

Chemistry 12

Reduction-Oxidation (Redox)
aka Electrochemistry

Oxidation and Reduction

What is a redox reaction?

Oxidation –

What type of substances tend to oxidize?

Reduction –

Hint with respect to oxidation and reduction:

In order for a redox reaction to occur, there must be an oxidation **AND** a reduction (ie. one substance has to first 'give-up' electrons in order for another substance to receive them).

All single replacement reactions are redox reactions. Take, for example, the reaction of iron metal in copper (II) chloride solution:



Iron starts as a metal with a charge of zero, and becomes an ion dissolved in solution with a charge of _____. Are electrons donated or accepted by Fe during its transformation to Fe^{2+} ? _____

Thus, Fe undergoes _____, and the *half-reaction* is:

Copper, as a reactant, is actually a dissolved ion with a charge of _____:

What does copper become, as a product?

Are electrons donated or accepted by the copper ion during its transformation to Cu? _____

Therefore, _____ undergoes _____, and the *half-reaction* is:

'Chlorine' actually begins as a dissolved ion (_____ or _____) as a reactant and remains so as a product, thus it does not take part in the redox reaction (it is simply a spectator ion).

To summarize:



Balancing electrons (here, we need to be sure that the amount of electrons *donated* equals the amount of electrons *accepted*):

Overall Net Redox Reaction:

So, for every iron atom that oxidizes, two electrons are released, which are enough to reduce one Cu^{2+} ion (hence, the 1:1 stoichiometry).

Note: the reactant that was a metal (iron) oxidized to become a positive cation, Fe^{2+} , as metals tend to do. Cu^{2+} , a metal cation, reduced to become a metal (the opposite process and therefore a reduction).

Some single replacement reactions involving metals and aqueous salt solutions are spontaneous (like our example above) and some are non-spontaneous (recall the *Activity Series* that you may have learned in Chemistry 11). Non-spontaneous reactions of this type require an injection of *electricity* in order for the reaction to occur.

A half-reaction specifies either the oxidation or reduction that occurred, whereas the net redox reaction is the combination of the two (with electrons balanced and subsequently canceled).

Silverware (silver/Ag) reacts with H₂S (hydrogen sulfide) that is present (in trace amounts) in the air in order to produce Ag₂S (tarnish). The '*cleaning*' (de-tarnishing) of silverware is a redox reaction:



*This reaction requires **heat** in order to overcome E_a and **water** to act as an electron transfer medium. Thus, the silverware is placed into a pan of water which is lined with aluminum foil and then heated gently in the oven.

Oxidation half-reaction:

Reduction half-reaction:

Net redox reaction:

*again...no electrons are noted in a net redox reaction → all are accounted for, and canceled, in the balancing process.

Oxidizing Agents and Reducing Agents

An **Oxidizing Agent** is a substance which _____ another substance. Therefore, an oxidizing agent itself undergoes _____.
What were the oxidizing agents in each of the previous examples?

A **Reducing Agent** is a substance which _____ another substance. Therefore, a reducing agent itself undergoes _____.
What were the reducing agents in each of the previous examples?

Practice Questions: For each of the following reactants, provide the

a) oxidation half-reaction b) reduction half-reaction

c) balanced redox reaction d) oxidizing agent e) reducing agent

*assume a metal ion reacts to become the corresponding metal (eg. in number 1, assume Ag^+ becomes Ag).

1) Na and Ag^+

2) Al and Cu^{2+}

3) Li and Fe^{3+}

4) Br_2 and Cr to produce Br^- and Cr^{3+}

Assignment 1: Read Hebden p.190 (start at 'Definitions') & 191 and do p.192 #1-2

Oxidation Numbers

An **Oxidation Number** is the _____ charge (for ions, ionic compounds, and neutral atoms/molecules) or _____ charge (for covalent compounds) that an atom possesses. It is very similar to _____.

Guidelines for Assigning Oxidation Numbers

The sum of the *positive* and *negative* oxidation numbers must equal the overall charge on the substance.

A) For neutral/non-polar covalent atoms/molecules, the oxidation number is 0.

Examples : Al C P₄ N₂ S₈
Oxidation #: ___ ___ ___ ___ ___

B) For ions, the oxidation number equals the charge on the ion.

Examples: Mn²⁺ Br⁻ S²⁻ Cu⁺ Al³⁺
oxidation #: ___ ___ ___ ___ ___

C) Polyatomic ions can be assigned a total oxidation number, which would be its ionic charge, or each element in the ion can be assigned its own oxidation number (part D will explain how to do this)

Find the total oxidation number: SO₄²⁻ OH⁻ PO₄³⁻
 ___ ___ ___

D) To assign individual elements an oxidation number in a compound or polyatomic ion, perform the following steps in order:

- 1) alkali metals are assigned a +1
- 2) alkaline earth metals are assigned a +2
- 3) Other metals with only one possible oxidation number (combining capacity)
- 4) oxygen is -2 (exceptions: peroxides (either X₂O₂ or XO₂, in general) → specifically: _____ or _____.
- 5) hydrogen is +1 (unless part of a *metal hydride* in which case -1)
 ex) CaH₂ (a metal hydride) → Ca is +2, so each H has to be ____.
- 6) halogens are -1 (but can be different in certain situations)
- 7) Lastly, assign any atom that is left over using arithmetic logic.

*Note: Since oxidation numbers are *apparent* for atoms in covalent compounds, sometimes an atom may possess a non-integer oxidation number.

Practice Questions: Determine the oxidation numbers of each element.

a) MnO_4^- b) SO_2 c) SO_4^{2-} d) PCl_5 e) Cu_2O f) HBiO_3 g) OCl^-

h) NH_2OH i) NO_3^- j) I_2 k) Cr^{3+} l) Cr m) N_2O_5 n) $\text{H}_4\text{P}_2\text{O}_7$

Now that we know how to find them, how are oxidation numbers helpful?

When an atom undergoes oxidation during a redox reaction, its oxidation number will _____ as it changes from reactant to product (it loses electrons – becomes more positive/less negative).

When an atom undergoes reduction during a redox reaction, its oxidation number will _____ as it changes from a reactant to a product (it gain electrons - becomes more negative/less positive).

Assigning oxidation numbers to reactants and products in a chemical reaction is helpful in determining whether the reaction is, in fact, a redox reaction, and if so, which reactant is oxidizing and which reactant is reducing.

*A Generalization that gave rise to the Terms:

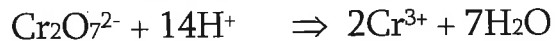
Species that undergo OXIDATION have their oxygen-to-other species ratio _____.

Species that undergo REDUCTION have their oxygen-to-other species ratio _____.

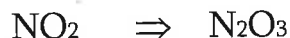
This generalization may only be considered when oxygen is actually observed in a reaction (in elemental or compound form).

Practice Questions

1. For the following balanced half-reaction (with electrons removed), how does the oxidation number of chromium change? Is the chromium oxidizing or reducing?

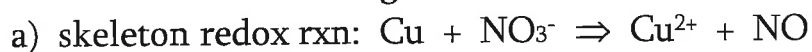


2. What happens to the oxidation number for nitrogen in the unbalanced (skeleton) half-reaction? Is the nitrogen, in nitrogen dioxide, oxidizing or reducing?

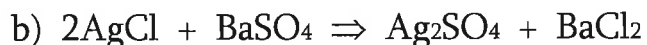
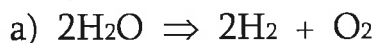


3. Use the generalization to determine whether CrO_4^{2-} oxidizes or reduces to form $\text{Cr}_2\text{O}_7^{2-}$. Then, use oxidation numbers to confirm. What do you notice? Conclusion?

4. Use oxidation numbers to identify which substance is oxidized and which is reduced in the following redox reactions:

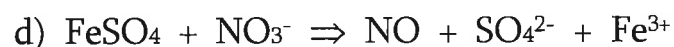
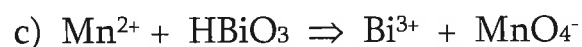
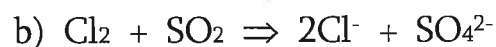
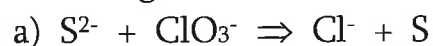


5. Use oxidation numbers to determine whether the following reactions are actually redox reactions.

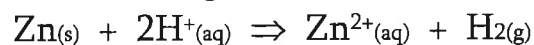


Assignment 2: Read Hebden p.193-194, do p. 194 #3-6, and the following questions:

1) For each unbalanced reaction, which species is being oxidized and which is being reduced?



2) Consider the following reaction:



The species being oxidized is: (circle the correct response)

- A. H_2 B. H^+ C. Zn D. Zn^{2+}

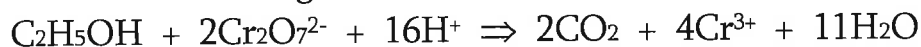
3) When SO_4^{2-} reacts to form $\text{S}_2\text{O}_6^{2-}$, the sulfur atoms

- A. lose electrons and are reduced
B. gain electrons and are reduced
C. lose electrons and are oxidized
D. gain electrons and are oxidized

4) In a reaction, the oxidation number of Cr decreases by 3. This indicates that Cr is

- A. reduced
- B. oxidized
- C. neutralized
- D. a reducing agent

5) Consider the following redox reaction:



Each carbon atom loses

- A. 2 electrons
- B. 4 electrons
- C. 6 electrons
- D. 12 electrons

Introduction to the Table of Standard Reduction Potentials

The last page of your data booklet...check it out!

On the left side, oxidizing agents (species that _____) are listed from strongest to weakest as you go _____ the table (sort of like acids in the acid/base table). Notice that from left to right, all reduction half-reactions show a gain of electrons.

In general, the strongest oxidizing agents (species that reduce) are halogens and many oxyanions.

On the right side, reducing agents (species that _____) are listed from strongest to weakest as you move _____ the table (sort of like bases in the acid/base table). Notice that the oxidation half-reactions, when read from right to left on the table, show electrons being lost.

Generally speaking, what type of substances seem to be the strongest form of reducing agent?

The double-arrow **does not** imply that the reactions are at equilibrium (nor does it imply that the reactions can reach equilibrium). The double-arrow simply means that the half-reactions can occur in *either* direction depending on the substances present in a reaction. Once you know the direction to use (oxidation or reduction) for a specific reaction, use only a one-way arrow when writing the half-reaction.

Why do some substances such as Cu^+ , H_2O_2 , & Fe^{2+} appear on both sides of the table?

Many of the metals have more than one common oxidation number, and therefore may have multiple half-reactions on the table (i.e. copper can have oxidation numbers of 0, +1, +2)

Some half-reactions require acidic conditions (H^+ from a STRONG acid must be present), while some require basic conditions (OH^- from a STRONG base must be present).

Predicting Spontaneity

How might you know whether a redox reaction is spontaneous or not?

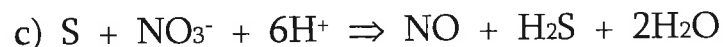
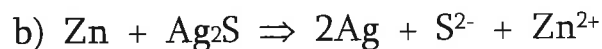
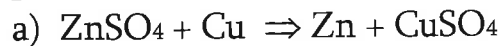
Recall: In order for a redox reaction to occur, there must be a reduction and an oxidation occurring simultaneously.

The first thing to do is figure out what substance is oxidizing, and what substance is reducing. Then, consider the reduction half-reaction and the oxidation half-reaction while taking into account the following:

1. If the reduction half-reaction is **higher** on the table than the oxidation half-reaction (remember that the oxidation half-reactions are written backwards (right-to-left) on the table), then the reaction is _____.
2. If the reduction half-reaction is **lower** on the table than the oxidation half-reaction (or, if on the same line), the reaction is _____.
3. **No redox reaction** is possible if the reactants can both *only* reduce or can both *only* oxidize (both found only on the same side of the table).

Practice Questions:

1. Classify the following reactions as being spontaneous, non-spontaneous, or not possible by any means (ie. no reaction at all).

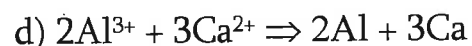
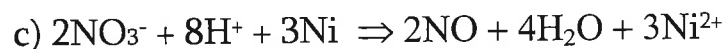
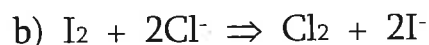
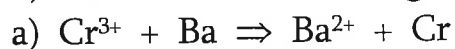


2) Which metal can be oxidized by I_2 but not by an acidic solution of SO_4^{2-} ? (Note: in future questions like this, assume that we are trying to discern the differences between spontaneous and non-spontaneous situations. If we were to consider answers where no reaction is even possible, the answer key would be infinitely long).

3) Which metal(s) can act as a reducing agent for Sn^{2+} but not for Co^{2+} ?

Assignment 3

1) Which of the following reactions occur spontaneously?



2) What products are formed when NO_3^- in acidic solution is reduced by $\text{Fe}_{(s)}$?

3) Read Hebden p.195-199 and do p.199 #8ace, 9ac, 10ac, 11aeg, 12(all)

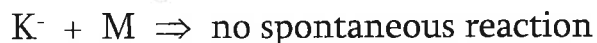
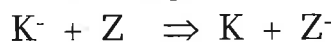
Redox Logic Problems

Strategy to solve redox logic problems:

- i) separate all substances into two columns, oxidizing agents and reducing agents;
- ii) list the reduction half-reactions to produce a 'crude' mini-redox table;
- iii) correct the table, if need be, using the information provided;
- iv) answer the pertaining question using your correct mini-redox table.

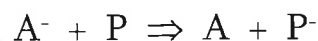
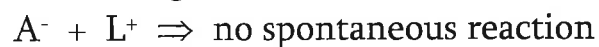
Examples:

1) Given the following information:



List the reducing agents from strongest to weakest (M is a nonmetal and becomes M^- when reduced).

2) Given the following information:

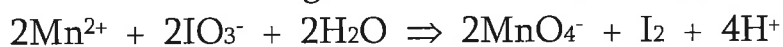


List the oxidizing agents from strongest to weakest (L is a metal and becomes L^+ when oxidized).

Assignment 4: Hebden p.200 #14-18

Assignment 5: Multiple Choice Review Practice

1. Consider the following oxidation-reduction reaction:



The reducing agent is

- A. I_2 B. IO_3^-
C. H_2O D. Mn^{2+}
2. Consider the reaction below:
$$\text{Cu}^{2+}(\text{aq}) + \text{Ni}(\text{s}) \Rightarrow \text{Ni}^{2+}(\text{aq}) + \text{Cu}(\text{s})$$

This reaction will proceed spontaneously because Cu^{2+}
A. is more easily oxidized than Ni^{2+}
B. is a weaker reducing agent than Ni^{2+}
C. is a stronger reducing agent than Ni^{2+}
D. gains electrons more readily than does Ni^{2+}
3. A piece of zinc metal is dropped into a solution of FeCl_2 . The result of this procedure is
A. no reaction B. the zinc is oxidized by Cl_2
C. the iron is oxidized by Zn^{2+} D. the zinc is oxidized by Fe^{2+}
4. Consider the redox reaction below:
$$2\text{BrO}_3^- + 10\text{Cl}^- + 12\text{H}^+ \Rightarrow \text{Br}_2 + 5\text{Cl}_2 + 6\text{H}_2\text{O}$$

The oxidation half-reaction involved in this reaction is
A. $2\text{Cl}^- \Rightarrow \text{Cl}_2 + 2\text{e}^-$
B. $2\text{H}^+ \Rightarrow \text{H}_2 + 2\text{e}^-$
C. $\text{BrO}_3^- + 6\text{H}^+ + 5\text{e}^- \Rightarrow 1/2\text{Br}_2 + 3\text{H}_2\text{O}$
D. $\text{BrO}_3^- + 6\text{H}^+ \Rightarrow 1/2\text{Br}_2 + 3\text{H}_2\text{O} + 5\text{e}^-$
5. Oxidation is the process involving a
A. gain of protons B. loss of protons
C. loss of electrons D. gain of electrons

6. In a reaction, the oxidation number of S changes from 6 to 4. This information tells us that sulfur has acted as
- a reducing agent, losing $2e^-$
 - a reducing agent, gaining $2e^-$
 - an oxidizing agent, losing $2e^-$
 - an oxidizing agent, gaining $2e^-$
7. Consider the reaction: $2H_2O + Al + MnO_4^- \Rightarrow Al(OH)_4^- + MnO_2$
The substance which undergoes reduction is
- Al
 - H_2O
 - MnO_4^-
 - $Al(OH)_4^-$
8. Consider the reaction: $2H^+ + 2e^- \Rightarrow H_2$
The reaction represents
- oxidation
 - reduction
 - electrolysis
 - replacement
9. Which of the following is non-spontaneous?
- $Pb(NO_3)_2 + Ni \Rightarrow Pb + Ni(NO_3)_2$
 - $2AgNO_3 + Ni \Rightarrow 2Ag + Ni(NO_3)_2$
 - $Co(NO_3)_2 + Ni \Rightarrow Co + Ni(NO_3)_2$
 - $2Au(NO_3)_3 + 3Ni \Rightarrow 2Au + 3Ni(NO_3)_2$
10. Which one of the following is the strongest reducing agent?
- Al
 - Ag
 - Ag^+
 - Al^{3+}
11. The oxidation number of an element decreases during a reaction. This implies that atoms of that element
- lost electrons
 - were oxidized
 - gained electrons
 - acted as a reducing agent
12. Which of the following is the strongest oxidizing agent?
- Cu^{2+}
 - Pb^{2+}
 - Ni^{2+}
 - Sn^{2+}

13. Metallic platinum reacts spontaneously with $\text{Au}^{3+}(\text{aq})$ but does not react with $\text{Ag}^{+}(\text{aq})$. The metals, in order of increasing strength as reducing agents, are
- A. Ag, Pt, Au B. Pt, Au, Ag
C. Au, Ag, Pt D. Au, Pt, Ag
14. Which of the following pairs of ions will react spontaneously in solution?
- A. Cu^{2+} and Fe^{2+} B. Pb^{2+} and Sn^{2+}
C. Co^{2+} and Cr^{2+} D. Mn^{2+} and Cr^{2+}
15. When NO_2 reacts to form N_2O_4 the oxidation number of nitrogen
- A. increases by 2 B. increases by 4
C. increases by 8 D. does not change

Writing Balanced Equations for Redox Reactions Using the Table

Steps:

- 1) Find the appropriate reduction and oxidation half-reactions from the table, and write them down, one above the other.
- 2) Balance electrons.
- 3) Cancel where appropriate and write the balanced equation. Electrons should cancel and not be written in the overall redox reaction (electrons should only be observed in half-reactions).

