
Electrochemistry

Chapter 10

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If a molecule is oxidized it loses H and changes the oxygen bond by either increasing the number of oxygens or by sharing more electrons. If it gains hydrogen it is reduced and also changes the oxygen bond, losing oxygens or reducing the number of shared electrons.

- The most general way to define oxidation and reduction is in terms of electron transfer. In oxidation electrons are lost and in reduction electrons are gained.

B. Terminology



This reaction is redox because electrons have been transferred.

Oxidation - loss of electrons, ox # increases, $\text{Zn} \rightarrow \text{Zn}^{+2}$

Reduction - gain of electrons, ox # decreases, $\text{Cu}^{+2} \rightarrow \text{Cu}$

Electrochemistry

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I. Applications of Oxidation/Reduction Reactions

A. History

- Oxygen combines with almost all elements to form oxides. It also reacts with various compounds. This process is called oxidation. Rapid oxidation which gives off much heat is called combustion. The atom or molecule that reacted with the oxygen is said to be oxidized and the oxygen itself is reduced.
- Another way to define oxidation with organic molecules (carbon containing) that contain H and O is to count the number of hydrogen atoms the molecule has.

Reducing agent - agent that allows reduction to occur, it is the substance that is oxidized and can provide electrons

Oxidizing agent - agent that allows oxidation to occur, it is the substance that is reduced and takes the electrons provided.

B. Examples

Corrosion

Combustion

Metabolism

Electrochemical cells (batteries)

Electrolysis

Electrochemistry

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II. Electrochemical cells (Batteries)

A. Theory of operation



This does not look like a battery because the electrons are being transferred directly between Cu^{+2} and the Zn strip. If we separate the reactions and force the electrons to travel through a circuit we could use these electrons as they try to get from the Zn to the Cu^{+2} .

ions are leaving on the right side (-). We must allow ions to flow to equalize the charge. This is the function of the salt bridge.

With the salt bridge the circle is complete. Electrons flow through the wire from Zn to Cu^{+2} and anions move from the right side to the left and cations move from left side to the right to equalize the charge. This total movement of charge, ions in the internal circuit and electrons in the external, completes the electrochemical cell.

B. Half Cell Potentials

We can measure the push of electrons (called the voltage) through the external wire for a voltaic cell. This voltage can be envisioned as a sum of 2 pushes - one for the oxidation and one for the reduction.

The push of the electrons to go from Zn to Cu^{+2} is called the voltage.

Voltage = work/charge $V = W/Q$

Volt [=] Joule/coulomb

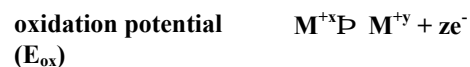
This push can be measured with a voltmeter.

Why do we need the salt bridge?

In the figure above the electrons from Zn \rightleftharpoons Zn^{+2} will move through the wire and over to the other side to the Cu^{+2} . Almost immediately the flow stops because of a charge buildup on both sides. Zn^{+2} ions are accumulating in the left compartment (+) and Cu^{+2}

$$E_{\text{cell}} = E_{\text{red}} + E_{\text{ox}}$$

The tendency for a metal to lose or gain electrons can be measured by these pushes - called the oxidation and reduction potentials. The larger the value the greater the tendency for that reaction to occur - or put another way the more positive the oxidation or reduction potential is the greater the tendency for that oxidation or reduction to occur. The activity series (see handout) is a listing of reduction potentials that gives a measure of how likely a reduction reaction is to occur.

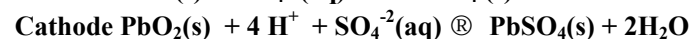
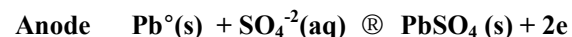


$$E_{\text{ox}} = - E_{\text{red}}$$

E. Example problems and questions using half cell potentials

- Will aluminum dissolve in a solution of Sn^{+4} ?
- Why do people who have dental fillings feel pain when chewing a piece of aluminum foil?
- Predict the voltage of an aluminum/zinc battery.
- Which is spontaneous, the reaction of iron with the cupric ion or the reaction of copper metal with ferrous ion?

