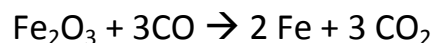


Unit 4: Electrochemistry

Oxidation and Reduction (pg 652)

Often metals do not exist as single elements, but exist bonded to another element in a compound. In prehistoric times, people learned to extract metals from their compounds through a variety of methods.

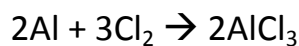
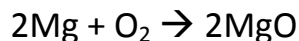
In metallurgy, the extraction of a metal from its compound is called *reduction*.



ie. Iron is extracted from iron oxide.

Furthermore, to extract the metal, a *reducing agent* is used to encourage the reduction reaction to occur. So in the reduction example above, CO is the reducing agent.

Additionally, metals could be reacted with oxygen (often through combustion) to produce a metal oxide. This led to the reaction being classified as an *oxidation*. In fact, it was discovered that other non-metals could react with metals in a similar oxidation process, hence not limiting the reaction to using only oxygen.



ie. Both of these reactions are oxidations!

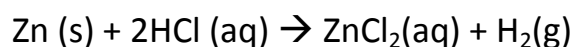
And to follow the trend above, the substance encouraging the oxidation reaction is called the *oxidizing agent*. So O₂ and Cl₂, are the oxidizing agents above.

Practice pg 653 # 2

Electron Transfer Theory (pg 654)

Oxidation and reduction reactions can be viewed in simpler terms, if you look at the movement of electrons. All of these reactions involve the transfer of electrons from one chemical species to another. Because “electrons” are involved in all these reactions, these changes are described as **electrochemical changes** and the study of these changes is called **electrochemistry**.

Single displacement reactions are beneficial to study first as they demonstrate a simplistic view of the movement of electrons. Lets look at the following reaction:



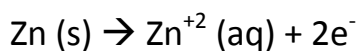
The zinc and hydrogen ions are switching places, but what is actually occurring in the reaction? To view this simply, we can use **half-reactions**.

- A half-reaction only represents what is happening to one reactant in an overall reaction

So, essentially you can view a single reaction as two half-reaction, and in this case the half reactions are the reaction of Zn and H.

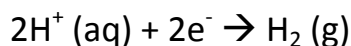
For Zinc:

Zinc metal is losing 2 electrons to react with Cl^- ions in solution, so the half-reaction is:



For Hydrogen:

Hydrogen is gaining electrons to separate from chlorine and form H_2 gas, so:



Note: both reactions are balanced by mass and by charge

Since reactions are more easily looked at in terms of the movement of electrons, we can now redefine reduction and oxidation:

Reduction: gain of electrons

Oxidation: loss of electrons

Hint: LEO the lion goes GER

L – lose	G – gain
E – electrons	E – electrons
O – oxidation	R – reduction

And theory states that the total number of electrons gained in a reaction must equal the total number of electrons lost. Hence, for this statement to work, it must be recognized that reduction and oxidation reactions must occur simultaneously, and simply are called **redox reactions**.

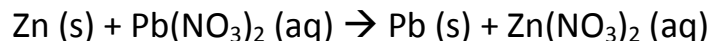
The equations for reduction and oxidation half-reactions and the overall (net) ionic equation summarize the electron transfer that is believed to take place during a redox reaction. And of course, these equations are balanced!

Example 1. (pg 655)

Write a balanced net equation for the reaction of copper metal with aqueous silver nitrate.

Example 2. (pg 656)

Write and label two balanced half-reaction equations to describe the reaction of zinc metal with aqueous lead (II) nitrate as given by the following chemical equation.



Practice pg 656 #8-10

Oxidation States (pg 657)

In order to describe oxidation and reduction of molecules and polyatomic ions, chemists have developed a method of “electron bookkeeping” to keep track of the loss and gain of electrons. The method is arbitrary and it does not usually represent an actual charge on an atom, but it works well.

Oxidation number: positive or negative number corresponding to the oxidation state assigned to an atom

Oxidation numbers are a systematic way of counting electrons. Therefore, the sum of oxidation numbers in a compound or ion must equal the total charge – zero for neutral compounds, and the ion charge for ions.