Practice Questions: Write a balanced reaction for the following reactants:

1. Cu and NO_3^- (acidic) to produce Cu^{2+} and NO

2. MnO_4^- (acidic) and H_2SO_3

Assignment 6: Write a balanced equation for each of the following

1. a) H_2O_2 (acidic) and $\text{N}_2\text{O}_4(\text{aq})$

b) Ag^+ and $\text{H}_2\text{S}(\text{g})$

c) IO_3^- (acidic) and H_2O_2

d) H_3PO_4 (acidic) and NO

2. You have an orange solution comprised of acidified $1.0\text{M Cr}_2\text{O}_7^{2-}$ and a green solution comprised of 1.0M Cr^{3+} . Non-acidified hydrogen peroxide (H_2O_2) is added to each solution and a redox reaction occurs in ONE of the solutions.
- Write the balanced equation for the redox reaction that occurs.
 - How might one qualitatively deduce that a reaction is actually occurring?

Balancing Half-Reactions Without the Use of the Reduction Table

Using the following guidelines, it is possible to build and balance half-reactions that are not on the redox table starting only with a skeleton half-reaction.

Guidelines: 'MAJOR HYDROXIDE' (MAJOR OH^- , actually)

- MAJORS: Balance all *major* elements (all elements except O and H).
- 'O': Balance oxygen by adding H_2O molecules to the applicable side.
- 'H': Balance hydrogen by adding H^+ ions to the applicable side.
- (e^-): Balance the charge by adding electrons to the applicable side.
- *5. If **necessary**: If the half-reaction is **basic**, you must use the equation $\text{H}_2\text{O} \Leftrightarrow \text{H}^+ + \text{OH}^-$ (may also be written the other way around) to cancel protons (which are acidic) from the half-reaction and end up with OH^- ions (which are basic).

Practice Questions: (other examples on p. 201-203):

1) Balance the half-reaction whereby NO is reduced to N₂O in acidic solution.

'Skeleton' half-reaction: $\text{NO} \Rightarrow \text{N}_2\text{O}$

2) Balance the half-reaction whereby Mn²⁺ is oxidized to MnO₂ in acidic solution 'Skeleton' half-reaction: $\text{Mn}^{2+} \Rightarrow \text{MnO}_2$

3) Balance the half-reaction whereby HO₂⁻ is oxidized to O₂ in **basic** solution.

'Skeleton' half-reaction: $\text{HO}_2^- \Rightarrow \text{O}_2$

4) Balance the following half-reaction in **basic** solution.

'Skeleton' half-reaction: $\text{Cu}_2\text{O} \Rightarrow \text{Cu}(\text{OH})_2$

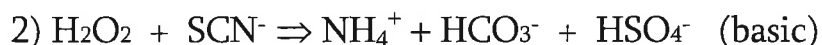
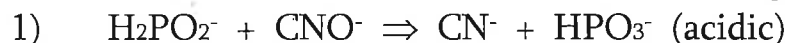
Assignment 7: Hebden p. 203 #19a-m

Balancing Full Redox Reactions not on the Table

Steps:

1. Figure out which reactant substances match up with which product substances to build skeleton half-reactions. Make sure all 'major' elements are present in a half-reaction from the start.
2. Balance each half-reaction using **MAJOR OH⁻** guidelines. However, do not convert to **basic** (if necessary) until after step 4 of this list.
3. Write newly constructed half-reactions one after the other and balance electrons.
4. Put half-reactions together and cancel where necessary (electrons should always cancel out).
- *5. **If necessary:** Convert to **basic** conditions in same manner as learned previously. If there are no H⁺ ions left to convert to basic conditions, then no conversion is possible or necessary.

Practice Questions: Balance each of the following redox reactions



Disproportionation Reaction: a redox reaction wherein the same substance is both reduced AND oxidized to make two different products.

3) Balance the following reaction (basic):

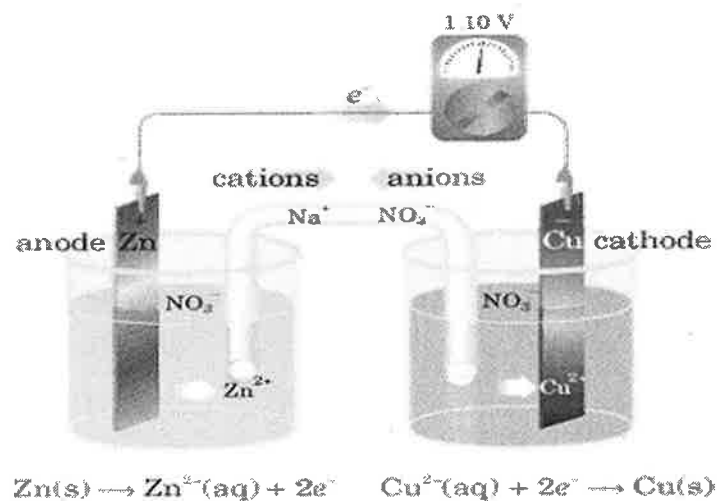


Assignment 8: Hebden p. 207 #24

The Electrochemical Cell

What is an electrochemical cell and how does it work?

What is another name for an electrochemical cell?



Key Terms

Electrode:

Anode:

Cathode:

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Wire:

Voltmeter:

Salt Bridge:

Summary of the Electrochemical Cell on the Previous Page

Oxidation takes place at the anode, as Zn metal atoms lose two electrons to become Zn^{2+} cations ($\text{Zn} \Rightarrow \text{Zn}^{2+} + 2\text{e}^-$), which then dissolve into solution (notice that a zinc salt is chosen as the electrolyte in a zinc half-cell). The electrons travel up the Zn electrode and through the wire to the cathode Cu electrode where they are used to reduce Cu^{2+} cations to Cu metal atoms ($\text{Cu}^{2+} + 2\text{e}^- \Rightarrow \text{Cu}$). The electrons travel from the oxidation to the reduction half-cell because they are being essentially 'pulled' in that direction by the Cu^{2+} ions, which are looking to be reduced. The Cu^{2+} ions are attracted to the cathode (Cu metal) by the negatively-charged electrons that are arriving through the wire. Thus, the anode Zn electrode loses mass (as Zn atoms oxidize to form Zn^{2+} ions that dissolve in solution) and the cathode Cu electrode gains mass (as Cu^{2+} ions reduce to form Cu atoms that plate on top of the existing electrode). The point of the whole process is to get electrons moving through the wire, which can be hooked up to electrically power a device such as a light bulb.

Salt-Bridge Explanation:

To balance the positive charge build-up in the solution at the Zn anode (due to production of Zn^{2+}), NO_3^- anions from the salt bridge migrate into the anode solution and Zn^{2+} cations migrate out of the anode solution into the salt bridge. To avoid negative charge build-up at the Cu cathode (due to loss of Cu^{2+}), Na^+ cations from the salt bridge migrate into the cathode solution and NO_3^- anions migrate out of the cathode solution into the salt bridge. If there is no salt bridge, the cell would cease to operate due to the resistance by the build-up of like charges (ie. Neutrality in each half-cell is pertinent to the cell functioning).

If the half-cells were not separated, the redox reaction between Zn and Cu^{2+} would occur directly in the solution (Cu^{2+} ions would be right beside the Zn metal taking Zn's electrons) and there would be no electron flow in the wire. Thus, the electrical energy from the cell could not be harnessed and subsequently used. (Cu would accumulate directly on the Zn)

Determining what redox reaction is occurring in an electrochemical cell:

Electrochemical cells are **spontaneous** (as opposed to electrolytic cells, which are non-spontaneous). Therefore, find the strongest reducing agent and the strongest oxidizing agent and they will be your key reactants in your cell.

Draw a Mg/Pb electrochemical cell (assume the lead ions are Pb^{2+}).

Half-Reactions

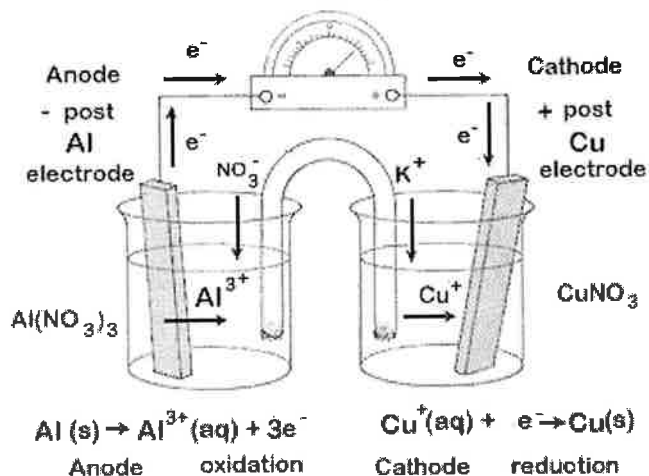
Any two half-reactions from the redox table can be put together to create an electrochemical cell. However, not all half-reactions include a metal. How can these reactions be set up in a half-cell? Through the use of _____ metals/conductors.

Draw a Mg/F₂ electrochemical cell.

Practice Questions:

1. Draw and label all parts of a Sn/Al electrochemical cell.
 - a) Identify a suitable electrolyte for the 'Al' half cell.
 - b) In which direction will electrons flow in the wire?
 - c) Which electrode will lose mass?
 - d) Toward which half cell will the K⁺ in the salt bridge migrate?
 - e) Write the half-reaction occurring at the anode.
 - f) Identify the cathode.
 - g) What happens to the [Al³⁺] in the aluminum half cell?
 - h) Write the net redox equation of the reaction.

2. Examine the following diagram of an electrochemical cell.



- Identify the cathode.
- What happens to the $[\text{NO}_3^-]$ in the aluminum half-cell as the cell is working?
- What happens to the $[\text{Cu}^+]$ in the copper half-cell as the cell is working?
- What is the role of K^+ from the salt bridge?
- Write the net redox reaction.

Assignment 9:

1. Draw an electrochemical cell with Mn and Pb electrodes and solutions of MnCl_2 and $\text{Pb}(\text{NO}_3)_2$ with a KNO_3 salt bridge.

- Identify the anode.
- Write the oxidation half-reaction.
- Write the half-reaction occurring at the cathode.
- Toward which electrode do the K^+ ions in the salt bridge migrate?
- Toward which electrode do the electrons travel in the wire?
- What will happen to the mass of the Pb electrode?

2. Draw an electrochemical cell with one half-cell having an iron electrode and iron II nitrate solution and the other half-cell having an inert platinum electrode with $\text{Cl}_{2(g)}$ being bubbled in. The electrolyte in that half-cell is aqueous sodium chloride. Use KNO_3 in the salt bridge.

- a) Identify the cathode.
- b) Write the half-reaction occurring in the iron half-cell.
- c) What happens to the $[\text{NO}_3^-]$ in the iron half-cell?
- d) Write the half-reaction occurring in the Cl_2 half-cell.
- e) What happens to the extra Cl^- ions being produced at the cathode?
- f) What is the function of the platinum electrode at the cathode?
- g) Write the net redox equation for this electrochemical cell.

3. Read Hebden p.215-217 and do #34-35

Standard Potentials

Cell potential, measured in volts (V), is the 'pull', or 'driving force' on electrons. Potential, or voltage, acts on electrons just like 'pressure' acts on water, or like gravity acts on objects. In an electrochemical cell, the substance that is reducing pulls the electrons through the wire, and this movement of electrons can be used to do work such as power a motor. One volt is defined as 1 joule of work per coulomb of charge transferred, so voltage gives an indication of how much work the electrochemical cell can do - the higher the voltage, the stronger the cell.

The magnitude of the voltage in an electrochemical cell depends on its half-reactions. If a substance that is very good at giving up electrons oxidizes (low on the right side of the table), and a substance that is very good at reducing gains the electrons (high on the left side), the cell will have a relatively large voltage (large gap between half-reactions on table). Generally speaking, the smaller the gap between the reduction and oxidation half-reactions, the smaller the voltage.

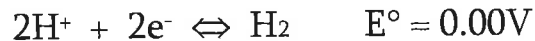
Find the cell voltage of a lithium/fluorine cell:

**When calculating cell voltage, switch the sign of the oxidation voltage:*

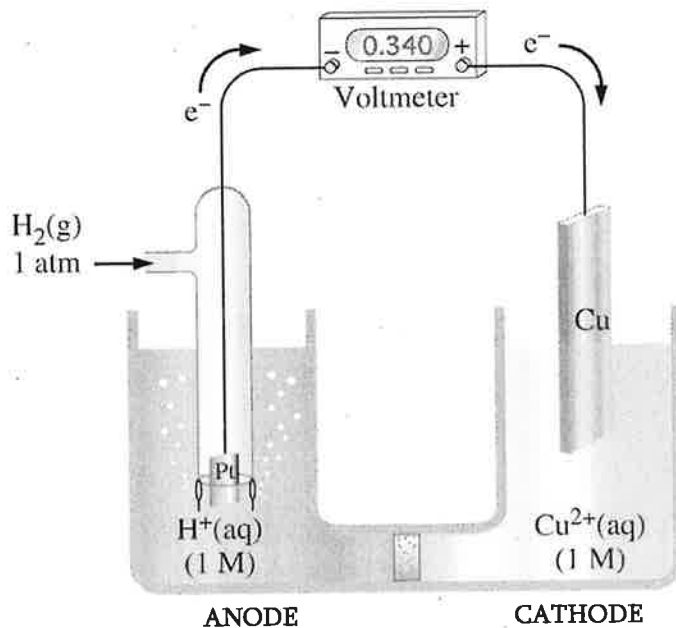
**Coefficients don't affect voltage, as it's joule per coulomb of charge (see p.221 Hebden)*

The E° values on the table are at 'standard state', meaning 25°C, 1 atm. pressure for gases ('room' pressure), 1M concentration for all solutions. If any of these conditions are altered, it is just an E value as it is no longer at standard state.

Notice that each half-reaction is assigned a certain voltage on the redox table. It is impossible to set up just a half-cell (without another half-cell) and get a voltage reading. You can only get a voltage from a complete cell with oxidation and reduction half-reactions. So where do these values on the table come from? The hydrogen half-cell at standard state was used as a reference, and every other half-cell was hooked up to a hydrogen half-cell and the voltage was recorded. Thus, the hydrogen half-cell was **arbitrarily** assigned a voltage of 0.00V (see table).

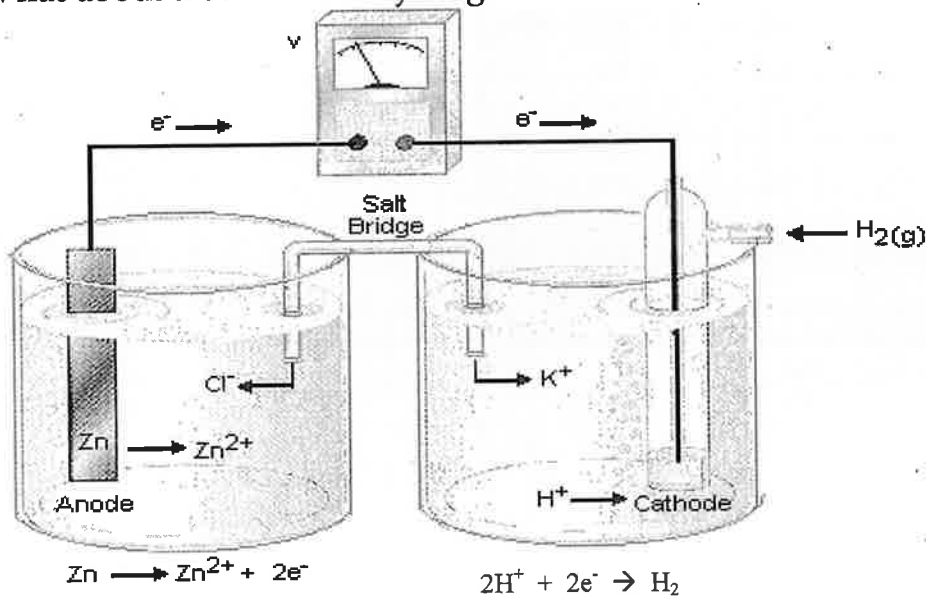


Below is an example with hydrogen and a Cu/Cu²⁺ half-cell:



To predict the cell voltage of two half-cells, simply add the two half-reaction voltages together: $E^0_{\text{cell}} =$

What about a cell with a hydrogen half-cell and a zinc half-cell?



Anode $E^0 =$
Cathode $E^0 =$
$E^0_{\text{cell}} =$

Any other half-reaction could have been chosen as the reference half-cell and been assigned 0.00V, but it was the hydrogen cell that was used.

The voltages given on the table are for reduction half-reactions. To determine **oxidation** half-reaction voltages, **reverse** the sign on the voltage measurement:
If Cu^{2+} is reduced (as above): $\text{Cu}^{2+} + 2\text{e}^- \Rightarrow \text{Cu} \quad E^\circ = 0.34\text{V}$

but, if Cu was oxidized in a cell: $\text{Cu} \Rightarrow \text{Cu}^{2+} + 2\text{e}^- \quad E^\circ = -0.34\text{V}$

Example (not involving Hydrogen half-cell): $\text{Br}_{2(l)} + 2\text{e}^- \Rightarrow 2\text{Br}^-$
 $\text{Pb}_{(s)} \Rightarrow \text{Pb}^{2+} + 2\text{e}^-$ _____
 $E^\circ_{\text{cell}} =$

A **spontaneous** reaction has a **positive** E°_{cell} and is an electrochemical cell.
A **non-spontaneous** reaction has a **negative** E°_{cell} or **zero** E°_{cell} and is an electrolytic cell (it won't occur unless supplied with voltage).

Examples:

1. Calculate the standard potential of the cell: $\text{Cu}^{2+} + \text{Co} \Rightarrow \text{Cu} + \text{Co}^{2+}$

2. Calculate the potential of the cell: $3\text{Zn}^{2+} + 2\text{Al} \Rightarrow 3\text{Zn} + 2\text{Al}^{3+}$

**Remember: Coefficients don't affect the voltage*

3. Write the complete redox equation and calculate the E°_{cell} of a Pb/Cr electrochemical cell.

Cells at Equilibrium (*Static*)

The E°_{cell} of a cell is the voltage at standard state, so solution concentrations are 1.0M. As the cell operates (as the battery runs), reactants are being used so their concentrations continually decrease, thus the voltage starts to decrease. When all reactants are used up, the cell will cease to operate, and the cell voltage will be zero. At this point, the cell is said to be at equilibrium. Therefore, the voltage of a cell at equilibrium is 0 V.

Assignment 10: Hebden p.224-225 #36abcdef, 37, p.226 #46

Cell Potential Practice Questions

1. Draw and label an electrochemical cell using a copper anode and having an E°_{cell} greater than 1.0V (The product of the oxidation is Cu^{2+}).
2. If the E° for $\text{Ni}^{2+} + 2e^- \Rightarrow \text{Ni}$ were set at zero volts, what would be the E° for $\text{Cu}^{2+} + 2e^- \Rightarrow \text{Cu}$?
3. What will happen to an aluminum spoon if it is used to stir a solution of $\text{Fe}(\text{NO}_3)_2$? Use E° values to support your answer.

4. Four metals were used to set up the following electrochemical cells:

Anode	Cathode	Cell Voltage
J	L	+0.30V
L	K	+1.60V
L	M	+1.30V

a) Identify the strongest reducing agent.

b) Identify the strongest oxidizing agent.

c) Calculate the voltage of a J/M cell.

5. Four half-cells are constructed by placing strips of the four metals W, X, Y, and Z in 1.00M solutions of their ions, W^+ , X^{2+} , Y^{3+} , and Z^{2+} respectively. Various combinations of these half-cells are connected, giving the following data:

Anode	Cathode	E°_{cell}
W	X	+0.20V
W	Y	+0.36V
Z	W	+0.14V

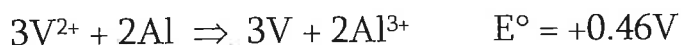
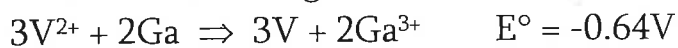
a) Which metal is the strongest reducing agent?

b) Which metal ion is the strongest oxidizing agent?

c) Write the balanced equation for the cell reaction that would occur when half-cells X and Y are connected.

d) Calculate the voltage produced when half-cells X and Y are connected to produce a spontaneous reaction.

6. Consider the following redox data:



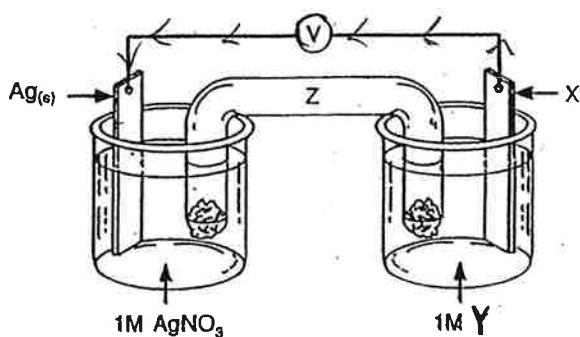
Based on these observations, a student concludes that Ga^{3+} and Al will react spontaneously. Evaluate this conclusion and support your answer with calculations.

Assignment 11

1. An electrochemical cell has electrodes of Pb in $Pb(NO_3)_2$ and Cr in $Cr(NO_3)_3$.

Calculate E°_{cell} .

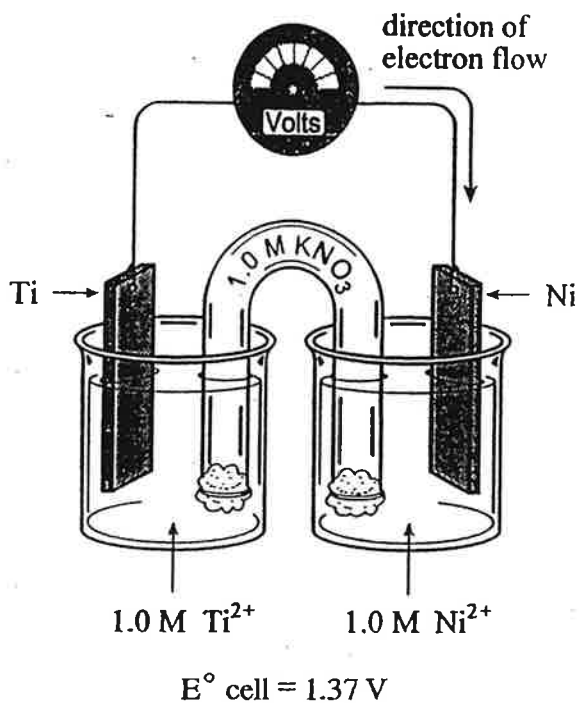
2. Use the following diagram of a cell at $25^\circ C$ to answer the questions:



The electrochemical cell produces an initial voltage of 0.93 V.

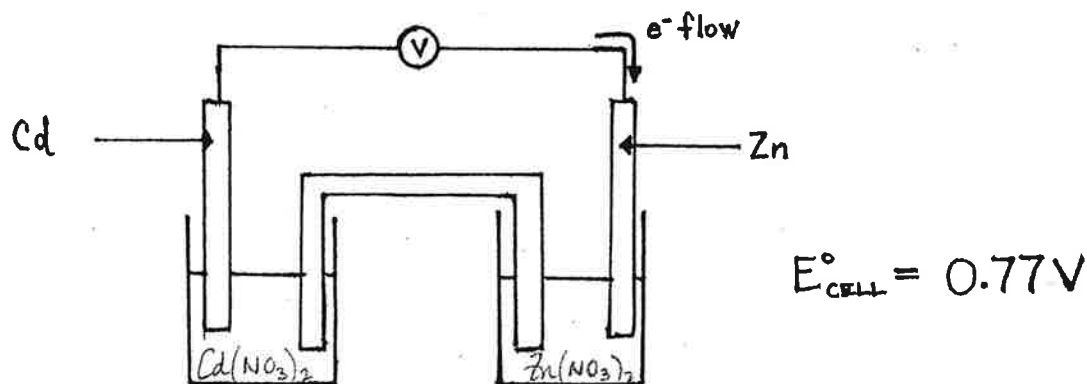
- Identify the metal "X"
- Identify a suitable electrolyte "Y"
- Identify a suitable electrolyte "Z"

3. Can $\text{Fe}_2(\text{SO}_4)_3$ be stored in a container made of nickel? Support with E° calculations.
4. Draw and label the parts of an operating electrochemical cell using a zinc anode that will produce an electric current having a voltage of 1.56V at standard conditions.
5. Consider the following electrochemical cell:



- a) Write the equation for the half-reaction that occurs at the anode.
- b) Calculate the reduction potential of Ti^{2+} .

6. Given the following diagram of an electrochemical cell, which is constructed in order to determine the reduction potential of a Cadmium half-cell, answer the questions provided:



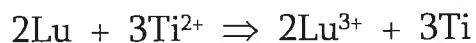
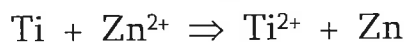
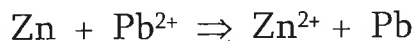
- Identify the cathode in the cell.
- Write the half-reaction occurring at the Cd electrode.
- Determine the E° for the half-reaction: $\text{Cd}^{2+} + 2\text{e}^{-} \Rightarrow \text{Cd}$

7. Four metals were used to set up the following electrochemical cells.

Anode	Cathode	Cell Voltage
A	B	+1.402V
A	C	+1.230V
Z	A	+0.080V

- Rank the metals from strongest reducing agent to weakest.
- Predict the E° of a Z/B cell.

8. The following reactions occur at 25°C with all substances present in 1.0M concentrations.



Predict whether each of the following reactions will occur:

- $\text{Pb} + \text{Ti}^{2+} \Rightarrow \text{Pb}^{2+} + \text{Ti}$
- $2\text{Lu} + 3\text{Pb}^{2+} \Rightarrow 2\text{Lu}^{3+} + 3\text{Pb}$
- $2\text{Lu}^{3+} + 3\text{Zn} \Rightarrow 3\text{Zn}^{2+} + 2\text{Lu}$

9. The metals Rh, Ti, Cr, and Pd are individually placed in 1.0M solutions of Rh^{2+} , Ti^{2+} , Cr^{2+} , and Pd^{2+} , and the cell voltages of the spontaneous reactions are determined.

ION METAL	Rh^{2+}	Ti^{2+}	Pd^{2+}	Cr^{2+}
Rh		no reaction	0.35 V	no reaction
Ti	2.23 V		2.58 V	?
Pd	no reaction	no reaction		no reaction
Cr	1.51V	no reaction	1.86 V	

- Arrange the metals in order of increasing strength as reducing agents.
- Determine the cell voltage for Ti in a 1.0M solution of Cr^{2+} .

10. Hebdén p. 225 #38, 40-41

Alkaline Dry Cell (Modified Version of Zinc/Carbon Dry Cell)

Same as zinc-carbon battery except the paste is manganese dioxide and potassium hydroxide.

The KOH electrolyte gives this battery its name (alkaline = basic). The half-reactions are the same as the zinc/carbon battery except they are under basic conditions. Alkaline batteries are the most common battery today.

