Lectures 23 and 24: Chemists and Chemical Engineers Make the World a Better Place: Catalysts and Batteries

Lecture 23: Two Famous Catalysts

As we discussed when examining the Arrhenius equation

 $K = A \exp(-Ea/RT)$

one important factor in the rate of reaction is the activation energy. The larger E_a , the smaller k and the slower the reaction. One of the thriving areas of research in chemistry is the search for ways to speed up reactions without increasing temperature (which is expensive.) Lowering the E_a with catalysts is one approach.

Catalyst, a definition: A material that speeds a rate of reaction by lowering the activation energy through a change of reaction mechanism. Catalysts do not show up in the overall chemical reaction (they are typically conserved to react over and over).

One class of catalysts are homogeneous catalysts which react in the same phase as the chemical reaction of interest. For example, a homogeneous catalyst is a:

liquid catalyst in a solution gas catalyst in the gas phase

A really important area of research is with heterogeneous catalysts. The catalysts are in a different phase than the overall reaction (usually a solid). For example

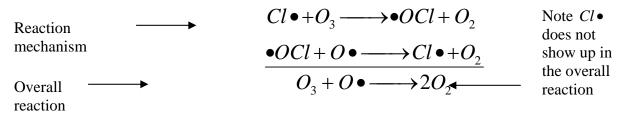
solids are common heterogeneous catalysts for gas and liquid phase reactions.

Two famous catalysts.

The hole in the ozone catalyst: Chlorine radical is a homogeneous catalyst that is reducing the size of the ozone. Chlorofluorocarbons are bad because they are volatile and typically find their way into the atmosphere. There they undergo photolytic degradation (photons from the sun break bands).

$$CF_3Cl \xrightarrow{hv}_{from} CF_3 \bullet + Cl \bullet$$

The Cl \bullet then participates as a catalyst in a reaction that eliminates ozone, O_3 .



The cleaner burning car catalyst: Catalytic converters in cars are heterogeneous catalysts. They are high surface area porous solids that do at least two things

An oxidation $\rightarrow CO \longrightarrow CO_2$ convert CO to CO_2

A reduction $\rightarrow NO_x \longrightarrow N_2$ convert nitrogen oxides to nitrogen

$$\begin{array}{c|c} NO_x \\ \hline CO & in \end{array} \end{array} \xrightarrow{\text{Magical}} \begin{array}{c} \text{out} & N_2 \\ \hline \text{heterogeneous catalyst} & CO_2 \end{array}$$

Note that the mechanism is not provided here, just know there is a heterogeneous catalyst. What are in the catalytic converters? Current generation automotive catalyst material consists of a ceramic or metallic substrate coated by an various combinations of aluminum oxides mixed with rare earth oxides and metals like platinum (Pt, Pd, Rh).

Lecture 24: Famous Batteries

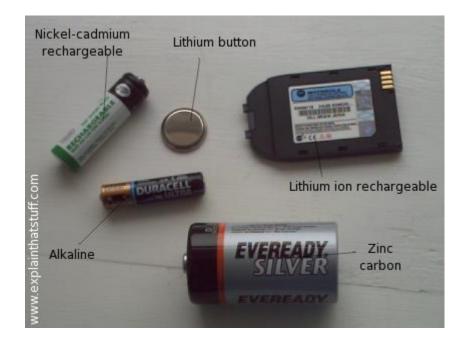
Having finished up redox reactions, note that the ones we are interested in are those that make useful things like batteries. In fact, a battery is simply a couple of redox half reactions that can be put together so that E is positive and some work can be done. So as you consider the electrochemical cell conventions below, understand that they are useful in helping to describe the following kinds of famous batteries:

And while they don't get a lot of press, batteries make our increasingly mobile world go round, and there is an enormous amount of energy that goes in to finding redox reactions that, among other things:

- produce a lot of energy
- produce a lot of current
- don't weigh very much or take up much space
- aren't toxic or environmentally dangerous
- have reversible reactions (are rechargeable)
- oh, and don't cost very much

Over the years a lot of progress has been made, and for example, these days people walk around with 5 to 10 batteries on their person and don't even know it. One thing is sure, the ability to make small, inexpensive power sources for our mobile world will be what drives changes in society.

So here are some batteries everyone should know:



Listed below are several famous batteries, distinguished by whether they are rechargeable or not.

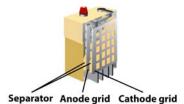
Primary batteries—these are not rechargeable, you throw them away when they reach equilibrium

Alkaline battery - Used in common Duracell and Energizer batteries. The electrodes are zinc and manganese-oxide, with an alkaline electrolyte. Inside an alkaline battery, manganese dioxide molecules are converted into manganese oxide and hydroxyl ions. The hydroxyl ions then react with zinc to form zinc oxide and water, releasing electrons. The electrons move toward the carbon rod and flow out around the circuit, producing an electric current. The battery stops producing electricity when all the manganese dioxide is used up.

Zinc-air battery – **Lightweight.** Zinc air batteries are small, non-rechargeable batteries with open circuit voltages of 1.15 to 1.4 V per cell. They use surrounding air (O_2) as the cathode. Zinc air batteries are long lasting, high performance batteries used in small devices such as hearing aids and pagers.

Secondary Batteries (Rechargeable.)

Lead-acid battery - Used in automobiles, the electrodes are made of lead and lead-oxide with a strong acidic electrolyte. They are rechargeable. Despite having the second lowest energy-to-weight ratio (next to the nickel-iron battery) and a correspondingly low energy-to-volume ratio, their ability to supply high surge currents means that the cells maintain a relatively large power-to-weight ratio. This, along with their low cost, makes them ideal for use in cars, as they can provide the high current required by automobile starter motors. Each cell contains (in the charged state) electrodes of lead metal (Pb) and lead (IV) oxide (PbO₂) in an electrolyte of about 37% (5.99 Molar) w/w sulfuric acid (H₂SO₄).



Nickel-cadmium battery - Uses nickel-hydroxide and cadmium electrodes, with potassium-hydroxide as the electrolyte. Rechargeable. Until recently, virtually all rechargeable batteries were nickel-cadmium (NiCd, usually pronounced "nicad"). Although very dependable, they need to be discharged fully before you charge them up or the amount of charge they will store (and their effective lifespan) can be greatly reduced.

Nickel-metal hydride battery - Rapidly replacing nickel-cadmium because it does not suffer from memory effect. Rechargeable. type of rechargeable battery similar to a nickel-cadmium (NiCd) battery but has a hydrogen-absorbing alloy for the anode instead of cadmium. Like in NiCd batteries, nickel is the cathode. A NiMH battery can have two to three times the capacity of an equivalent size NiCd and the memory effect is not as significant. However, compared to the lithium-ion battery, the volumetric energy density is lower and self-discharge is higher. Applications of NiMH type batteries includes hybrid vehicles such as the Toyota Prius

Lithium-ion battery - Very good power-to-weight ratio, often found in high-end laptop computers and cell phones. Rechargeable. High discharge rates don't significantly reduce its capacity, nor does it lose very much capacity after each cycle, still retaining 80% of its energy capacity after 500 recharge cycles. Early versions were prone to exploding in the labs and people still claim there is a risk with these batteries.