



Electrochemistry

(Hebden Unit 5)

Electrochemistry

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Electrochemistry is the study of the interchange of chemical energy and electrical energy.

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We will cover the following topics:

- Review oxidation states and assigning oxidation numbers
- Redox Half-reactions
- Identify redox reactions
- Define the following terms:
 - Oxidizing agent
 - Reducing agent
 - Redox couples
- Balancing redox reactions

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Oxidation-Reduction (REDOX)

- **O**xidation – loss of electrons
 - occurs at the **a**node
- **R**eduction – gain of electrons
 - occurs are the **c**athode
- Reducing agent – electron donor
 - is oxidized (causes reduction)
- Oxidizing agent – electron acceptor
 - is reduced (causes oxidation)

OIL RIG
Oxidation **I**s **L**ost
Reduction **I**s **G**ained



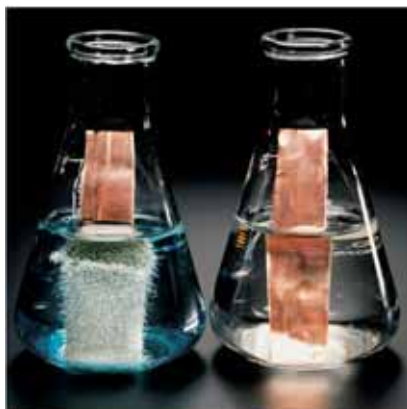
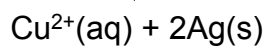
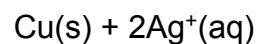
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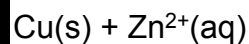
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Oxidation-Reduction Reaction



(a)

(b)



No reaction

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Oxidation-Reduction Reaction

- When copper wire is placed in a silver nitrate solution, a redox reaction occurs.
 - A reaction is observed to occur because the solution changes color and crystals form on the surface of the copper wire.
- When copper wire is placed in a zinc nitrate solution, no reaction occurs.

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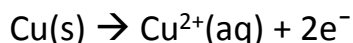
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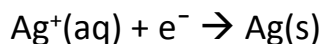
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Oxidation-Reduction Reaction

- The solution's blue color is indicative of Cu^{2+} ions in solution.
 - Cu^{2+} is formed when a copper atom loses two electrons.
 - The copper metal is oxidized.



- The crystals forming on the surface of the copper wire are silver metal.
 - Silver is formed when a silver cation gains an electron.
 - The silver cation is reduced.



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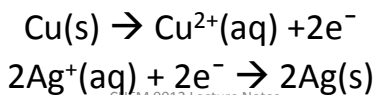
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Oxidation-Reduction and Half-Reactions

- For the reaction between silver cation and copper metal, two *half-reactions* are written.
 - One for the oxidation of copper and one for the reduction of silver.
 - Neither half-reaction can occur without the other.
- The half-reactions as written indicate that Ag^{+} only accepts one electron whereas Cu loses two electrons.
 - The electron transfer must balance, so the reduction half-reaction is multiplied by 2.



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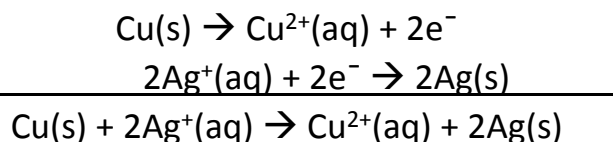
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Oxidation-Reduction and Half-Reactions

- Add the two half-reactions together, the electrons cancel out, leaving the *net ionic equation* for the redox reaction.



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1. Oxidation Numbers

- To understand which atoms are receiving the e^{-} 's (*reduction*) & which atoms are losing the e^{-} 's (*oxidation*) we can use the concept of *oxidation numbers (oxidation states)*
- Oxidation number is the charge that an atom would have if the chemical species was made up of ions.

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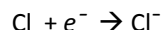
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Oxidation Numbers

Non-metals tend to gain electrons.



Metals tend to lose electrons.



Reducing agents

Oxidizing agents

We use the Oxidation Number to keep track of the number of electrons that have been gained or lost by an element.

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Rules for Oxidation Numbers (ON)

1. The sum of all the ON over all the atoms in a chemical species is equal to the charge on the chemical species
2. In their compounds, the alkali metals and the alkaline earths have ON of +1 and +2 respectively.
3. In compounds the ON of fluorine is *almost always* -1
4. In compounds, the ON of hydrogen is *usually* +1
5. In compounds, the ON of oxygen is *usually* -2.
6. In binary (two-element) compounds with metals:
 - i. Group 7A have ON of -1,
 - ii. Group 6A have ON of -2 and
 - iii. Group 5A have ON of -3.

Whenever two rules appear to contradict one another follow the rule that appears *higher* on the list.

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Determine the oxidation number of the atoms in

- a. H_2S $\text{H} = +1, \text{S} = -2$
- b. S_8 $\text{S} = 0$
- c. SO_2 $\text{O} = -2, \text{S} = +4$
- d. H_2SO_4 $\text{H} = +1, \text{O} = -2, \text{S} = +6$
- e. $\text{Mg}(\text{ClO}_4)_2$ $\text{Mg} = +2, \text{O} = -2, \text{Cl} = +7$
- f. $\text{Fe}^{2+}, \text{Fe}^{3+}$ $\text{Fe}^{2+} = +2, \text{Fe}^{3+} = +3$
- g. $\text{NO}_3^-, \text{NO}_2^-$ $\text{NO}_3^- (\text{O} = -2, \text{N} = +5); \text{NO}_2^- (\text{O} = -2, \text{N} = +3)$
- h. $\text{N}_2\text{H}_4, \text{N}_2\text{F}_4$ $\text{N}_2\text{H}_4 (\text{H} = +1, \text{N} = -2); \text{N}_2\text{F}_4 (\text{F} = -1, \text{N} = +2)$

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1. Oxidation Number of Nitrogen in Different Species

Compound or ion	Oxidation state
NO_3^-	+5
N_2O_4	+4
NO_2^-	+3
NO	+2
N_2O	+1
N_2	0
NH_2OH	-1
N_2H_4	-2
NH_3	-3

This species cannot be oxidized further

This species cannot be reduced further

Oxidation half-reaction (reducing agent)

Reduction half-reaction (oxidizing agent)

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2. Redox Half-reactions

For every redox reaction, it is made up of two half-reactions.

(a) Oxidation half-reaction: LOSING electron(s)

(b) Reduction half-reaction: GAINING electron(s)

LEO the lion says GER

Losing Electron(s) OXIDATION

Gaining Electron(s) REDUCTION

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2. Redox Half-reactions

(a) Oxidation half-reaction: LOSING electron(s)

A balanced reaction showing a reactant losing electrons. The oxidation number of the reactant becomes more positive.

(b) Reduction half-reaction: GAINING electron(s)

A balanced reaction showing a reactant gaining electrons. The oxidation number of the reactant becomes more negative.

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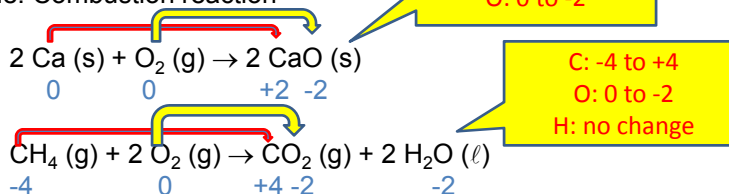
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3. Identify redox reactions

- Many reactions involve the transfer of electrons. As a result, there is an accompanying change in oxidation states in the atoms/ions involved.
- Many reactions involving oxygen as a reactant are referred to as “oxidations”. It is important to remember that there is a simultaneous exchange of electrons between reactants.