Rules for assigning Oxidation Numbers

- i) The Oxidation # of all elements = "0"
- ii) The Oxidation # of any simple ion = **charge**
- iii) The Oxidation # of any compound = "0"
- iv) The Oxidation # of any polyatomic ion = **overall charge**
- v) The Oxidation # of Hydrogen = **+1**, oxygen = **-2**
- vi) The Oxidation # of Oxygen = **-2 (except in peroxide = -1)**

Example 1. (pg 658)

What is the oxidation number of carbon in methane, CH₄?

Example 2. (pg 658)

What is the oxidation number of manganese in a permanganate ion, MnO₄⁻?

Example 3. (pg 659)

What is the oxidation number of sulfur in sodium sulfate?

Practice pg 659 # 12-14 **Note:** #14b – glucose = C₆H₁₂O₆

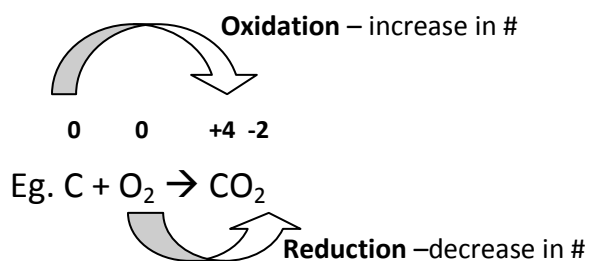
Oxidation Numbers and Redox Reactions (pg 660)

In a redox reaction, oxidation numbers change. So:

An oxidation is an increase in oxidation number

A reduction is a decrease in oxidation number

If there is no change in number then no electrons were transferred.



Example 1. (pg 660)

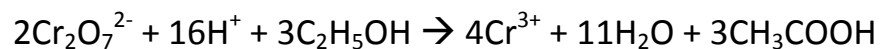
Identify the oxidation and reduction in the reaction of zinc metal with hydrochloric acid.

Example 2. (pg 661)

When natural gas (CH_4) burns in a furnace, carbon dioxide and water form. Identify oxidation and reduction in this reaction.

Example 3. (pg 661)

Identify the oxidation and reduction in the following chemical reaction:



Practice pg 662 #18-21

Balancing Redox Equations – Using Oxidation Numbers(pg 664)

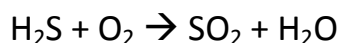
1. Assign oxidation numbers and identify atoms/ions whose oxidation numbers change.
2. Using the change in oxidation numbers, write the number of electrons transferred per atom.
3. Using the chemical formulas, determine the number of electrons transferred per reactant. (use subscripts)
4. Calculate the simplest whole number coefficients for the reactants that will balance the total number of electrons transferred. Balance the reactants and products.
5. Balance the O atoms using H₂O (l) and then balance the H atoms using H⁺(aq).

For basic solutions only:

6. Add OH⁻(aq) to both sides equal in number to the number of H⁺ present.
7. Combine H⁺ and OH⁻ on the same side to form H₂O (l) and cancel the same number of H₂O (l) on both sides.

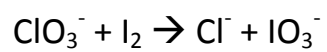
Example 1. (Pg 664)

Balance the following equation using oxidation numbers.



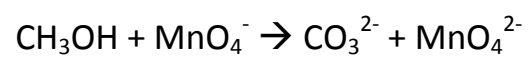
Example 2. (pg 666)

Balance the following redox reaction:



Example 3. (pg 666)

Balance the following basic solution:



Practice pg 668 #2-4

Half-Reaction Method (pg 668)

1. Write the chemical formulae for the reactants and products.
2. Balance all atoms, other than O and H.
3. Balance O by adding H_2O (l).
4. Balance H by adding H^+ (aq).
5. Balance the charge on each side by adding e^- and cancel anything that is the same on both sides.

For basic solutions only:

6. Add OH^- (aq) to both sides equal in number to the number of H^+ present.
7. Combine H^+ and OH^- on the same side to form H_2O (l) and cancel the same number of H_2O (l) on both sides.

Example 1. (pg 669)

Nitrous acid can be reduced in an acidic solution to form nitrogen monoxide gas. What is the reduction half-reaction for nitrous acid?

Example 2. (pg 670)

Aqueous permanganate ions are reduced to solid manganese (IV) oxide in a basic solution. Write the half-reaction equation.

Practice pg 671 #5

Balancing Redox Equations using Half-Reaction Equations (pg 671)

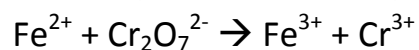
1. Separate the skeleton equation into the start of two half-reaction equations.
2. Balance each half-reaction equation.
3. Multiply each half-reaction by simple whole numbers to balance the electrons lost and gained.
4. Add the 2 half-reaction equations, cancelling the electrons and anything else that is exactly the same on both sides of the equation.

For basic solutions only:

5. Add $\text{OH}^-(\text{aq})$ to both sides equal in number to the number of H^+ present.
6. Combine H^+ and OH^- on the same side to form $\text{H}_2\text{O}(\text{l})$ and cancel the same number of $\text{H}_2\text{O}(\text{l})$ on both sides.

Example 1. (pg 671)

Balance the following equation using half-reaction equations.



Example 2. (pg 672)

Permanganate ions and oxalate ions react in a basic solution to produce carbon dioxide and manganese (IV) oxide. Write the balanced redox equation for this reaction.

Practice pg 673 # 6-7

Technology of Cells and Batteries (pg 685)

Electric cell: device that continuously converts chemical energy into electrical energy

Battery: group of two or more electric cells connected in series

Alessandro Volta invented his electric cell in the year 1800, but these cells produced very little electricity. He eventually redesigned his methods and linked several cells together, creating the battery. His battery looked similar to **Figure 1, pg 685**, and consisted of several bowls of aqueous sodium chloride (salt water!) linked together by metallic strips. From this he was able to obtain a steady flow of electric current. He then revised this by stacking the metal strips and replacing the bowls with leather soaked in the salt water. Then he connected the two ends of the stack with a copper wire to create an even more efficient battery! Although simplistic, Volta's battery led to many advances in several fields of science and he was also able to produce a steady current – which no other device could do!

Basic Cell Design and Properties (pg 686)

Each electric cell is composed of two electrodes and one electrolyte.

Electrolyte: aqueous electrical conductor (eg. Battery acid)

Electrode: solid electrical conductor, usually metal

Cathode: positive electrode (releases positive particles – **cations**)

Anode: negative electrode (releases negative particles – **anions**)

Electricity is the flow of electrons. If you recall, electrons are negatively charged, so they flow from the anode (negative) to the cathode (positive).

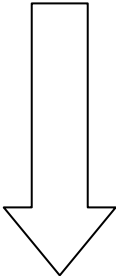
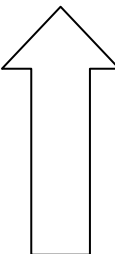
Diagram of an Electric Cell

Some Key Quantities in Electricity

Quantity	Description	Symbol	Unit	Unit Symbol	Meter
Charge	-				-
Current	Rate of flow of charge (electrons) past a point				
Potential difference (voltage)	Energy difference between any 2 points on a circuit				
Power	Rate of energy change				-
Energy density	Energy available in a specific mass	-	-		-

Strength of Oxidizing & Reducing Agents (pg 676)

Use the following table to predict elements as being oxidizing or reducing agents.