Anode half-reaction: $\text{Zn} + 2\text{OH}^- \Rightarrow \text{ZnO} + \text{H}_2\text{O} + 2\text{e}^-$

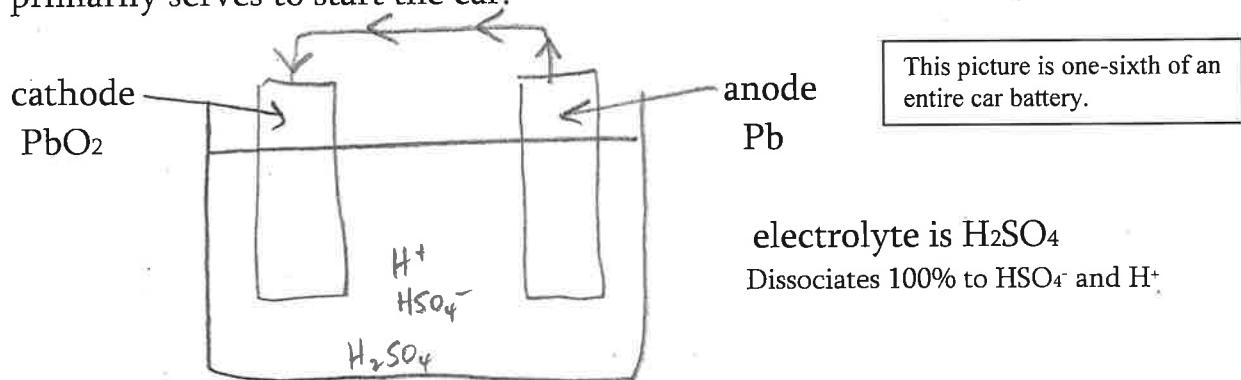
Cathode Half-Reaction: $2\text{MnO}_2 + \text{H}_2\text{O} + 2\text{e}^- \Rightarrow \text{Mn}_2\text{O}_3 + 2\text{OH}^-$

Advantages: - more efficient ion transport in basic (alkaline) electrolyte
- more constant voltage than zinc/carbon battery

Disadvantages: - materials more expensive

Lead-Acid Storage Battery (Car Battery)

This is the type of battery found in cars etc. It is made up of 6 individual cells connected in series, with each cell producing 2 volts (making a 12 volt battery). Each cell consists of one Pb plate and one PbO₂ plate immersed in Sulfuric Acid. The cathode and anode do not need separate compartments since both Pb and PbO₂ are solids, thus they cannot come in direct contact. This battery primarily serves to start the car.



Discharging half-reactions:

Anode: $\text{Pb}_{(s)} + \text{HSO}_4^- \Rightarrow \text{PbSO}_{4(s)} + \text{H}^+ + 2\text{e}^-$

Cathode: $\text{PbO}_{2(s)} + 3\text{H}^+ + \text{HSO}_4^- + 2\text{e}^- \Rightarrow \text{PbSO}_{4(s)} + 2\text{H}_2\text{O}$

*Re-charging half-reactions would be the reverse of the discharging rxns

Notice that solid PbSO_4 is a product of each half-reaction. It sticks to both electrodes and serves as the reactant when the battery is recharged, which is accomplished by applying a voltage to reverse the half-reactions. The *alternator* does this; it is powered by the motor to convert its mechanical energy to chemical energy, which then provides the necessary voltage to the non-spontaneous recharging reaction). Eventually, PbSO_4 can 'flake-off' of the electrodes, due to bumps, erratic driving etc, and fall to bottom of the H_2SO_4 bath. This loss of reactants disallows the battery from fully re-charging. Eventually, a new battery is required.

Assignment 12: Read Hebden p. 228-233 Do #52-53, 55a

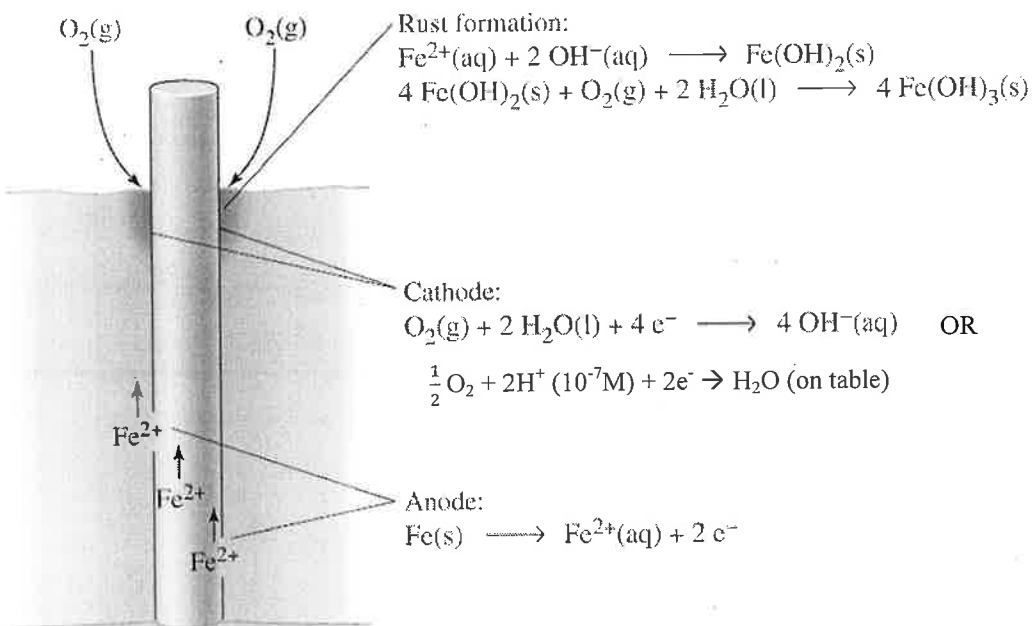
Corrosion of Iron

What must be present in order for iron to rust?

Iron corroding is actually a redox reaction. What happens to the Fe metal?

Where do the resulting electrons go?

So what serves as the anode? The cathode?

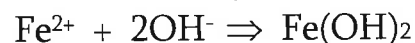


Anode Half-Reaction: $\text{Fe} \Rightarrow \text{Fe}^{2+} + 2\text{e}^-$

Cathode Half-Reaction (not on table): $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \Rightarrow 4\text{OH}^-$

Cathode Half-Reaction (on table): $\frac{1}{2}\text{O}_2 + 2\text{H}^+ (10^{-7}\text{M}) + 2\text{e}^- \Rightarrow \text{H}_2\text{O}$

The Fe^{2+} created at the anode follows the electrons to the cathode and dissolve in the water present. This helps maintain neutrality as the negatively charged OH^- is produced at the cathode. In fact, Fe^{2+} combines with the hydroxide ion, producing solid Iron (II) hydroxide.



The Iron (II) hydroxide then further reacts with oxygen and water to make $\text{Fe}(\text{OH})_3$. Then $\text{Fe}(\text{OH})_3$ decomposes to $\text{FeO}(\text{OH}) + \text{H}_2\text{O}$, and then two $\text{FeO}(\text{OH})$ molecules collide to make $\text{Fe}_2\text{O}_3 + \text{H}_2\text{O}$.

Rust is actually Fe_2O_3 as well as its hydrated form, $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$. This accounts for the different colours in rust (the darker the colour, the more hydrated (the higher x is), the poorer the integrity of the solid).

Protection from Corrosion

There are two protection types: **Physical and Electrochemical**

Physical Protection

What is physical protection from corrosion?

What are some different types of physical protection?

Electrochemical Protection

What is electrochemical protection from corrosion?

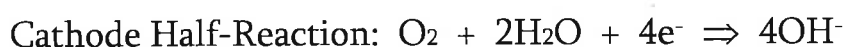
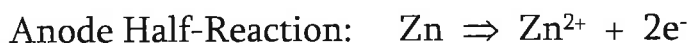
There are two types of electrochemical protection:

1. Cathodic Protection *with* a Sacrificial Anode

eg: The placing of zinc strips on the iron hull of a boat

Explanation:

Zinc oxidizes more readily than iron (see your table). Therefore, if zinc is available, it will oxidize to Zn^{2+} before any iron starts to oxidize. Attaching zinc strips to a piece of iron will prevent iron from rusting as the zinc will oxidize before the iron, and the electrons from zinc will conduct through the iron to the cathode. The zinc is called a **sacrificial anode** (it sacrifices itself for the iron). Zinc 'provides' Fe with electrons and Fe acts as the cathode to conduct electrons to O_2 and H_2O , thus the zinc does not have to completely cover the iron.



The oxidation of the Zn will decrease its mass. Regularly replacing the sacrificial anode (Zn strips) will ensure that the iron will not corrode.

2. Cathodic Protection *without* a Sacrificial Anode

Some ships will supply a low voltage electric current (a stream of electrons) to the iron hull. This prevents the iron hull from having to oxidize to supply electrons to oxygen and water, thereby preventing corrosion. This low voltage current's source can either be a battery or it could come from the running of the engine.

Assignment 13: Corrosion Exercises

1. Can Zn be used as a sacrificial anode for Al? Explain.
2. Would it be smart to use a tin based paint on the bottom of an aluminum boat? Why or why not?
3. The Statue of Liberty consists of an iron frame covered with a copper skin. Discuss the reasons for the rapid corrosion in this structure.
4. Why has the Titanic's hull's integrity survived so long?
5. To prevent an environmental disaster, how could you stop an underground iron septic tank from rusting through without actually having to dig the entire tank up?
6. Why does most car-rust begin in or around the wheel wells?

Electrolysis

Recall that a spontaneous cell (a battery) is called an **electrochemical cell**.

What is an **electrolytic cell**?