Example: Combustion reaction



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4. Define the terms

(a) Oxidizing agent

- A reactant that is reduced is an oxidizing agent.
- There are varying strengths of oxidizing agents.

(b) Reducing agent

- A reactant that is oxidized is a reducing agent.
- Elemental metals will act as reducing agents because metals tend to oxidize (lose electrons).
- There are varying strengths of reducing agents.

The Activity Series of Metals displays the tendency of metals being oxidized. Metals at the TOP of the table has the highest tendency to be oxidized. They are **STRONG** reducing agents.

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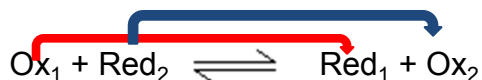
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4. Define the terms

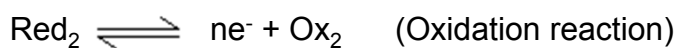
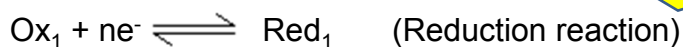
In general, an exchange of electrons occurs in a redox reaction.



Species 1 becomes reduced. This is the oxidizing agent.

Species 2 becomes oxidized. This is the reducing agent.

Separate the redox reaction into half-reactions e⁻ on the left side



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e⁻ on the right side

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4. Define the terms

(c) Redox Couples

In general, an exchange of electrons occurs in a redox reaction.



Ox_1/Red_1 and Ox_2/Red_2 are called the REDOX COUPLES.

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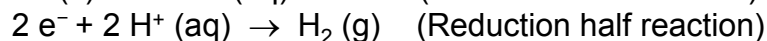
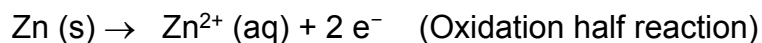
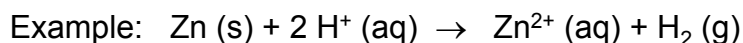
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4. Define the terms

(c) Redox Couples

In general, an exchange of electrons occurs in a redox reaction.

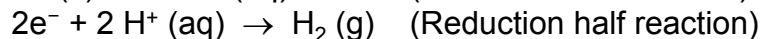
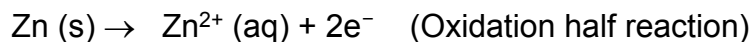
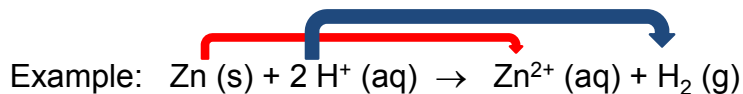


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Many electrochemical processes are useful for:

- The production of chemicals
- Making a battery
- Dissolving metals

Corrosion of metals is a result of electrochemical reactions. Corrosion prevention, maintenance and electroplating metals are common electrochemical processes.

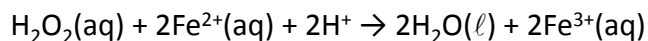
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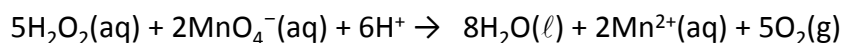
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3. Identifying Oxidizing and Reducing Agents



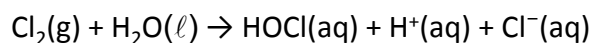
Iron is Oxidized and Peroxide is Reduced.

Iron is Reducing Agent and Peroxide is Oxidizing Agent.



Permanganate is Reduced and Peroxide is Oxidized.

Permanganate is Oxidizing Agent and Peroxide is Reducing Agent



Disproportionation reaction is a redox reaction in which one substance (Cl_2) is both oxidized and reduced. Cl_2 is both the Oxidizing and Reducing Agents.

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Balance half reactions:

In acidic solutions

- Balance major elements (atoms other than O and H)
- Balance O using H_2O
- Balance H using H^+
- Balance charge using electrons, e^-

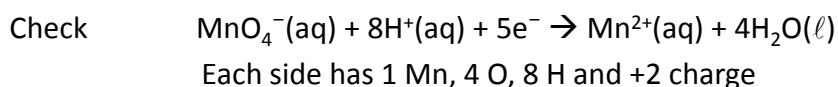
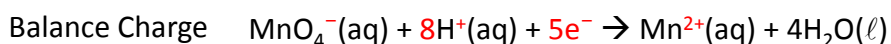
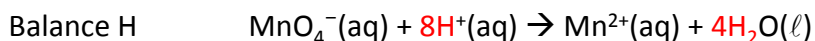
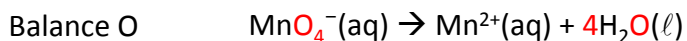
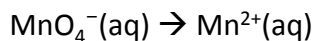
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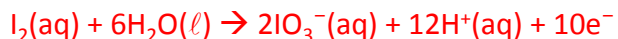
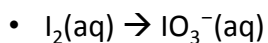
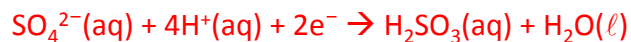
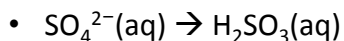
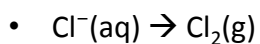
Balance the following half reaction in acidic solution:



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Balance the following half reactions in acidic solution:



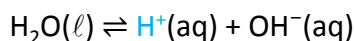
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Balance half reactions:

In **basic** solutions

- Balance major elements, O, H and charge as in acidic solution
- Cancel all the H^+ by adding the water dissociation equilibrium



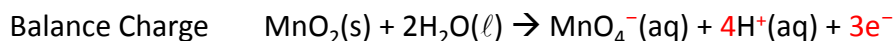
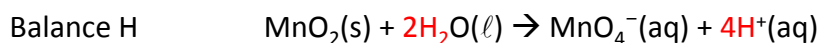
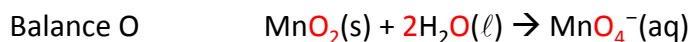
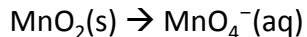
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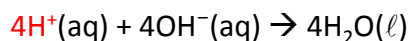
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Balance the following half reaction in basic solution:



Add $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$ to cancel the H^+

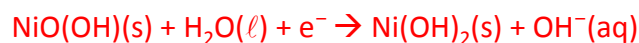
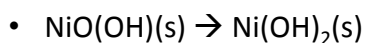
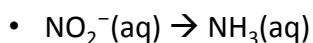
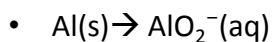


Check 1 Mn, 6 O, 4 H and -4 charge

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Balance the following half reactions in basic solution:



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Balancing redox reactions:

- Break redox reaction in to its half reactions
- Balance the half reactions
- Multiply the half reactions by numbers so that the the number of electrons lost or gained is the same
- Add the half reactions together
- Check that elements and charges are balanced

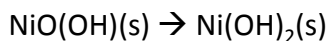
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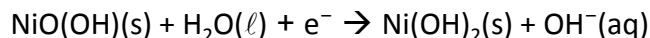
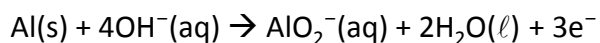
Balance the following redox reaction in basic solution:



The half reactions are:



The balanced half reactions are (from the previous slides)



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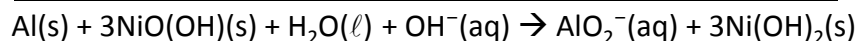
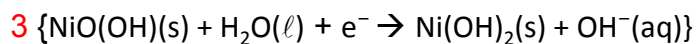
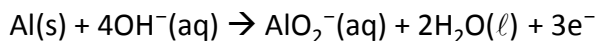
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Balance the following redox reaction in basic solution:



Multiply to balance out electrons and add half reactions



Check: 1 Al, 3 Ni, 8 O, 6 H and -1 charge

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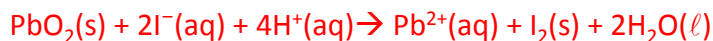
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Balance the following reactions:

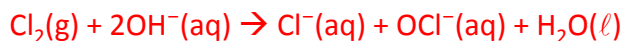
- $\text{PbO}_2(\text{s}) + \text{I}^-(\text{aq}) \rightarrow \text{Pb}^{2+}(\text{aq}) + \text{I}_2(\text{s})$ in acidic solution



- $\text{S}_2\text{O}_3^{2-}(\text{aq}) + \text{Cl}_2(\text{g}) \rightarrow \text{SO}_4^{2-}(\text{aq}) + \text{Cl}^-(\text{aq})$ in acidic solution



- $\text{Cl}_2(\text{g}) \rightarrow \text{Cl}^-(\text{aq}) + \text{OCl}^-(\text{aq})$ in basic solution



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Cell Terminology

- Galvanic cells.
 - Produce electricity as a result of spontaneous reactions.
 - Converts chemical energy into electrical energy.
- Electrolytic cells.
 - Non-spontaneous chemical change driven by electricity.
 - Converts electrical energy into chemical energy.
- Electromotive force, E_{cell} .
 - The cell voltage or cell potential.
 - The “pull” or driving force on the electrons

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Building a Galvanic Cell

- To harness electricity from a galvanic cell, each half-reaction is prepared separately in half-cells.
 - Cu metal immersed in Cu^{2+} solution is one half-cell.
 - Ag metal immersed in Ag^+ solution is the second half-cell.
- Current flows by the migration of ions in solution.
 - To transfer current between the half-cells, a salt bridge is used.
 - The *salt bridge* contains a strong electrolyte that allows either cations or anions to migrate into the solution where they are needed to maintain charge neutrality.
 - A metal wire cannot transport ions and cannot be used.

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Building a Galvanic Cell

- For a salt bridge composed of NH_4Cl :
 - NH_4^+ will flow into the Ag^+ beaker to offset the removal of Ag^+ from solution.
 - Cl^- will flow into the Cu^{2+} beaker to offset the production of Cu^{2+} in solution.
- The circuit is completed by connecting wires to each metal strip.
 - A voltage potential of 0.46 V will be measured for the described cell.

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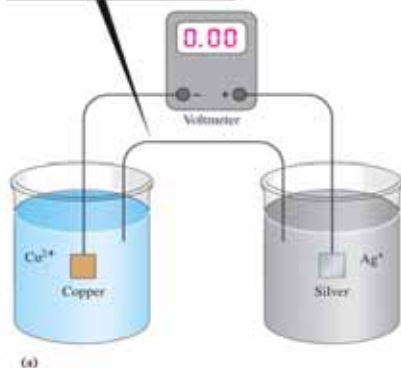
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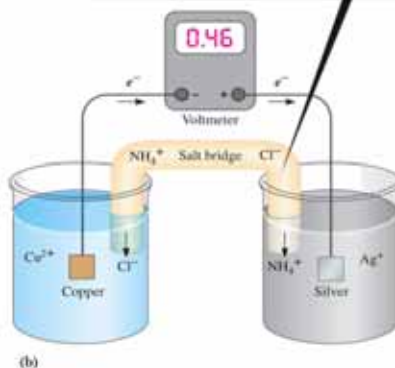
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Building a Galvanic Cell

If a wire connects the half-cells, no voltage is measured. The wire cannot transport ions to close the circuit.



If the wire is replaced with a salt bridge, the release of ions at both ends of the bridge closes the circuit. Current can flow, and the cell voltage is measured.



- A salt bridge is crucial to a galvanic cell. The salt bridge allows ions to flow between each half-cell, completing the circuit. Anions flow toward the anode and cations toward the cathode.

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Cell Terminology

- Electrodes* are the electrically conducting sites at which either oxidation or reduction occurs.
 - The electrode where **oxidation** occurs is the **anode**.
 - The electrode where **reduction** occurs is the **cathode**.
 - Electrons** flow from the **anode** to the **cathode**
 - Cations** flow from the **anode** to the **cathode**
 - Anions** flow from the **cathode** to the **anode**
- Cell notation* - a shorthand notation for the specific chemistry of an electrochemical cell.
 - Cell notation lists the metals and ions involved in the reaction.
 - A vertical line, |, denotes a *phase boundary*.
 - A double vertical line, ||, denotes a *salt bridge*.
 - The **anode** is written on the **left**, the **cathode** on the **right**.

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Electrochemistry

Hebden – Unit 5

Cell Terminology

- General form of cell notation
 $\text{anode} \mid \text{anode electrolyte} \parallel \text{cathode electrolyte} \mid \text{cathode}$
- For the previous example of copper and silver
 $\text{Cu(s)} \mid \text{Cu}^{2+}(\text{aq}) (1\text{M}) \parallel \text{Ag}^{+}(\text{aq}) (1\text{M}) \mid \text{Ag}$
 - The electrolyte concentration is also given.
- An electrochemical cell is at its *standard state* when the electrolyte concentrations are 1 M.
- For half-cells that generate or consume a gas, a partial pressure of 1 atm is required for the standard state.

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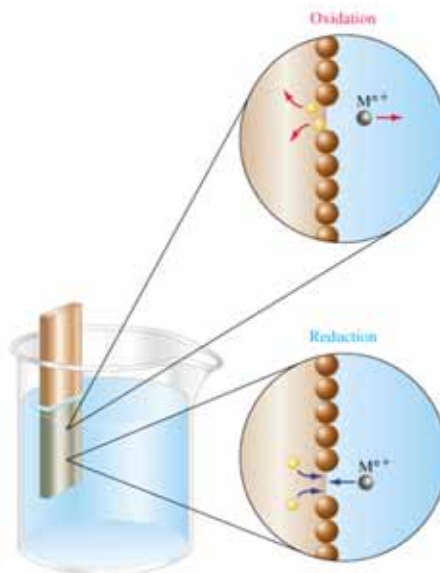
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Electrochemistry

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Atomic Perspective on Galvanic Cells

- Before half-cells are connected by a salt bridge, a small build up of charge occurs for each half-cell at the interface between the electrode and the electrolyte.
 - At the anode, some oxidation occurs and cations dissolve into solution, leaving a negative charge on the anode.
 - At the cathode, some reduction occurs and cations are removed from solution, leaving a positive charge on the cathode.



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Atomic Perspective on Galvanic Cells

- An equilibrium can be described for each half-cell, the *half-reaction equilibrium*.
 - Not an oxidation-reduction equilibrium.
- The build up of charge on the electrode means there is potential for electrical work.
 - This potential is the *cell potential*, or *electromotive force (EMF)*.
- EMF is related to the maximum work obtainable from an electrochemical cell.
 - $w_{\max} = qE$
 - q is the charge, E is the cell potential.

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Electrochemistry

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Cell Potentials

- A *voltmeter* measures the size of the electrical potential and also its polarity - the locations of the negative charge (negative pole) and the positive charge (positive pole).
- An electric potential has a fixed polarity and voltage.
 - Reversing the poles of a battery with respect to a voltmeter changes the sign on the measured voltage but does not influence the electrochemical reaction in the battery.

