

Chapter 11

There are many types of chemical reactions. In this chapter we will begin with combustion reactions and end with oxidation/reduction reactions. Along the way we examine various aspects of reactions.

Reading Assignment: Read the entire chapter.

Homework: see the web site for homework.

http://web.fccj.org/~smilczan/psc/Homework7_11.htm

There are many types of chemical reactions. In this chapter we will begin with combustion reactions and end with oxidation/reduction reactions. Along the way we examine various aspects of reactions.

Combustion reactions:

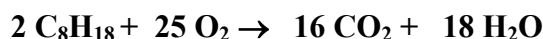
All combustion reactions fall into the pattern:



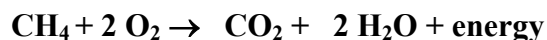
The coefficients of the balanced equation will change depending on the fuel. The fuel can be almost anything including methane (CH_4), propane (C_3H_8), butane (C_4H_{10}), octane (C_8H_{18}) or sugar ($\text{C}_6\text{H}_{12}\text{O}_6$).

The balanced equation for methane is $\text{CH}_4 + 2 \text{O}_2 \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O}$

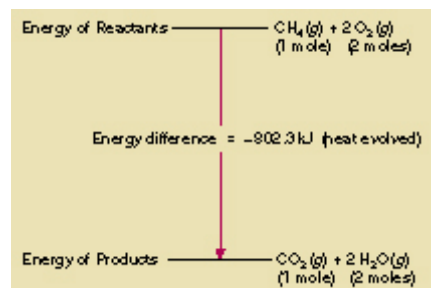
The balanced equation for octane is



The combustion of methane or octane is exothermic; it releases energy.



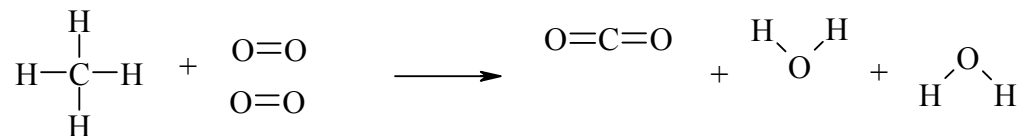
The energies of the products are lower than the energies of the reactants. The excess energy is released as heat and light.



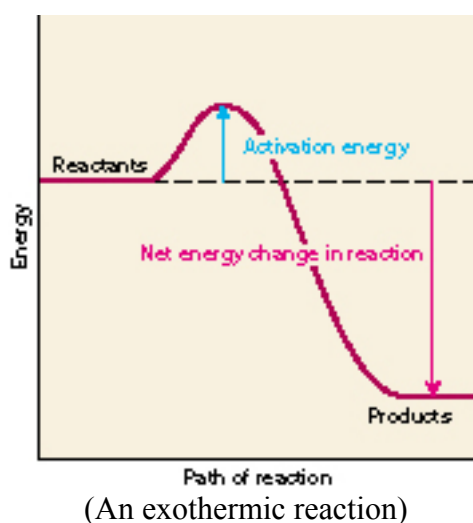
Matter tends to move to lower energy states. A good analogy for a reaction is a ball falling down a hill. Exothermic reactions are more likely to occur. Endothermic reactions absorb energy. In these reactions the products are higher in energy than the reactants. Endothermic reactions are less likely to occur. You seldom see a ball spontaneously going uphill. Endothermic reactions can occur when entropy drives the reaction (pushes the ball up the hill). These reactions are far less common. An exothermic reaction occurs in a chemical hot pack. (Skiers know about hand and foot warmers.) An endothermic reaction occurs in a chemical cold pack.

Activation energy

If you mix methane and oxygen together, a reaction does not occur right away. There is a barrier to the reaction. This barrier is due to the fact that to make CO₂ and H₂O we have to break 4 carbon-hydrogen bonds and some oxygen-oxygen bonds. From this initial energy investment however we get a larger energy payoff when the carbon-oxygen and hydrogen-oxygen bonds are formed.



The energy barrier is called the activation energy. The net energy of the reaction is the energy that is released as the methane burns. How do you overcome the initial energy barrier? Typically we light the reactants with a lighter or a spark. Once we start the reaction, the energy released can let other reactions overcome their activation energy and the fire is underway.



Please watch the **animation 11.1: Reactions and Energy on your CD**

Other oxidation reduction reactions

Organic chemists give the following definition to oxidation reactions:

Oxidation: A reaction that increases the number of bonds to oxygen.

reduction: A reaction that decreases the number of bonds to oxygen.

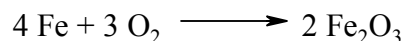
Organic chemists classify combustions reactions as oxidation reactions

There is another method of classifying oxidation/reduction reaction

Oxidation: When a species loses electrons and becomes more positively charged.

reduction: When a species gains electrons and becomes more negatively charged.

The following is an oxidation/reduction reaction (redox) reaction.