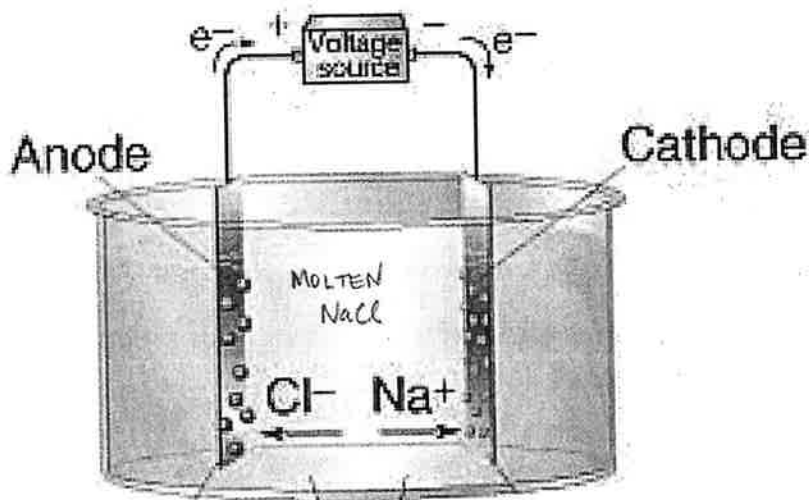
How does an electrolytic cell function?

Why don't electrolytic cells need separate half-cells?

Molten Electrolytic Cell- Electrolysis of a Molten (Liquid) Binary Salt

*Binary refers to a two ion salt; a cation and an anion

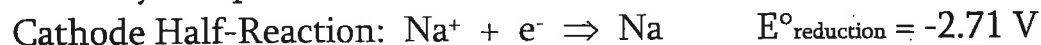
A molten salt means that the salt has been melted to a liquid, so no water is present in the cell. This takes very high temperatures, and is expensive.



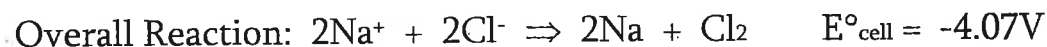
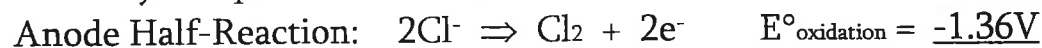
The inert cathode electrode becomes negatively charged because the battery's anode pumps electrons to it. The negative charge draws Na⁺ ions to the cathode to be reduced.

The inert anode electrode becomes positively charged because the battery's cathode pulls electrons away from it. The positive charge draws Cl⁻ ions to the anode to be oxidized.

The only component of the cell that can reduce is Na⁺:



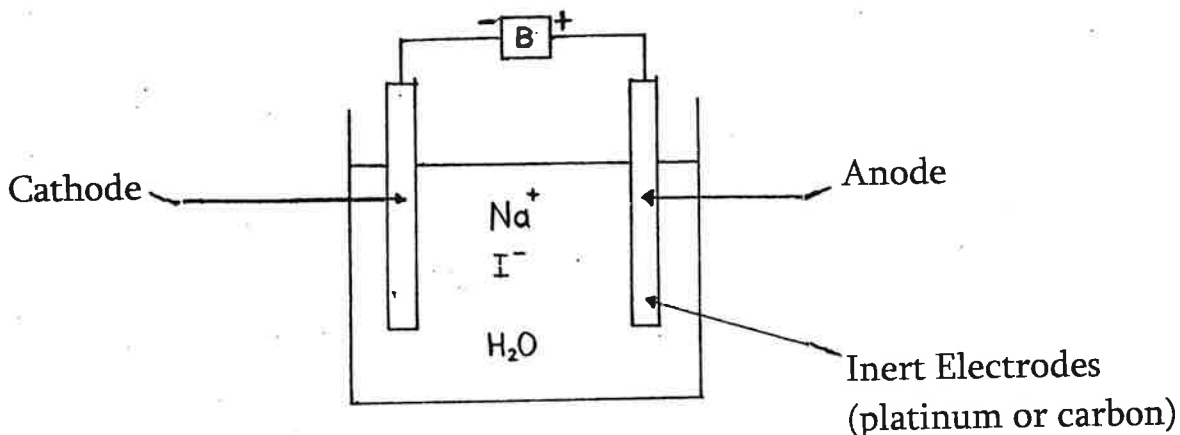
The only component of the cell that can oxidize is Cl⁻:



Slightly more than 4.07V would have to be supplied by the battery in order to make this cell function.

Aqueous Electrolytic Cell - Electrolysis of an Aqueous Salt (a salt solution)

For an aqueous electrolytic cell, water is present with the salt ions, so it may oxidize or reduce before the ions. Use the table to find which half-reaction will occur at the cathode and anode.



Cathode Half-Reaction:

Voltage =

Anode Half-Reaction:

Voltage =

Overall Reaction:

$E^\circ_{\text{cell}} =$

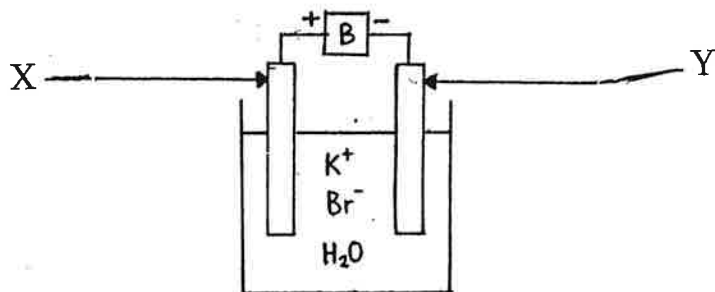
The battery must provide a voltage of slightly more than _____, in order for this cell to function.

What colour would the solution eventually become if phenolphthalein was added?

Why?

Practice Questions:

1. Consider the following cell for the electrolysis of 1M KBr.



- Identify the anode.
- Which species in the cell could act as reducing agents?
- Which of the above reducing agents will be preferentially oxidized at the anode? Why?
- Which species in the cell could act as oxidizing agents?
- Which of the above oxidizing agents will be preferentially reduced at the cathode? Why?
- Write the overall redox reaction.
- What minimum voltage will be required to operate the cell?

2. Draw an electrolytic cell that will perform the electrolysis of water to make H_2 and O_2 .

a. Why must an aqueous salt still exist within the cell?

b. Write the net redox reaction.

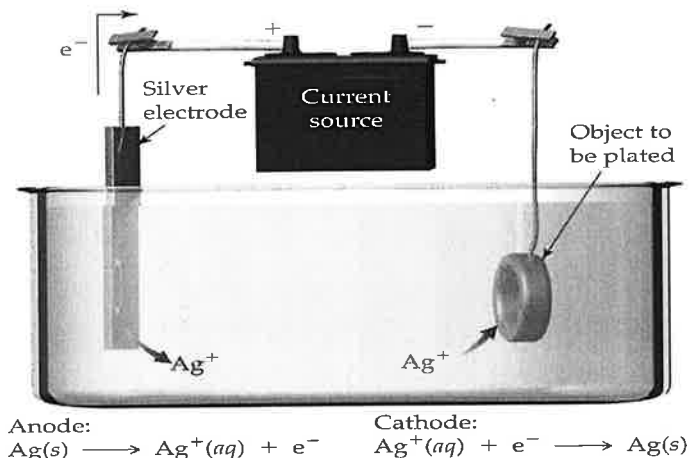
c. What voltage would be required to run this cell?

d. Why can water be 'electrolyzed' with Sulfuric Acid serving as the electrolyte? Explain using half-reactions.

Assignment 14: Hebden p.238 #64ab, p.242 #65abc, 67, 69, 71

Electroplating

Electroplating is an electrolytic process where a metal is 'plated' onto another metal for protection or decoration.



The metal that will be used for plating is first oxidized at the anode (from metal to ion). It then travels across the electrolyte as a cation (it's attracted to the electrons waiting at the cathode) and is reduced at the cathode (from ion back to metal).

What is the overall reaction of the electroplating cell above?

What is the point of electroplating if there is no overall reaction?

For an electroplating cell, what is the anode and what is the cathode?

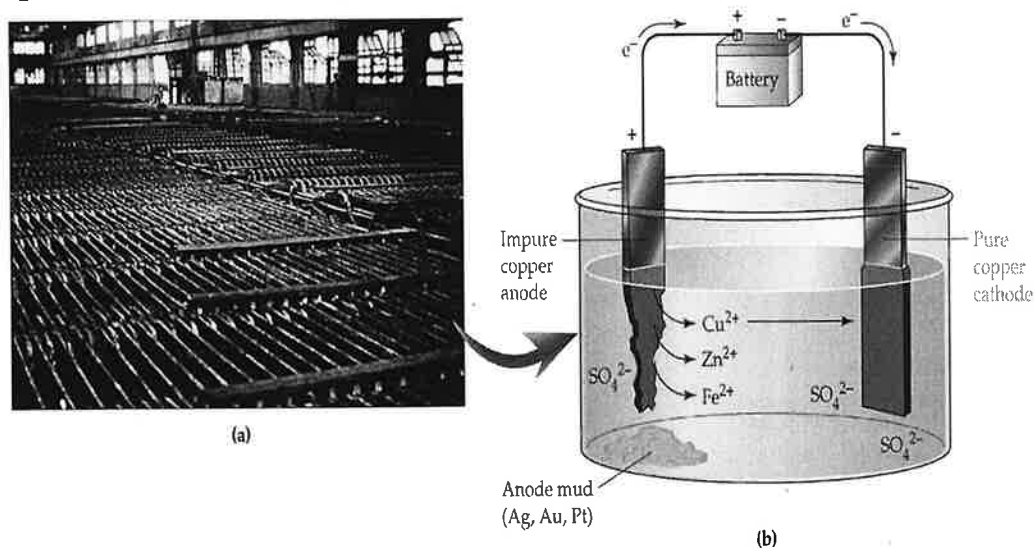
What should the electrolyte be made up of?

What voltage must be supplied by the battery in order for the electroplating to occur?

Design an electrolytic cell which will result in a nickel coin being plated with copper. Label the anode, cathode, and electrolyte. Give the half-reactions, the overall reaction, the voltage, and the voltage required for the process to occur.

Electrorefining

An electrolytic process where impure metal ore becomes pure metal. Below is an example of electrorefining copper:



The impure copper ore anode contains various amounts of zinc, iron, silver, platinum, and gold, but mostly copper. What order will these metals oxidize?

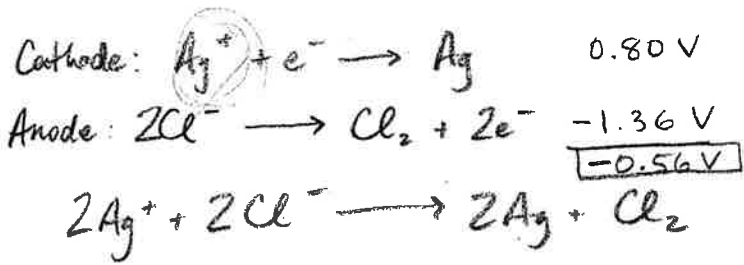
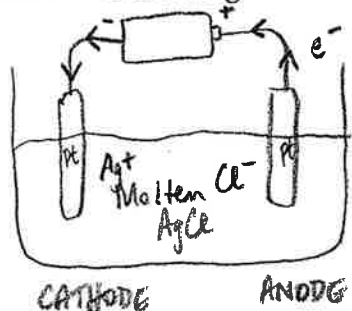
Because copper will always be on the surface of the anode (since the anode is *mostly* copper), silver, platinum, and gold will never get a chance to oxidize, and will fall to the bottom of the cell making the 'anode mud'. Therefore, when zinc is still in existence within the ore, it will oxidize, then Fe, then Cu. Therefore, what three cations will exist in the solution?

What ion out of the three listed above is the strongest oxidizing agent, and thus, best at reducing?

Once all of the copper is reduced, the cell is terminated. The electrolyte is $\text{CuSO}_{4(\text{aq})}$, in order to have extra Cu^{2+} ions in solution.

Assignment 15: Hebden p.244 #73,75,76, Read p.245-246 and do #77

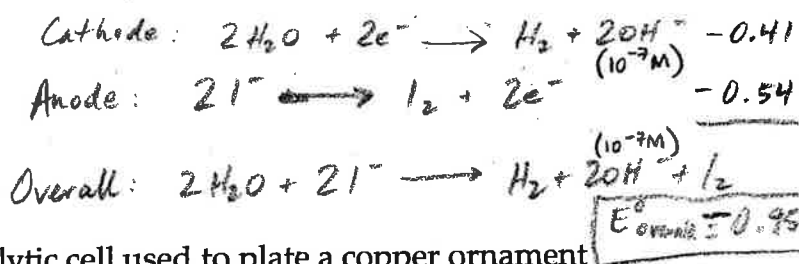
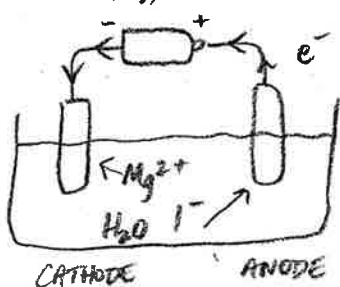
1. Draw and label all parts of an electrolytic cell used for the electrolysis of molten AgCl. Show the direction of electron flow, give the anode and cathode half reactions including E° , and the overall reaction including E°_{cell} . (4)



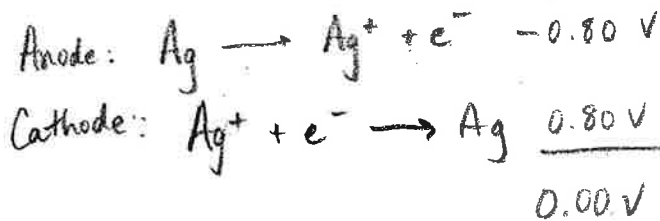
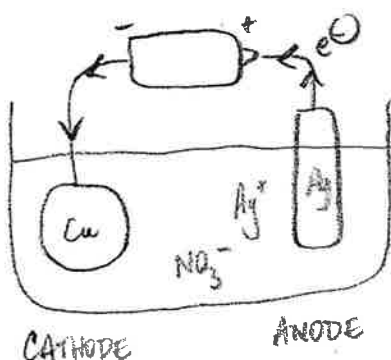
2. Describe what is meant by the phrase 'cathodic protection using a sacrificial anode'. Use an example to help with your explanation. (2)

Zinc strips on iron hulls. *Using a stronger reducing agent metal to protect another. Zn is more readily oxidized (anode) than Fe, thus Fe is protected from oxidation. It simply serves as the cathode allowing O_2 and H_2O to be reduced. (e⁻ conductor)

3. Give the anode and cathode half reactions and the overall reaction including E° values for a 1M MgI_2 electrolytic cell. Suggest suitable electrolytes. (4)

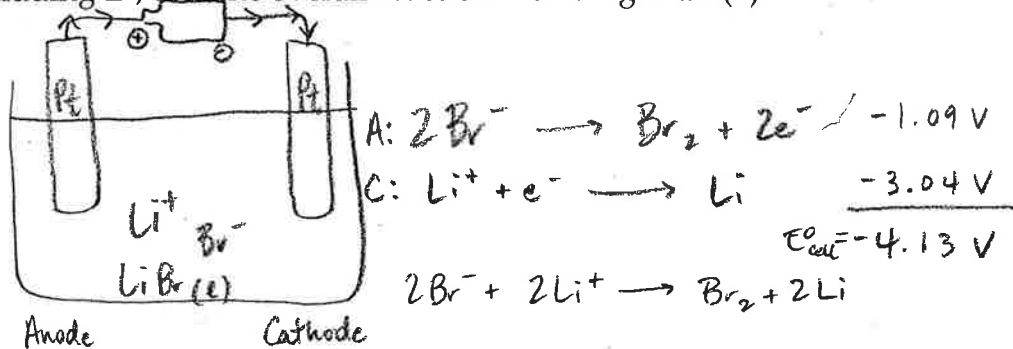


4. Draw and label all parts of an electrolytic cell used to plate a copper ornament with silver. Give anode and cathode half reactions as well as the voltage necessary to have the cell functioning. (4)



Any voltage!

1. Draw and label all parts of an electrolytic cell used for the electrolysis of molten LiBr. Show the direction of electron flow, give the anode and cathode half reactions including E° , and the overall reaction including E°_{cell} . (4)

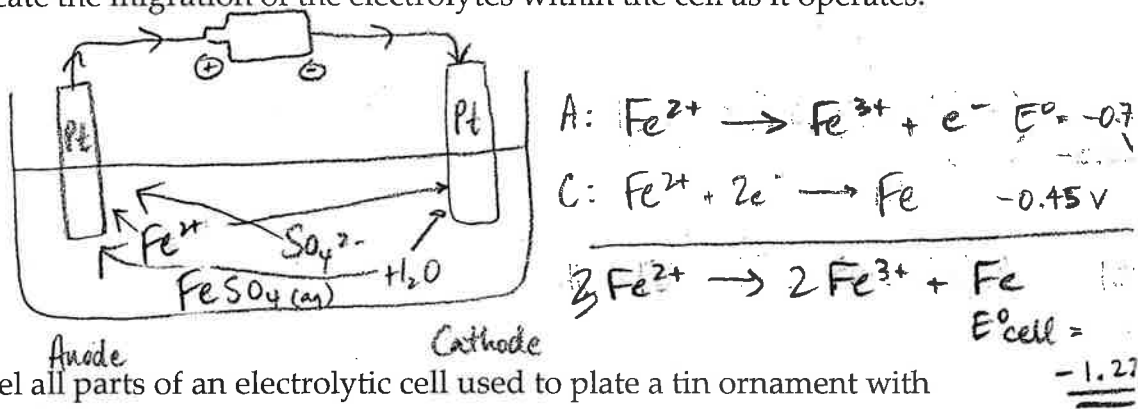


2. Describe what is meant by the phrase 'cathodic protection using a sacrificial anode'. Use an example to help with your explanation. (2)

A metal that is a stronger Reducing Agent is preferentially oxidized before the original anode/cathode metal.

eg: Zn strips on Fe boat hull

3. Give the anode and cathode half reactions and the overall reaction including E° values for a 1M ~~FeSO4~~ electrolytic cell. Draw a picture of this cell and use arrows to indicate the migration of the electrolytes within the cell as it operates. (4)



4. Draw and label all parts of an electrolytic cell used to plate a tin ornament with silver. Give anode and cathode half reactions as well as the voltage necessary to have the cell functioning. (4)