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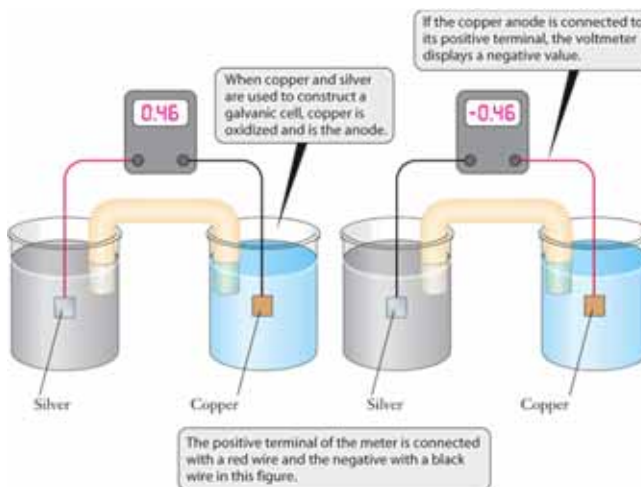
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Cell Potentials

Just like a commercial battery, a galvanic cell has a fixed polarity. Electrons flow through the external circuit from the anode to the cathode. Reversing the leads of the voltmeter changes the sign of the reading, but does not influence the flow of current.



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Electrochemistry

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Standard Electrode Potentials

- Cell voltages, the potential *differences* between electrodes, are among the most precise scientific measurements.
- The potential of an individual electrode is difficult to establish.
- Arbitrary zero is chosen.
 - The Standard Hydrogen Electrode (SHE)

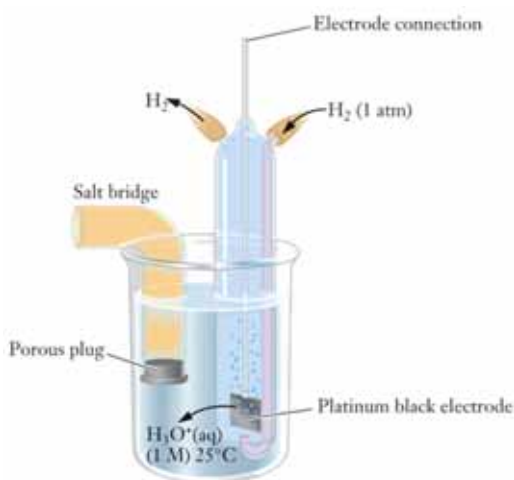
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- The *standard hydrogen electrode (SHE)* is the choice for the standard component in cell potential measurements.
- The cell is constructed of a platinum wire or foil as the electrode.
 - The electrode is immersed in a 1 M HCl solution through which H₂ gas with a pressure of 1 atm is bubbled.
- The SHE has been chosen as the reference point for the scale of standard reduction potentials, and assigned a potential of exactly zero volts.



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- For the Standard Hydrogen Electrode, SHE
 - The half-reaction for the SHE is: $2 \text{H}^+(\text{aq}) + 2 \text{e}^- \rightarrow \text{H}_2(\text{g})$.
 - The half-cell notation is: $\text{Pt}(\text{s}) \mid \text{H}_2(\text{g}, 1 \text{ atm}) \mid \text{H}^+ (1 \text{ M})$.
 - The half-cell is assigned a potential of exactly zero volts.
 - The cell potential is attributed to the other half-reaction.

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Electrochemistry

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Measuring Cell Potential

- For some galvanic cells, the SHE acts as the anode and for other galvanic cells, the SHE acts as the cathode.
- The anode is the site of oxidation, releasing electrons and creating a negatively charged electrode.
 - If the anode is connected to the positive terminal of the voltmeter, a negative potential is measured.
- The cathode is the site of reduction, consuming electrons and creating a positively charged electrode.
 - If the cathode is connected to the positive terminal of the voltmeter, a positive potential is measured.

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Measuring Cell Potential

- When the SHE is always connected to the positive terminal, the sign of the potential tells us the direction of the redox reaction.
 - When the potential is negative, the SHE is the anode, and H_2 is oxidized to $\text{H}^+(\text{aq})$.
 - When the potential is positive, the SHE is the cathode, and $\text{H}^+(\text{aq})$ is reduced to H_2 .

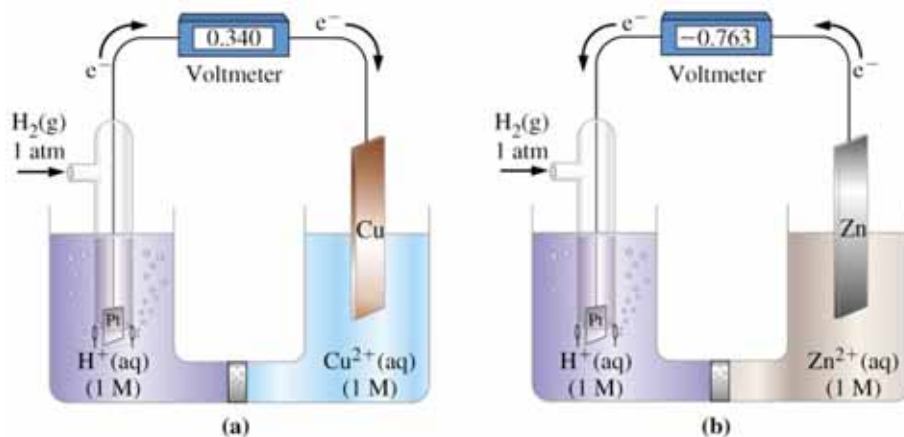
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Measuring Standard Reduction Potential



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Standard Reduction Potentials

- To compare the oxidation-reduction trends of species used in electrochemistry, all half-cell potentials are written as reductions.
 - A table of *standard reduction potentials* lists the potential of any half-reaction when connected to a SHE.
 - All materials are 1 M for aqueous species and 1 atm partial pressure for gases.
 - Where no metallic substance is indicated, the potential is established on an inert metallic electrode (ex. Pt).

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Electrochemistry

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Standard Reduction Potentials

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STANDARD REDUCTION POTENTIALS OF HALF-CELLS
Ionic Concentrations are at 1 M in Water at 25°C

STRENGTH OF OXIDIZING AGENT	OXIDIZING AGENTS	REDUCING AGENTS	POTENTIALS	STRENGTH OF REDUCING AGENT
strong	$F_2 + 2e^- \rightleftharpoons 2F^-$		+2.87	weak
	$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$		+1.36	
	$Br_2 + 2e^- \rightleftharpoons 2Br^-$		+1.07	
	$I_2 + 2e^- \rightleftharpoons 2I^-$		+0.54	
	$CrO_4^{2-} + 2H^+ + 2e^- \rightleftharpoons Cr^{3+} + H_2O$		+1.33	
	$NO_3^- + 4H^+ + 3e^- \rightleftharpoons NO + 2H_2O$		+0.96	
	$NO_2^- + H^+ + 2e^- \rightleftharpoons NO_2 + OH^-$		+0.80	
	$NO_2^- + H^+ + e^- \rightleftharpoons NO + OH^-$		+0.80	
	$NO_2^- + H^+ + 2e^- \rightleftharpoons NO_2 + OH^-$		+0.80	
	$NO_2^- + H^+ + 2e^- \rightleftharpoons NO_2 + OH^-$		+0.80	
weak	$Li^+ + e^- \rightleftharpoons Li$		-3.04	strong
	$K^+ + e^- \rightleftharpoons K$		-2.93	
	$Rb^+ + e^- \rightleftharpoons Rb$		-2.93	
	$Ca^{2+} + 2e^- \rightleftharpoons Ca$		-2.87	
	$Na^+ + e^- \rightleftharpoons Na$		-2.71	
	$Mg^{2+} + 2e^- \rightleftharpoons Mg$		-2.37	
	$Al^{3+} + 3e^- \rightleftharpoons Al$		-1.66	
	$Zn^{2+} + 2e^- \rightleftharpoons Zn$		-0.76	
	$Fe^{2+} + 2e^- \rightleftharpoons Fe$		-0.44	
	$Sn^{2+} + 2e^- \rightleftharpoons Sn$		-0.14	

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Standard Reduction Potentials

- Although the half-reactions are listed as reductions in the table, one half-reaction in any electrochemical cell must be an oxidation and, therefore, reversed from what appears in the table.
 - The cell potential sign must be changed when writing the half-reaction as an oxidation.
- Some half-reactions have positive potentials, whereas others have negative potentials.