3. Lead storage (2.0V)

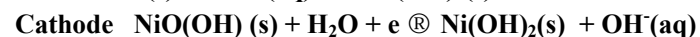
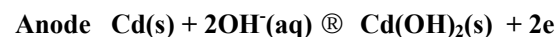


Net reaction



- can be recharged because the lead (II) sulfate product is an insoluble product which stays at the electrodes.

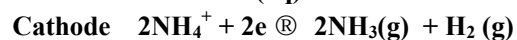
4. Nickel/Cadmium (1.3 V)



- can be recharged due to the fact that products are insoluble hydroxides that stay at the electrode surface
- this battery produces a constant voltage until completely discharged

C. Common Batteries

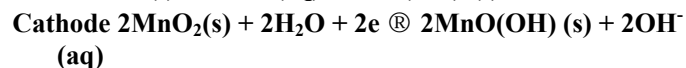
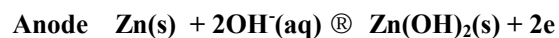
1. Dry Cell (1.5 V)



The hydrogen gas is a problem so MnO_2 is added; gaseous ammonia reacts with the Zn^{+2} ion.

- decline in voltage under high load

2. Alkaline (1.5 V)

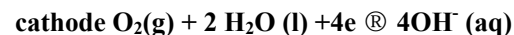


no gases are formed

- no decline in voltage under high load

C. Fuel Cell

a special type of electrochemical cell in which the reactants are continually supplied from an external source; the best known is the hydrogen / oxygen fuel cell used in the space program



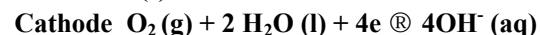
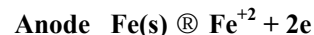
An explosion does not occur because the reaction is carried out at low temperature on a platinum catalyst. The net cell reaction is simply the production of water.

III. Corrosion

- A. Defined as the oxidation of a metal that results in a loss of structural strength and that is a result of exposure to the environment.

The most common is the corrosion of iron (rusting). Many metals oxidize but only those which form scaly oxidize coatings corrode. For example aluminum oxidizes readily but does not corrode easily.

B. Reactions for rusting



This gives the net reaction



Further reaction with oxygen gives the red-brown hydrated iron (III) oxide - $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}(\text{s})$

Cathodic protection - force the metal to become a cathode instead of the anode. This is accomplished by attaching a more readily oxidized metal, such as zinc, to the metal being protected. The iron is said to be galvanized. A current example is the dipping of the steel frame of a car in a solution of zinc phosphate to prevent corrosion.

C. Requirements

- Anodic areas occur at cracks in the metal surface exposing pure metal.
- Cathodic areas can be anywhere else on the metal.
- Water is a necessary ingredient to form a salt bridge between anode and cathode.
- Chlorides dissolved in the water such as salt speed up corrosion by enhancing the salt bridge.

D. Protection

Anodic inhibition - coat the surface of the metal to prevent exposure. More recent treatments involve chromate and phosphate baths to form a tight film of iron and chromium oxides and phosphates on the surface.

IV. Electrolysis

- A. This is the opposite process from the galvanic cell. We use an electric current to force a nonspontaneous reaction.

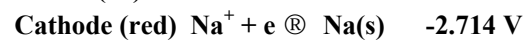
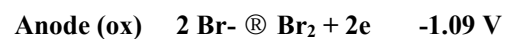
<u>Cell</u>	<u>Electrode</u>	<u>Function</u>	<u>Polarity</u>
Battery	Anode	oxidation	negative
	Cathode	reduction	positive
Electrolysis	Anode	oxidation	positive
	Cathode	reduction	negative

B. Applications

1. Production of elements such as sodium and chlorine
2. Plating of metals over another metal (or suitably prepared substance) for protection or beauty

C. Predicting reactions

1. Molten NaBr

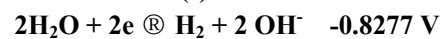
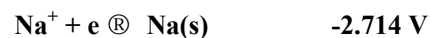


2. An aqueous solution of NaBr

Possible anode reactions



Possible cathode reactions



The bromide oxidation and the water reduction have the greatest tendency to occur (most positive potentials) so the result is:

