

Introduction

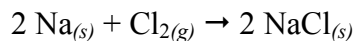
Oxidation/reduction reactions involve the exchange of an electron between chemical species.

The species that loses the electron is oxidized.

The species that gains the electron is reduced.

“LEO” the lion says “GER”

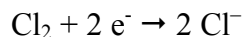
Loss of Electrons is Oxidation. Gain of Electrons is Reduction.



Sodium loses an electron to become sodium ions (oxidation):



Chlorine atoms gain electrons to become chloride ions (reduction):



Sodium is oxidized. Sodium is also the reducing agent because it causes the other reactant to be reduced.

Chlorine is reduced. Chlorine is also the oxidizing agent because it causes the other reactant to be oxidized.

We keep track of electrons by using oxidation numbers.

In purely ionic compounds oxidation numbers are simply the ionic charge of the species.

In covalent compounds, the oxidation numbers (or change in oxidation numbers) indicate if the access to electrons is increasing or decreasing.

Covalent compounds are treated as ionic for determining oxidation numbers.

To determine oxidation numbers:

1. An element is assigned 0
2. A monatomic ion is assigned its charge
3. A compound or polyatomic compound must have its oxidation numbers sum to its charge.
4. Hydrogen is +1 (ex. hydride)
5. Oxygen is -2 (ex. Peroxides -1)
6. Halogens are usually -1 (F is always -1)

Balancing Redox Reactions

Oxidation — reduction reactions are often examined as two half reactions: the oxidation half reaction, and the reduction half reaction.

A half reaction must start with the species that is oxidized or reduced.

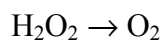
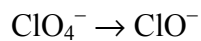
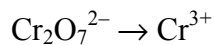
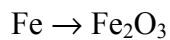
Other species can then be added to balance the reaction.

Balance acidic half reactions through these steps:

1. Balance major atoms (not H or O)
2. Balance O atoms with H_2O .
3. Balance H atoms with H^+ ions.
4. Balance charge with electrons e^- .
5. Check if the change in oxidation number equals the number of electrons.

Example 1:

Balance the following half reactions in acidic solutions:



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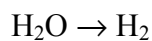
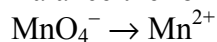
In Basic solutions, there is one additional step.

The half reaction is balanced as if it were in acidic solution. Then, an “OH⁻” is added to both sides of the equation for each “H⁺” present.

These combine to form water.

Example 2:

Balance the following in basic solution:



An overall redox reaction is balanced by first balancing the half reactions.

To separate a reaction into half reactions, determine what is oxidized and what is reduced.

Balance the half reactions.

Multiply the half reactions by whole numbers so the number of electrons in the reduction equals the number of electrons in the oxidation.

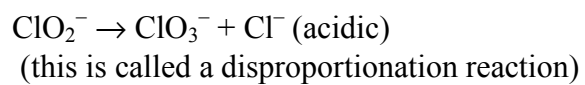
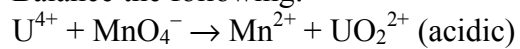
The reduction and oxidation half reaction are combined.

If a reaction is in a basic solution, the step to convert the H⁺ to OH⁻ can be completed at any step in this process. However, it is easiest to do as the last step.

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Example 3:

Balance the following:



Follow Up Problems 21.1
Problems 21.1, 3, 10, 12, 14

Spontaneous Redox Reactions

A redox reaction is an exchange of an electron from one species to another that has a stronger attraction for the electron.

The table of reduction potentials arranges the reactions with the strongest oxidizing agent on the bottom left, and the strongest reducing agent on the top right.

We can use this to predict if a reaction will occur.

We examine all the species present in a mixture. An oxidizing agent on the left will react with a reducing agent that is on the right and above it on the table.

- Some species appear more than once: Cu^+ , Cu^{2+} , Fe^{2+} .
- If H^+ is present in the reaction the reaction must be in an acidic environment.

Example 1:

Predict if a reaction is spontaneous, and products if there is a reaction:

Cu and Zn

Cu^{2+} and Zn and Zn^{2+}

Cl_2 and Br^-

Acidified hydrogen gas and Sn^{2+}

acidified MnO_4^- and Hg

Cu^+

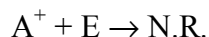
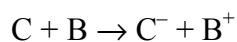
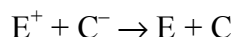
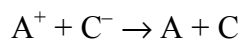
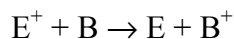
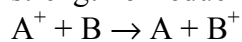
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If we are given information about spontaneous reactions, we can rank different species by their strength as reducing agents.

To remind yourself of the order of reducing and oxidizing agents, use the data table.

Example 2:

Given the following spontaneous reactions, rank the species by strength of reducing agents.