Electrochemistry

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Standard Reduction Potentials

- The tendency for the chemicals involved in a half-reaction to be an oxidation or reduction depends on the value of the reduction potential.
 - A large, positive value for the standard reduction potential implies the substance is reduced readily and a good oxidizing agent.
 - A large, negative value for the standard reduction potential implies the substance is oxidized readily and a good reducing agent.

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Electrochemistry

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Standard Reduction Potentials

- For a galvanic cell, the half-reaction with the more positive reduction potential will be the cathode.
 - The half-reaction with the more negative reduction potential will be the anode.
- The standard reduction potential for any pair of half-reactions, E_{cell}° , is calculated from the standard reduction potentials for the cathode and anode.

$$E_{\text{cell}}^{\circ} = E_{\text{red}}^{\circ} - E_{\text{ox}}^{\circ}$$

- E_{red}° is the standard reduction potential for the cathode and E_{ox}° is the standard reduction potential for the anode.

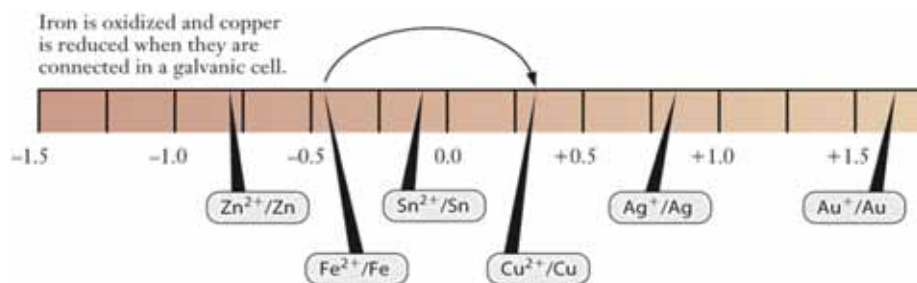
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Standard Reduction Potentials



- For standard reduction potentials arranged horizontally, the anode and cathode for a galvanic cell can easily be determined. The reduction potential furthest to the left is the anode.

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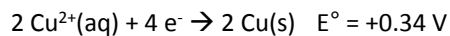
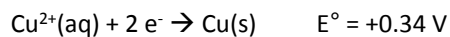
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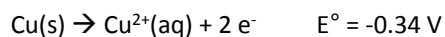
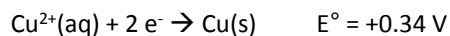
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Properties of Standard Reduction Potentials

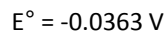
- E° values are **unaffected** by **multiplying** half-equations by a constant.



- E° for the **reverse** reaction is **$-E^\circ$**



- Note E° for a **half reaction** is **not equal** to the **sum** of E° of reactions that equate to the half reactions



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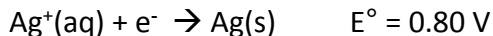
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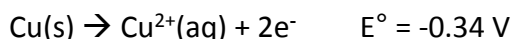
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Relating Electrode Potentials to Cell Potential

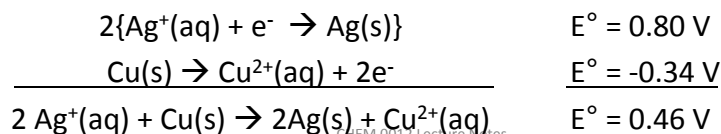
- Write proposed *reduction* half-equation and standard potential to describe it, E° .



- Write proposed *oxidation* half-equation and standard potential to describe it, $-E^\circ$.



- Combine the half-equations into a net redox equations. Add the half-cell potentials to obtain E°_{cell} .



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Galvanic Cell Example

Aluminum metal displaces Zn^{2+} ions from aqueous solutions

- Write oxidation and reduction half-equations and a net equation for this oxidation-reduction reaction.



- Draw a cell diagram for a galvanic cell in which this reaction would occur.



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Half Cell Example at Standard Conditions

Identify the reduction & oxidization half-cells in the following electrochemical cells. Also calculate E°_{cell}

- $\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$ & $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$



- $\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$ & $\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$



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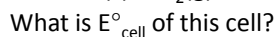
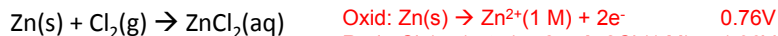
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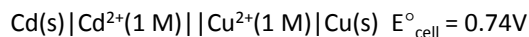
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E° Examples

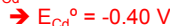
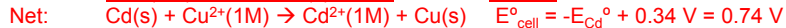
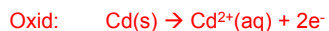
1. A battery system being considered for possible use in electric vehicles is the zinc-chlorine battery. The net reaction producing electricity in this galvanic cell is



2. Cadmium is usually found in small quantities wherever zinc is found. Unlike zinc, which is an essential element for life, Cd is a poison. To measure Cd^{2+} we need to know the E° for the Cd^{2+}/Cd couple. The following cell is constructed and its voltage is measured.



What is the standard potential for the Cd^{2+}/Cd electrode?



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Spontaneous Change

- $E_{\text{cell}} > 0$
 - Reaction proceeds spontaneously as written.
- $E_{\text{cell}} = 0$
 - Reaction is at equilibrium.
- $E_{\text{cell}} < 0$
 - Reaction proceeds in the *reverse* direction spontaneously.

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Electrochemistry

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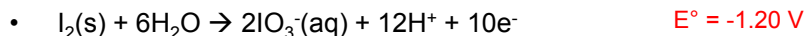
Spontaneous Reaction Example

Dichromate ion, $\text{Cr}_2\text{O}_7^{2-}$ in acidic solution is a very good oxidizing agent. Which of the following oxidations can be accomplished with dichromate ion in acidic solution?



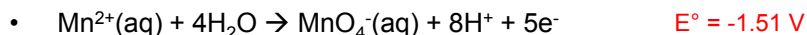
$$E^\circ_{\text{cell}} = 1.23\text{V} - 0.150\text{V} = -0.27\text{V} < 0$$

Therefore Au(s) cannot be oxidized by $\text{Cr}_2\text{O}_7^{2-}$.



$$E^\circ_{\text{cell}} = 1.23\text{V} - 1.20\text{V} = +0.03\text{V} > 0$$

Therefore I_2 can be oxidized by $\text{Cr}_2\text{O}_7^{2-}$.



$$E^\circ_{\text{cell}} = 1.23\text{V} - 1.51\text{V} = -0.28\text{V} < 0$$

Therefore Mn^{2+} cannot be oxidized to MnO_4^- by $\text{Cr}_2\text{O}_7^{2-}$.

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Spontaneous Reaction Example

Peroxodisulfate ion ($\text{S}_2\text{O}_8^{2-}$) are strong oxidizing agents used as bleaching agents for fats, oils and fabrics. The usually starting materials for the preparation of peroxodisulfates is Na_2SO_4 . If it works, one of cheapest ways to produce peroxodisulfates would be to pass $\text{O}_2(\text{g})$ through a solution of sulfate ion. Will oxygen gas oxidize sulfate ion to peroxodisulfate ion, with $\text{O}_2(\text{g})$ being reduced to water?



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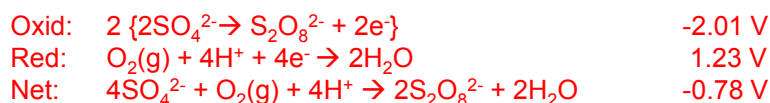
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Spontaneous Reaction Example

Will oxygen gas oxidize sulfate ion to peroxodisulfate ion, with $\text{O}_2(\text{g})$ being reduced to water?

Must identify the oxidation and reduction half-reactions and their half-cell potentials



The negative value of E°_{cell} indicates that $\text{O}_2(\text{g})$ will not oxidize SO_4^{2-} to $\text{S}_2\text{O}_8^{2-}$ to any significant extent.

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Electrochemistry

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Spontaneous Reaction Example

Why does platinum dissolve in aqua regia (a mixture of concentrated HNO_3 and HCl) but not in either concentrated HNO_3 or HCl individually?

	E°
Rxn 1: $\text{Pt}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Pt}(\text{s})$	1.188 V
Rxn 2: $\text{NO}_3^-(\text{aq}) + 4\text{H}^+(\text{aq}) + 3\text{e}^- \rightarrow \text{NO}(\text{g}) + 2\text{H}_2\text{O}(\ell)$	0.965 V
Rxn 3: $\text{PtCl}_4^{2-}(\text{aq}) + 2\text{e}^- \rightarrow \text{Pt}(\text{s}) + 4\text{Cl}^-(\text{aq})$	0.755 V
Rxn 4: $2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$	0 V

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Electrochemistry

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Spontaneous Reaction Example

Platinum in HNO_3

	E°
$\text{Pt}(\text{s}) \rightarrow \text{Pt}^{2+}(\text{aq}) + 2\text{e}^-$	-1.188 V
<u>$\text{NO}_3^-(\text{aq}) + 4\text{H}^+(\text{aq}) + 3\text{e}^- \rightarrow \text{NO}(\text{g}) + 2\text{H}_2\text{O}(\ell)$</u>	<u>0.965 V</u>
$3\text{Pt}(\text{s}) + 2\text{NO}_3^-(\text{aq}) + 8\text{H}^+(\text{aq}) \rightarrow 3\text{Pt}^{2+}(\text{aq}) + 2\text{NO}(\text{g}) + 4\text{H}_2\text{O}(\ell)$	-0.223 V
Since $E^\circ < 0$ reaction is not spontaneous	

Platinum in HCl

	E°
$\text{Pt}(\text{s}) + 4\text{Cl}^-(\text{aq}) \rightarrow \text{PtCl}_4^{2-}(\text{aq}) + 2\text{e}^-$	-0.755 V
<u>$2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$</u>	<u>0 V</u>
$3\text{Pt}(\text{s}) + 2\text{NO}_3^-(\text{aq}) + 8\text{H}^+(\text{aq}) \rightarrow 3\text{Pt}^{2+}(\text{aq}) + 2\text{NO}(\text{g}) + 4\text{H}_2\text{O}(\ell)$	-0.755 V
Since $E^\circ < 0$ reaction is not spontaneous	

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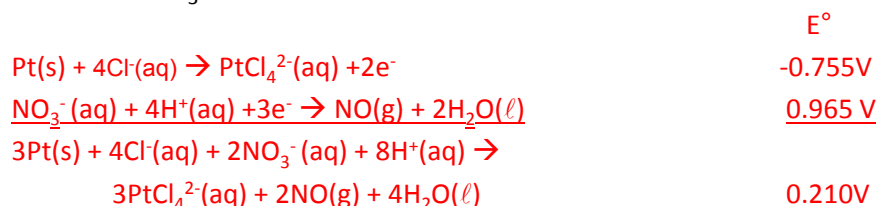
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Spontaneous Reaction Example

Platinum in HNO₃ and HCl



Since $E^\circ > 0$ reaction is spontaneous i.e. Pt will dissolve in a mixture of HNO₃ and HCl

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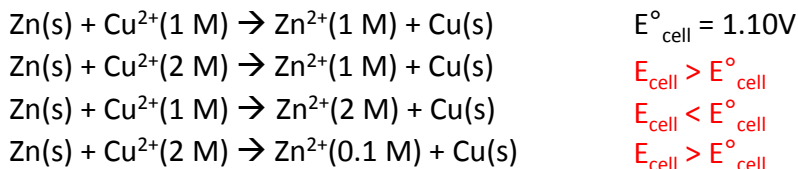
Electrochemistry

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Effect of Concentration on Cell Potential

- Qualitatively the value of E_{cell} relative to E°_{cell} may be predict from LeChatelier's principle
($E_{\text{cell}} > E^\circ_{\text{cell}}$ or $E_{\text{cell}} < E^\circ_{\text{cell}}$)

- Consider



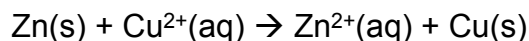
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Electrochemistry

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Effect of Concentration on Cell Potential



The Nernst Equation:

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{nF} \ln(Q)$$

R = ideal gas constant

T = temperature (K)

n = number of electrons transferred

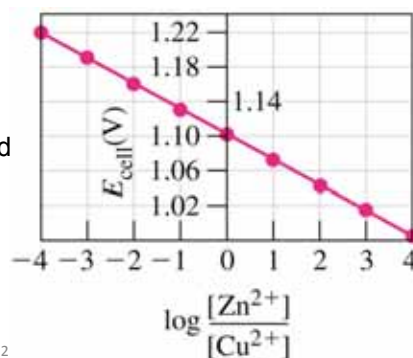
F = Faraday's constant:

At 25°C

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.05916 \text{ V}}{n} \log(Q)$$

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$$Q = \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

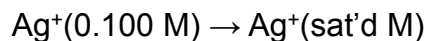
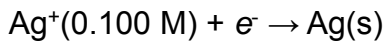


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Electrochemistry

Hebden – Unit 5

Measurement of K_{sp}



If $E_{\text{cell}} = 0.417\text{V}$, what is K_{sp} for AgI?

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Electrochemistry

Hebden – Unit 5

Measurement of K_{sp}

If $E_{cell} = 0.417V$, what is K_{sp} for AgI? $AgI(s) \rightarrow Ag^+(aq) + I^-(aq)$

Let $[Ag^+]$ in a saturated Ag^+ solution be x : then $[I^-] = x$

and $K_{sp} = (x)(x) = x^2$

Cell reaction is: $Ag^+(0.100 M) \rightarrow Ag^+(sat'd M)$

$$E_{cell} = E_{cell}^{\circ} - \frac{0.05916 V}{n} \log(Q) = E_{cell}^{\circ} - \frac{0.05916 V}{n} \log\left(\frac{[Ag^+]_{sat}}{[Ag^+]_{0.10M}}\right)$$

$$0.417 V = 0 - \frac{0.05916 V}{1} \log\left(\frac{x}{0.10}\right)$$

$$\log\left(\frac{x}{0.10}\right) = \frac{0.417 V}{0.05916 V} = 7.048 \Rightarrow \frac{x}{0.10} = 10^{7.048}$$

$$x = (0.10)(10^{7.048}) = 8.94 \times 10^{-9} M$$

$$\therefore K_{sp} = x^2 = 8.94 \times 10^{-9} = 7.99 \times 10^{-17}$$

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Corrosion

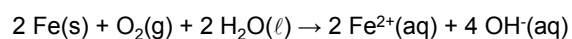
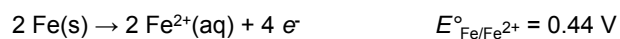
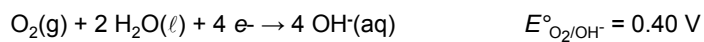
- Oxidation of metals
 - Metals tend to be easily oxidized
 - Most metals have standard reduction potentials that are less than oxygen
 - 0.40 V in basic solutions
 - 1.23 V in acidic solutions
 - The oxidation of most metal by O_2 will have a positive E_{cell} , so they will spontaneously occur
 - Some metals, such as copper, gold, silver and platinum, are relatively difficult to oxidize. These are often called **noble metals**.