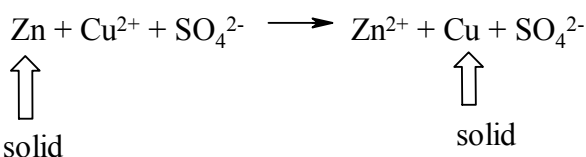


Iron is Fe and Fe₂O₃ is red rust. O₂ is oxygen. You might think that water is required for this process but it is not, it merely speeds it up. Notice that the iron is now bound to the oxygen. It has gone from its elemental state with no charge (Fe⁰) to its ionic state (Fe³⁺) Because the iron has lost electrons and become positively charged, it has been oxidized. The oxygen has been reduced. The electrons from the iron went to the oxygen. Every oxidation process has to have a corresponding reduction. We call these redox reactions, the word redox combining **reduction** and **oxidation**.

We can write half reactions for this total reaction:



Some metals are more stable in their elemental state than others. Gold, Platinum and silver are hard to oxidize. Other metals such as lithium magnesium and aluminum are easy to oxidize. When they oxidize they change into their ionic state. If you put Zn metal into a solution of Cu²⁺ and SO₄²⁻ an interesting thing happens. The zinc goes into solution and the copper begins to plate out as solid copper (Cu⁰). The equation for this is



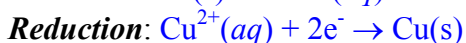
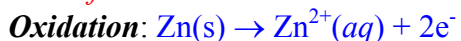
The zinc and the copper are solids and the ions are in solution. Notice that the sulfate (SO₄²⁻) is not changing during the reaction. We call these ions spectator ions. Why does this reaction occur? Copper is more stable than zinc. Copper is below zinc on the activity series.

The activity series.

Metal	Oxidation Reaction
Lithium	Li → Li ⁺ + e ⁻
Potassium	K → K ⁺ + e ⁻
Barium	Ba → Ba ²⁺ + 2e ⁻
Calcium	Ca → Ca ²⁺ + 2e ⁻
Sodium	Na → Na ⁺ + e ⁻
Magnesium	Mg → Mg ²⁺ + 2e ⁻
Aluminum	Al → Al ³⁺ + 3e ⁻
Zinc	Zn → Zn²⁺ + 2e⁻
Chromium	Cr → Cr ³⁺ + 3e ⁻
Iron	Fe → Fe ²⁺ + 2e ⁻
Cobalt	Co → Co ²⁺ + 2e ⁻
Nickel	Ni → Ni ²⁺ + 2e ⁻
Tin	Sn → Sn ²⁺ + 2e ⁻
Lead	Pb → Pb ²⁺ + 2e ⁻
Hydrogen	H ₂ → 2H ⁺ + 2e ⁻
Copper	Cu → Cu²⁺ + 2e⁻
Silver	Ag → Ag ⁺ + e ⁻
Mercury	Hg → Hg ²⁺ + 2e ⁻
Platinum	Pt → Pt ²⁺ + 2e ⁻
Gold	Au → Au ³⁺ + 3e ⁻



The *redox half-reactions* for the above reaction would be:



The oxidation of a Zinc atom releases 2 electrons

The reduction of a Copper ion is achieved by the acceptance of 2 electrons

Thus, there would appear to be a movement, or flow, of electrons from the Zinc metal to the Copper ions

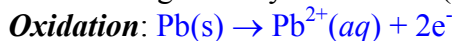
We can capture the power energy produced in this reaction in a battery. The battery can use this flow of electrons to do work. Please read about voltaic cells at

<http://wine1.sb.fsu.edu/chm1046/notes/Electro/Voltaic/Voltaic.htm>

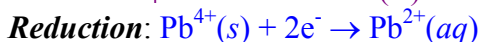
or

<http://sciborg.uwaterloo.ca/~cchieh/cact/c123/battery.html>

The lead-acid storage battery uses lead 0 (elemental) and lead 4+.

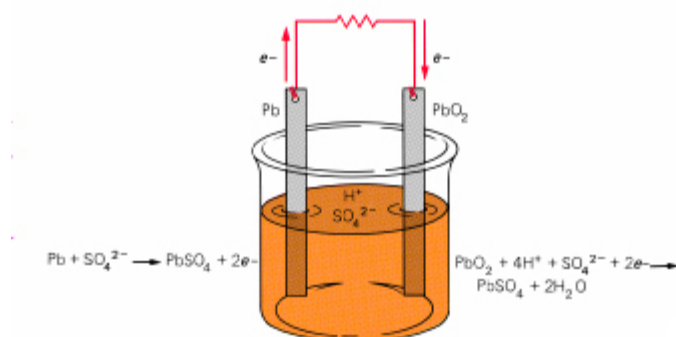


The lead gives away two electrons through the wire and becomes Pb^{2+} which combines with SO_4^{2-} to become lead(II)sulfate.



The lead here starts as Pb^{4+} as it combines with 2O^{2-} . It can take the two electrons from the wire and become Pb^{2+} which combines with SO_4^{2-} to become lead(II)sulfate.

Again, as the electrons pass through the wire they create a voltage which can be used to do work.



How do reactions occur?