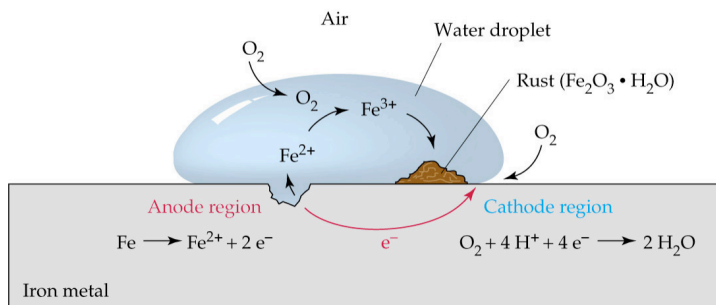


A commonly identified spontaneous redox reaction is corrosion. Iron will rust spontaneously to form iron(III)oxide.

The anode reaction is the oxidation reaction.
The cathode reaction is the reduction reaction.
These two reactions are separated. The electrons must be able to move from the anode to the cathode.

The colour of the rust will vary with the hydration of the $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$.

What factors would affect the rate of this reaction?



Follow Up Problems 21.4 (ignore voltage)

Problems 21.26, 40, 42, 44, 46, 48, 50 (ignore voltage)

8.4 Redox — Voltaic Cells

The most useful application of electrochemistry is a voltaic or electrochemical cell. This cell (or battery when combined) converts chemical energy into electrical energy. The basic form is to separate the reduction reaction and the oxidation reaction so that the transfer of electrons is external to the chemical reactions. These electrons can be made to do work.

The half cell that has the oxidation reaction is called the anode.

The half cell that has the reduction reaction is called the cathode.

The direction of the electron flow can be determined from the reactivity series.

Electrons flow from the anode to the cathode.

The salt bridge (or a porous barrier) is to allow the charge to balance.

Electrons moving to the cathode would quickly build up a charge and stop the electron flow. The salt bridge (or porous barrier) allow ions to move to balance the charge.

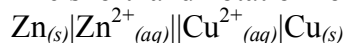
Positive ions (cations) move to the cathode, negative ions (anions) move to the anode.

The voltage of a cell can be calculated from the standard electrode potentials.

These voltages are based on standard cells that have all solutions at 1.0 M, all gasses at 101.3 kPa.

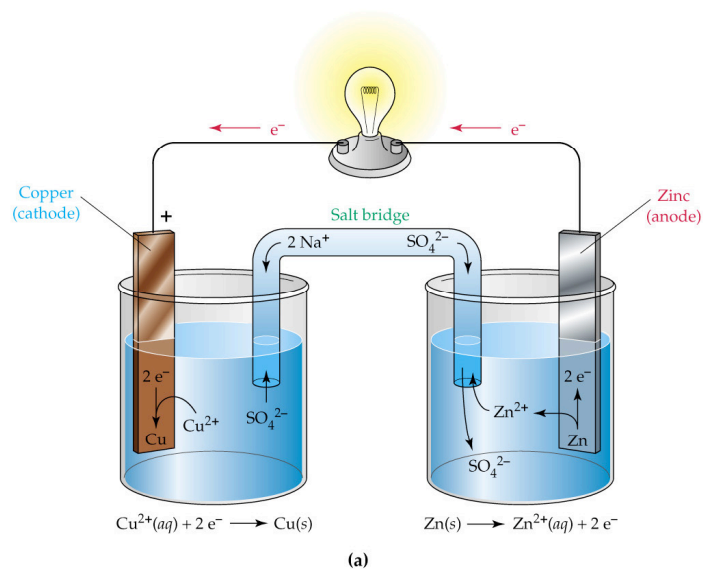
A cell with a positive voltage will indicate a spontaneous reaction (It would have a negative ΔG).

The shorthand notation for the copper/zinc voltaic cell is:



The single line represents a phase change. The double line represents the salt bridge.

The anode is written and then the cathode.



Example 1:

Construct a cell with a silver electrode and a copper electrode.
Label the cell and calculate its voltage.

What will happen to the concentrations and the voltage of this cell
as it reacts?

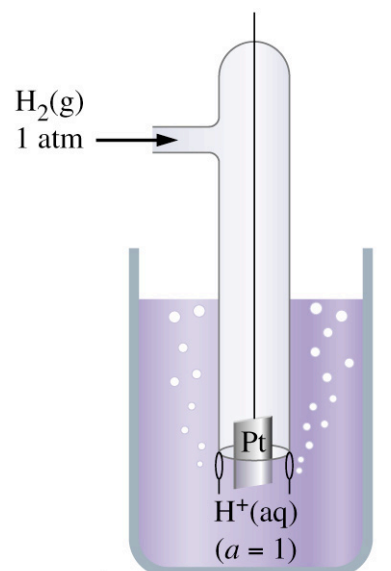
The voltage values are the difference in voltage between two
different half cells.

To give the half cells specific values, the hydrogen half cell is
defined as zero volts.

To determine the voltage of a half cell, it is connected to the
standard hydrogen half cell and the voltage is measured.