Electrochemistry

Hebden – Unit 5

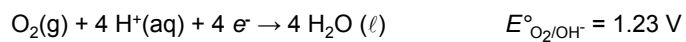
Corrosion: Unwanted Galvanic Cells

In basic solution:



$$E^\circ_{\text{cell}} = 0.84 \text{ V}$$

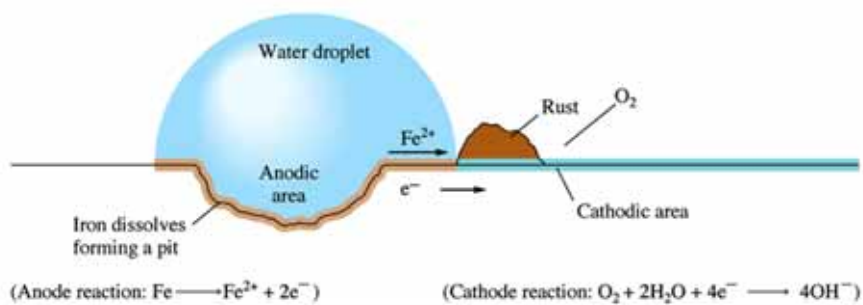
In acidic solution:



Electrochemistry

Hebden – Unit 5

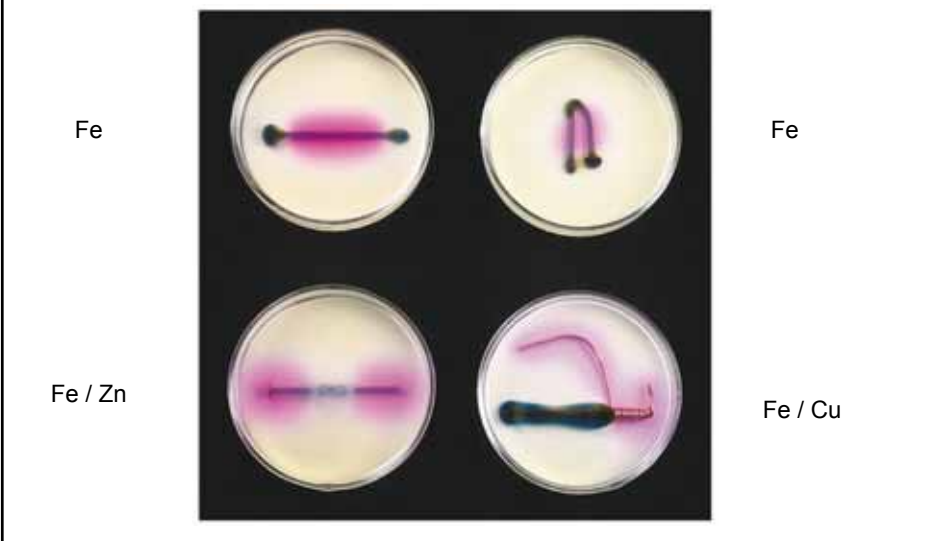
The Electrochemical Corrosion of Iron



Electrochemistry

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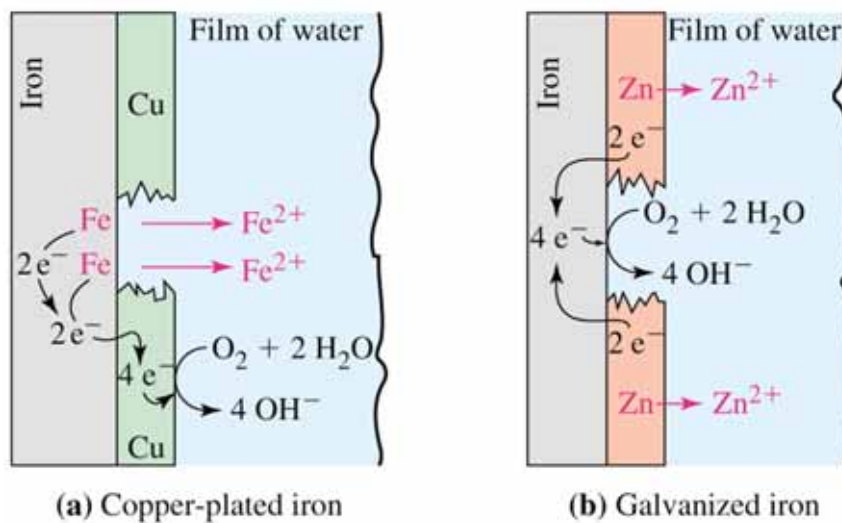
Corrosion



Electrochemistry

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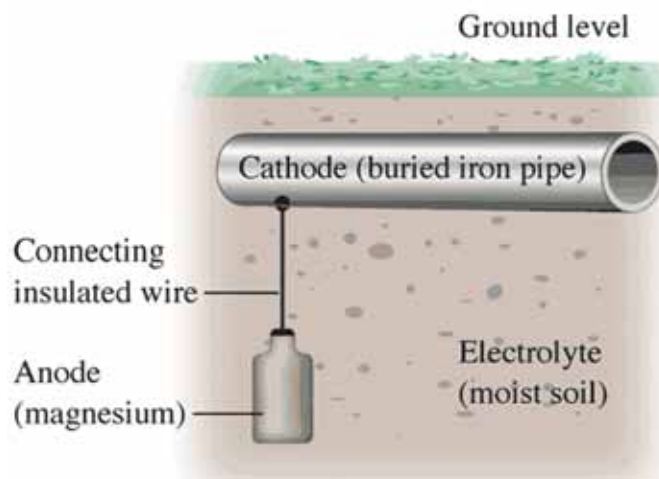
Corrosion Protection



Electrochemistry

Hebden – Unit 5

Cathode Protection of an Underground Pipe



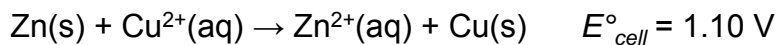
Electrochemistry

Hebden – Unit 5

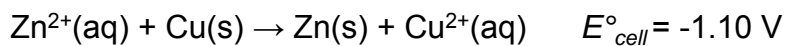
Electrolysis:

Causing Non-spontaneous Reactions to Occur

Galvanic Cell:



Electrolytic Cell:

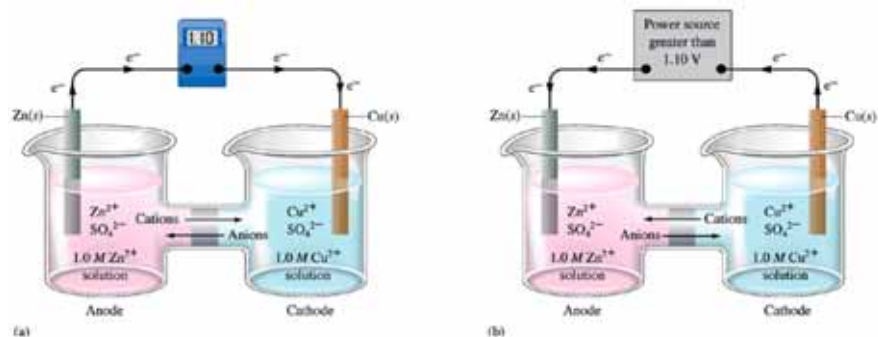


Electrolysis is forcing a current through a cell to produce a chemical change for which the cell potential is negative.