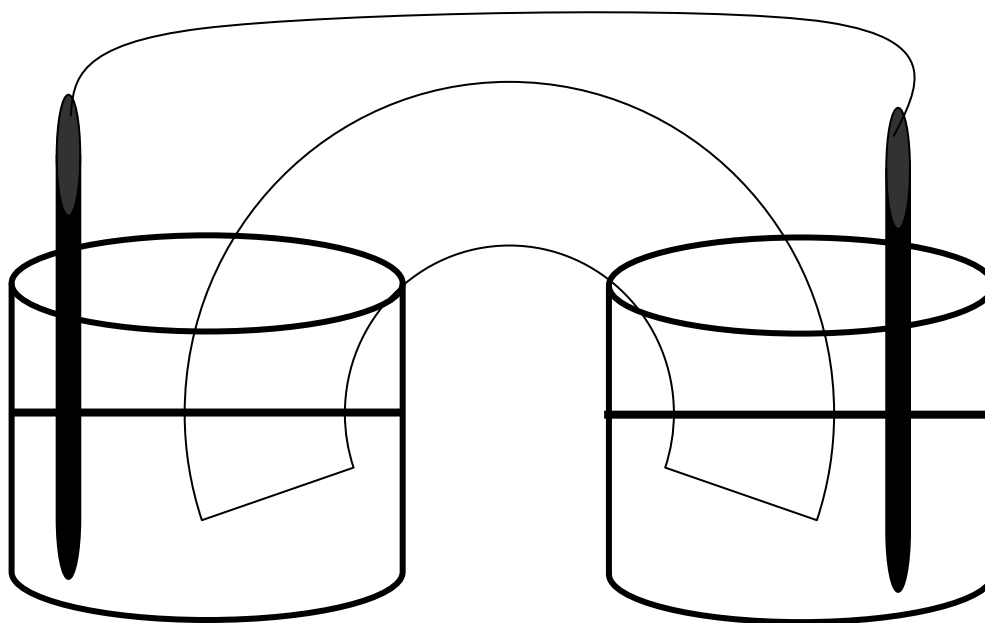
Decreasing reactivity of oxidizing agents		$\text{Ag}^+ + \text{e}^- \rightleftharpoons \text{Ag}$ $\text{Cu}^{2+} + 2\text{e}^- \rightleftharpoons \text{Cu}$ $\text{Pb}^{2+} + 2\text{e}^- \rightleftharpoons \text{Pb}$ $\text{Zn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Zn}$		Decreasing reactivity of reducing agents
-------------------------------------------	-----------------------------------------------------------------------------------	------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------	-------------------------------------------------------------------------------------	------------------------------------------

See also table on pg 805 of text or back of senior periodic table
* in text is reduction potentials, on table is oxidation potentials

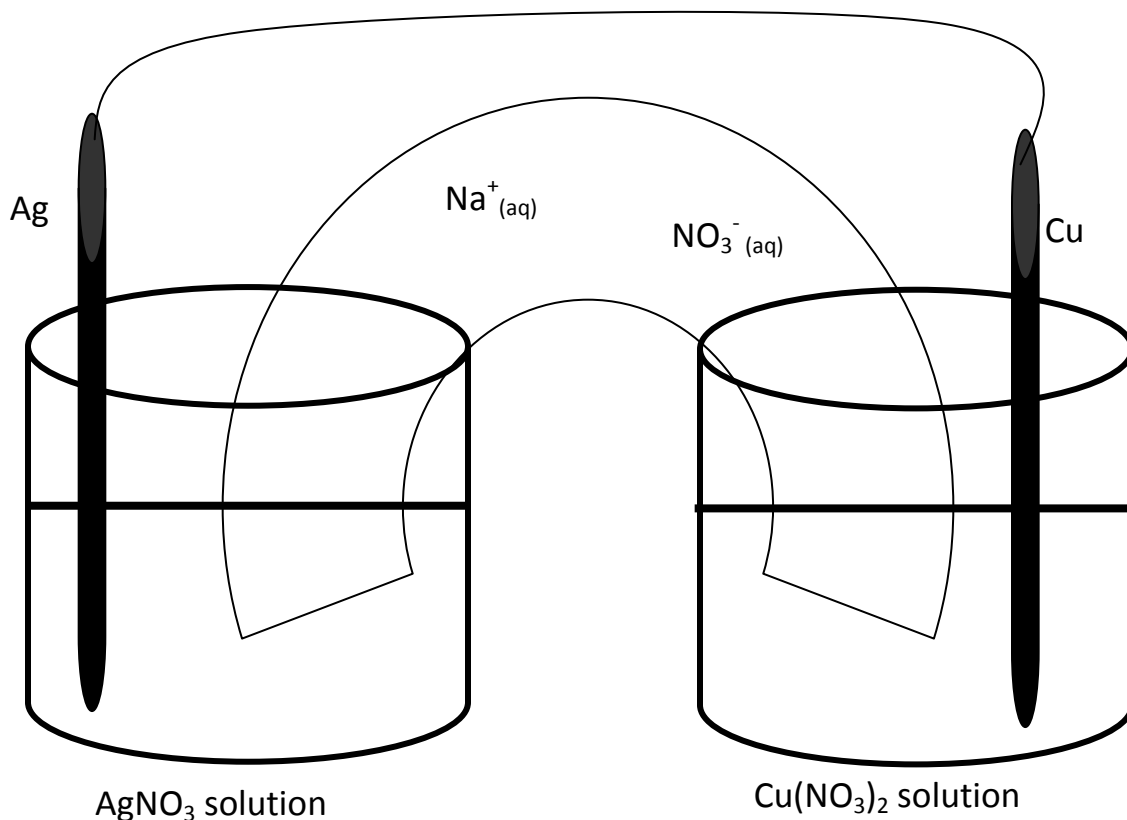
Galvanic Cells (pg 695)