Follow Up Problems 21.2, 3

Problems 21.22, 25, 27, 29, 31, 33, 48



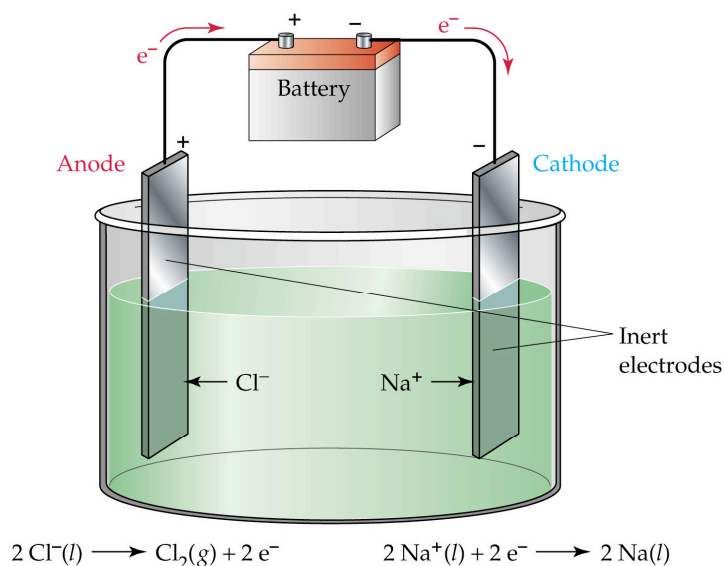
8.5 Redox — Electrolytic Cells

An electrolytic cell is a non-spontaneous redox reaction that is forced to occur by an external power source.

An electrolytic cell converts electrical energy into chemical energy.

The species in an electrolytic cell will have a negative voltage. This is the minimum voltage that is required to force the non-spontaneous reaction to occur. It would have a positive ΔG value.

The simplest electrolytic cell electrolyzes a molten salt. The only species to oxidize is the anion. The only species to reduce is the cation. Ions move to conduct the current.



The cathode is still the electrode where reduction takes place, and the anode is where the oxidation takes place.

Determining the cathode and anode can be done by identifying the negative and positive terminal of the power source.

The negative terminal of the power source is a source of electrons. It will provide the electrons for reduction.

The positive terminal will cause the oxidation.

The amount of product at an electrode will depend on several factors:

- Greater current means more electrons will be involved in the reaction.
- More time means that more electrons will react.
- A species that needs one electron to react will produce twice the moles as a species that required two electrons (other factors being equal).

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A more complicated electrolytic cell involves aqueous solutions or mixtures of solutions and electrodes.

If solutions are close to 1M, the standard electrode potentials chart can be a guide. The combination of reactants that requires the lowest voltage to react will probably react first.

The concentration of a solution can have an affect on the products of electrolysis. A dilute NaCl solution will produce H_2 at the cathode and O_2 (from water) at the anode.

A concentrated NaCl solution will still produce H_2 at the cathode (voltage for Na^+ is much lower) but will produce Cl_2 at the anode (voltage for water and Cl^- are very close).

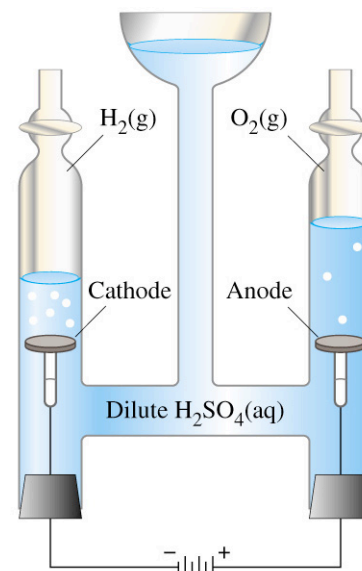
Other than the labels, how could you determine that the left is hydrogen and the right in oxygen?

What would be produced if concentrated sulfuric acid were used?

Example 1:

An electrolytic cell electrolyzes molten sodium chloride. In 1.00 h, the cell can produce 125 g of sodium. Draw this cell. How much chlorine gas (at STP) would also be collected?

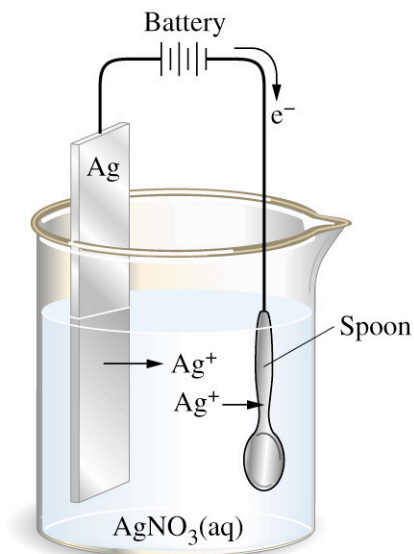
Under the same conditions, how many grams of magnesium would be produced by electrolyzing magnesium chloride?



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Electroplating is a common application of electrolytic cells. Many metals can be reduced from ions in solution to form a coating of metal on the cathode.

Why is a silver anode used in this apparatus?



An aqueous solution can be used to electroplate only with metals that are between the water species on the electrode potentials chart. Why?

Expectations for Electrolytic cells:

- Draw and label a complete cell with equations at anode and cathode.
- How is it different than a voltaic cell.
- Explain how it is used in electroplating.
- Determine the products at the cathode and the anode for salts and solutions.
- Explain how charge, current and time affect the amount of products.
- Determine relative amounts of products.

Follow Up Problems 21.8, 9

Problems 21.85, 87, 89, 93, 95, 97