Three things must happen for a reaction to occur.

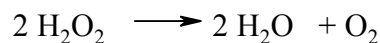
- 1) Molecules must collide.
- 2) Molecules must collide with enough energy to begin to break the old bonds so new bonds can form. (Remember activation energy)
- 3) Molecules must collide with the correct orientation.

How can we speed up reactions?

- 1) Increase concentration. This increases the number of collisions. The more collisions per second, the faster the reaction.
- 2) Increase temperature. This increases the number of collisions because the molecules are moving faster. It also means that more of the collisions have enough energy for a reaction to occur. A higher % of collisions will have enough energy. A rule of thumb is that at about room temperature, an increase in 10° C will double the rate.
- 3) Use a catalyst. A catalyst lowers the barrier to the reaction. It lowers the activation energy. A catalyst speeds up a reaction but is unchanged at the end of the reaction.

Please watch **Animation 11.4: Catalysts.**

In the first animation we are looking at the decomposition of peroxide;



Iodide (I⁻) catalyzes this reaction. After the iodide has catalyzed one reaction it is unchanged so it can catalyze another, and another, and another and so on.....

By lowering the energy barrier to the reaction, more of the collisions will be successful and the reaction will occur faster.

Enzymes are examples of catalysts in our body.

Equilibrium

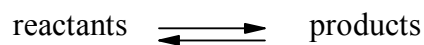
Equilibrium is defined as an exact balancing of two processes that are opposite of each other. Think of a tetter totter.



Notice that the weights of the two animals is not the same but by shifting their position they can achieve equilibrium.

Chemical equilibrium is defined as a dynamic state where the concentration of all reactants remains constant. They may not be equal but they are not changing.

In a chemical reaction, a double arrow indicates an equilibrium situation. Reactants are on the left and products are on the right.



We have made an implicit assumption... that reactions react to completely transform reactants to products.

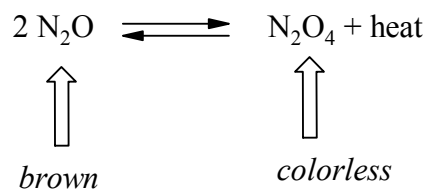
- In some reactions, this is true, but in most reactions it is inaccurate. The majority of reactions are reversible, meaning that a certain amount of reactant remains at the end of the reaction.
- Reversible reactions occur until equilibrium is established, meaning that they achieve a sort of balance between amounts of reactant and product.
- If the reactants and products are equal in energy, at equilibrium, they will have the same concentration. If the products are lower in energy, there will be a higher % of the products in the equilibrium mixture. If the reactants are lower in energy, there will be a higher % of the reactants in the equilibrium mixture.

Equilibrium is...

1. A state in which the concentrations of reactant and product are no longer changing, for a reversible reaction.
2. A state in which the rate of the forward reaction is equal to the rate of the reverse reaction; reactant is being consumed to form product at the same rate at which product is being degraded to form reactant.
3. Individual molecules are constantly being converted from one form to another, but no overall change in the concentrations of any species is observed.

What do we mean by dynamic?

An example of an equilibrium reaction is



By dynamic we mean that N_2O is constantly going to N_2O_4 and N_2O_4 is constantly going to N_2O . They are just balancing each other out. This reaction is exothermic so heat can be considered a product.

We can perturb a system at equilibrium. (Remember our tetter-totter. We can add some cheese to the mouse side). How will this affect the relative ratios? Le Châtelier's Principle says the following:

"A system at equilibrium, when stressed, will shift to offset the stress"

This means if we add reactant, equilibrium goes right, away from the reactant.

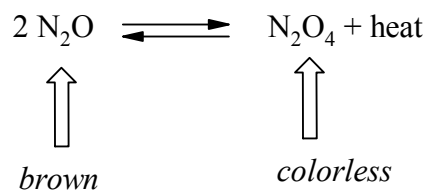
If we add product, equilibrium goes left, away from the product.

If we remove product, equilibrium goes right, making product.

If we remove reactant, equilibrium goes left, making reactant.

Please watch **Animation 11.3: Shifting Equilibrium**

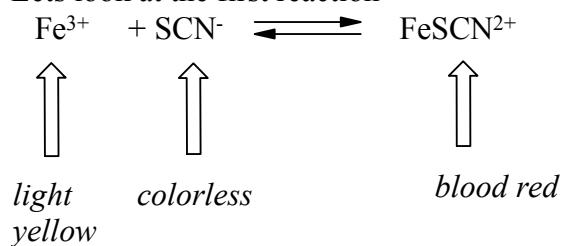
Notice that in the second video we are watching this reaction



By cooling we are removing heat and the equilibrium shifts right and the color gets lighter because we are converting N_2O to N_2O_4 .

By heating we are adding heat and the equilibrium shifts left and the color gets darker because we are converting N_2O_4 to N_2O .

Lets look at the first reaction



By adding iron (Fe^{3+}) or thiocyanate (SCN^-) we shift the equilibrium to the right making more blood red iron/thiocyanate complex and the solution gets darker.