Half-cell: electrode & an electrolyte forming half of a complete cell

Galvanic cell: arrangement of 2 half-cells that can produce electricity simultaneously



Look at the following diagram of a silver-copper galvanic cell (with NaNO_3 salt bridge) & examine how e^- flow through the cell.



- The strongest oxidizing agent in the cell always undergoes a reduction at the cathode
- The strongest reducing agent in the cell always undergoes an oxidation at the anode

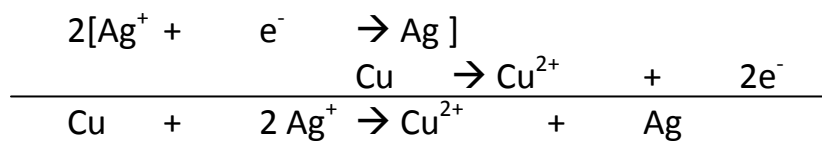
Cell Notation

Galvanic cells are written in the following format to represent the contents of the cell:

- Cathode 1st
- Anode 2nd
- Ions written in the middle

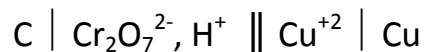


You can also write half-equations & a net equation to demonstrate the reaction that is occurring in the cell.



Example 1. (pg 699)

Write half-reactions & the overall reaction that occur in the following cell:



Draw a diagram of the cell, labelling electrodes, electrolytes, the direction of electron flow, and the direction of ion movement.

Practice pg 700 #3, 6a

Standard Cells and Cell Potentials (pg 701)

Standard cell potential: maximum electric potential difference (voltage) of a cell operating under standard conditions

Standard reduction potential: E_r° represents the ability of a standard half-cell to attract electrons in a reduction half-reaction

*Note your senior periodic table has standard oxidation potential values. To convert to E_r° , change the sign in front of the number.

ΔE°	=	E_r°	-	E_r°
Cell		cathode		anode

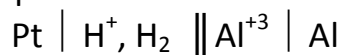
* ΔE° = standard cell potential

Standard Hydrogen Half-Cell (pg 701)

- Has a standard cell potential of exactly zero
- Represented by **Pt | H⁺, H₂** (platinum electrode immersed in H ions)
- Represented by the half-reaction **H₂ → 2e⁻ + 2H⁺**

Measuring Standard Reduction Potentials (pg 702)

Eg. Calculate the standard cell potential for the following cell:



Notes:

- When balancing the half-reactions, you multiplied the reaction by coefficients, but **do not change the reduction potential!**
 - The potentials are unaffected by balancing the reaction
- A positive cell potential ($\Delta E > 0$) indicates that the net reaction is spontaneous – this is required for all galvanic cells!