Electrochemistry

Hebden – Unit 5

Galvanic Cell vs Electrolytic Cell



- a) A standard galvanic cell based on the spontaneous reaction

$$\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)}$$
- b) A standard electrolytic cell. A power source forces the opposite reaction:

$$\text{Zn}^{2+}(\text{aq}) + \text{Cu(s)} \rightarrow \text{Zn(s)} + \text{Cu}^{2+}(\text{aq})$$

Electrochemistry

Hebden – Unit 5

Electrolysis

The electrolysis of water produces hydrogen gas at the cathode (on the right) and oxygen gas at the anode (on the left).



Electrochemistry

Hebden – Unit 5

Complications in Electrolytic Cells



- Overpotential.
- Competing reactions.
- Non-standard states.
- Nature of electrodes.

Electrochemistry

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Predicting Electrolysis Reactions

- The half-reactions having the greatest tendency to reduce and greatest tendency to oxidize are preferred
 - The preferred reaction will be the one requiring the lowest voltage
- During the electrolysis of aqueous solutions, the oxidation or reduction of H_2O must be considered
 - $2\text{H}_2\text{O}(\ell) \rightarrow \text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4e^-$ $-0.82 \text{ V @ pH} = 7$
 - $2\text{H}_2\text{O}(\ell) + 2e^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$ $-0.41 \text{ V @ pH} = 7$

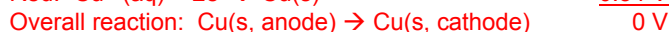
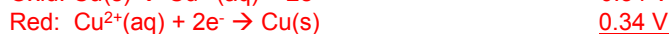
Electrochemistry

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Predicting Electrolysis Reactions

Consider the electrolysis of a $\text{CuSO}_4(\text{aq})$ solution. The cathode is made of copper. What would be the electrode reactions and net electrolysis reactions when the anode is made of

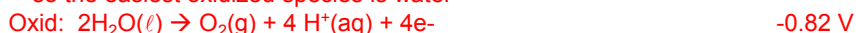
a) Copper



So only a very slight voltage is need to transfer the copper from the anode to the cathode

b) Platinum

Platinum metal is inert, oxidation of SO_4^{2-} to $\text{S}_2\text{O}_8^{2-}$ is not very feasible ($E^\circ = -2.01\text{V}$) so the easiest oxidized species is water

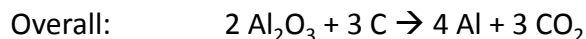
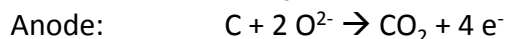
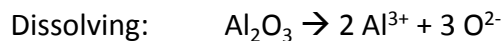


So 0.48 V is need, copper plates out at the cathode and O_2 is generated at the anode

Electrochemistry

Hebden – Unit 5

Electrolytic Production of Al



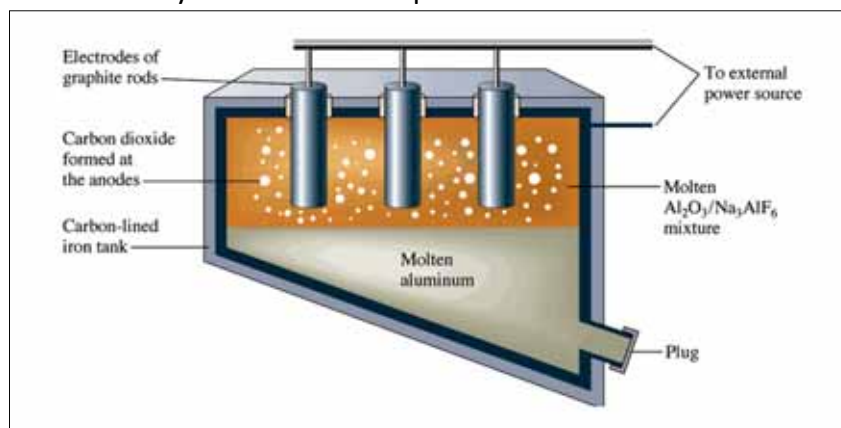
- Reactor cell (cathode) and anode are made of graphite.
- As the Al_2O_3 is used up more is added (continuous smelting process)
- The electrical current maintains the cryolite bath in its molten state.
- Use low voltage $\sim 4 \text{ V}$
- High current $\sim 150,000 \text{ A}$
- Takes $\sim 16 \text{ kWh}$ of electricity to produce 1 kg of Al

Electrochemistry

Hebden – Unit 5

Electrolytic Production of Al

A schematic diagram of an electrolytic cell for producing aluminum by the Hall-Heroult process

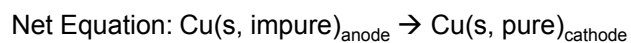


Electrochemistry

Hebden – Unit 5

Electrorefining (Purification of Metals)

Ultrapure copper sheets that serve as the cathodes are lowered between slabs of impure copper that serve as the anodes into a tank containing an aqueous solution of copper sulfate (CuSO_4).

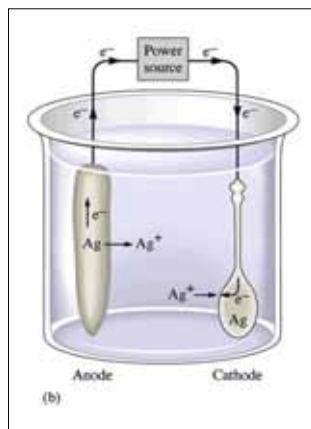


Transfer of material from the impure anode to the cathode

Electrochemistry

Hebden – Unit 5

Electroplating



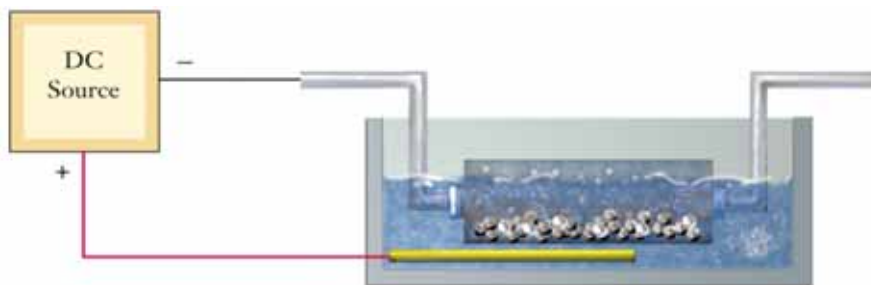
Net Equation: $\text{Ag(s)}_{\text{anode}} \rightarrow \text{Ag(s)}_{\text{cathode}}$

Transfer of material from the anode to the cathode

Electrochemistry

Hebden – Unit 5

Electroplating



- Barrel plating is often used to apply coatings to small parts.

Membrane Potential

- (a) Solutions of KCl separated by a membrane that is permeable to both K^+ and Cl^- .
- (b) Solutions of KCl separated by a membrane that is only to K^+ .

