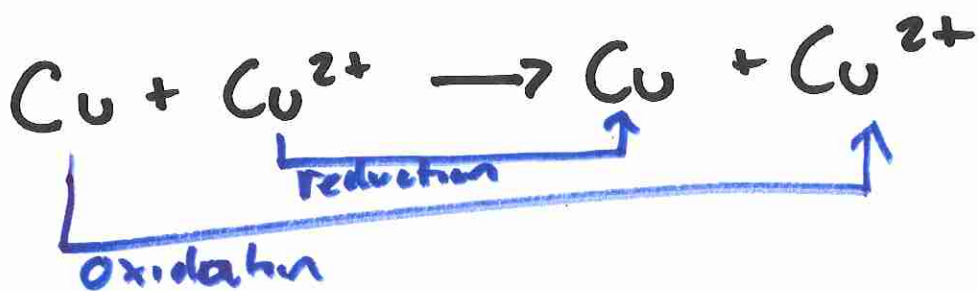
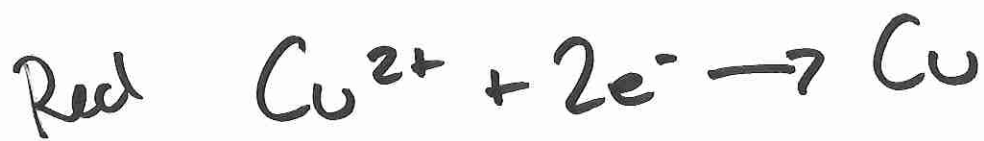
Salt bridge
 cations → cathode
 anions → anode



$$\mathcal{E} = \mathcal{E}^0 - \frac{0.05916}{n} \log Q$$

$$Q = \frac{[\text{Sn}^{2+}] \cdot P_{\text{H}_2}}{[\text{H}^+]^2}$$

- (1) Added H_2 gas $Q \uparrow, \mathcal{E} \downarrow$
- (2) Add Pt Q, \mathcal{E} same
- (3) Remove Sn^{2+} $Q \downarrow, \mathcal{E} \uparrow$
- (4) Increase the pH $[\text{H}^+] \downarrow, Q \uparrow, \mathcal{E} \downarrow$



$$Q = \frac{[\text{Cu}]_{\text{anode}}}{[\text{Cu}^{2+}]_{\text{cathode}}}$$

↳ only for simple concentration cells

$$E = - \frac{0.05916}{n} \log Q$$

$E (+)$ when $[\text{Cu}^{2+}]_{\text{cathode}} > [\text{Cu}^{2+}]_{\text{anode}}$

~~$Q > 1$~~ $Q < 1$