Example 2. (pg 706)

A standard dichromate-lead cell is constructed. Write the cell notation, label the electrodes, write & balance the half- reactions & net equation, **and** calculate the standard cell potential.

Practice pg 708 #10ab

Electrolysis (pg 730)

If you recall, galvanic cells must be spontaneous ($\Delta E > 0$) for them to work.

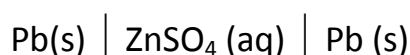
Electrolysis is the process of supplying electrical energy to force a non-spontaneous redox reaction to occur. These types of cells are referred to as **electrolytic cells**.

Galvanic vs. Electrolytic Cells

	Galvanic Cell	Electrolytic Cell
Spontaneity	Spontaneous	Non-spontaneous
Standard Cell Potential, ΔE°	Positive	Negative
Cathode	-Strongest oxidizing agent present undergoes a reduction -Positive electrode	-Strongest oxidizing agent present undergoes a reduction -Negative electrode
Anode	-Strongest reducing agent present undergoes an oxidation -Negative electrode	-Strongest reducing agent present undergoes an oxidation -Positive electrode
Direction of electron movement	Anode \rightarrow cathode	Anode \rightarrow cathode
Direction of ion movement	Anions \rightarrow anode Cations \rightarrow cathode	Anions \rightarrow anode Cations \rightarrow cathode

** secondary cells act as electrolytic cells when they are being recharged!

All calculations are the same as before! However notation is a little bit different.



- the two outside entities are the electrodes
- the inside substance is the solution

Example 1. (pg 734)

An electrolytic cell containing cobalt (II) chloride solution and lead electrodes is assembled.

a) Write the cell notation and predict the reactions at the cathode & anode, and in the overall cell.

b) What is the minimum voltage that must be applied to this cell to make it work?

Practice pg 735 #1a, 2a

Stoichiometry of Cell Reactions (pg 747)

Since these reactions involve transfer of electrons it is important to be able to measure the number of electrons being transferred. However, this is quite difficult so the number of electrons has to be measured indirectly. To do this, we must first measure charge.

$$q = It$$

q = charge (measured in coulombs, C)

I = current (measured in amperes, A)

t = time (measured in seconds)

Example 1. (pg 747)

The technology of Hall-Heroult cell for producing aluminum has improved considerably since the first industrial factory. Modern electrolytic cells may use up to 300kA of current. What is the charge that passes through one of these cells in a 24-h period?

Practice pg 748 #1-4

Faraday's Law (pg 748)

Faraday's Law: the mass of a substance formed or consumed at an electrode is directly related to the charge transferred

Therefore you will get **Faraday's constant**, which represents charge/mol.

$$F = 9.65 \times 10^4 \text{ C/mol}$$

And this now leads to the next equation:

$$n_{e^-} = q/F \text{ or } n_{e^-} = It/F$$

n_{e^-} = moles of electrons (in moles, mol)

q = charge (in coulombs, C)

F = Faraday's constant (9.65×10^4 C/mol)

Example 1. (pg 748)

What amount of electrons is transferred in a cell that operates for 1.25 h at a current of 0.150 A?

Example 2. (pg 749)

How long, in minutes, will it take a current of 3.50 A to transfer 0.100 mol of electrons?

Practice pg 749#5-7.

Half-Cell Calculations (pg 750)

Further calculations can be made to determine values from different parts of a half-cell equation. For these, you must consider the ratio between the electrons and the element to complete your calculation.

Example 1. (pg 750)

What is the mass of copper deposited at the cathode of a copper electrorefining cell operated at 12.0 A for 40.0 min?

Example 2. (pg 751)

In a silver electroplating cell, 0.175g of silver is to be deposited from a silver cyanide solution in a time of 10.0 min. Predict the current required.

Practice pg 751 #8-10