Electrochemistry

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I. Applications of Redox Reactions

A. **Terminology**

$Zn\ (s)\ +\ Cu^{+2}(aq)\ ®\ Zn^{+2}\ (aq) + Cu\ (s)$

This reaction is redox because electrons have been transferred.

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

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

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

Voltaic cells (batteries)

Electrolysis

B. Balancing Redox Reactions

Oxidation reduction reactions are sometimes very difficult to balance. Mass, charge, and # of electrons must be balanced. The following method for balancing is slightly different from the book.

1. Write reaction in ionic form and assign oxidation numbers
2. Separate into half cells
3. Balance # of atoms of oxidized and reduced species
4. Balance # of electrons of oxidized and reduced species
5. Make sure electrons lost in the oxidation = electrons gained in the reduction
6. Balance charge in each half cell using H^+ if in acid and OH^- if basic
7. Balance # of H and O using water molecules.

II. Voltaic cells (Batteries)

A. Theory of operation

$$Zn(s) + Cu^{+2}(aq) \ \circledR \ Zn^{+2}(aq) + Cu(s)$$

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}.

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 ® 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} 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 voltaic cell.

B. The notation for the cell is

M (electrode)½M$^+$(solution)½½N$^+$(solution) ½N(electrode)

       anode   cathode
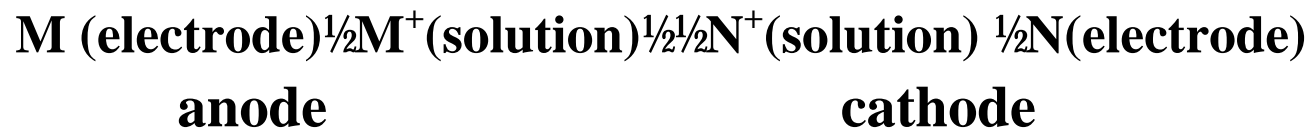
C. Thermodynamics and the Cell Potential

Standard Potential - When all reactants and products present are pure solid or in solution at 1.0 M (or gases at 1.0 Atm) the conditions are standard and the measured voltage is called the standard potential E°. This E° is a measure of the tendency of pure reactants to become products, sort of like DG^o. There is a relationship between the two:

Under standard conditions $\quad DG° = -nF\ E°$

Under any conditions $\quad DG = -nF\ E$

Since spontaneous reactions have a positive E° there must be a negative sign in the proportionality. n represents the number of moles of electrons (also called Faradays) transferred in the balanced equation. F is a conversion between Joules, Volts and moles of electrons. It is called Faraday's constant. $F = 96,500$ coulombs/mole

D. 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.

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

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.

oxidation potential $\qquad$ $M^{+x} \rightarrow M^{+y} + ze^-$
(E_{ox})
reduction potential $\qquad$ $M^{+y} + ze^- \rightarrow M^{+x}$
(E_{red})
$E_{ox} = - E_{red}$

The problem is that we cannot measure each individual push so we cannot measure the absolute cell potential. So we define a cell potential to be zero and measure all others against it. This allows the calculation of all other potentials. The actual zero potential that has been agreed upon is the $H_2 \rightleftharpoons 2H^+ + 2e^-$.

E. Rules of thumb for using half cell potentials

1. $E°$ values are normally tabulated as reduction potentials

2. If you need to find the oxidation potential simply reverse the algebraic sign of $E°$. All reactions are reversible

3. The more positive the value of $E°$ is the more likely the process is to occur. Since the reduction process is the agent of oxidation, the elements at the top of the reduction table are the best ox agents and the species at the bottom (for the reverse oxidation reaction) are the best reducing agents.

4. Under standard conditions (1M or 1Atm) any substance will spontaneously oxidize any other substance underneath it in the reduction table.

5. Potentials are intensive properties. Changing the stoichiometric coefficients for a half-rxn does not change the value of E.

6. To predict the spontaneity of a rxn, add E° of the red rxn and E° of the ox rxn together. If E° is positive the rxn is spontaneous under standard conditions.

F. 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?

G. Voltaic cells at nonstandard conditions

What if the concentrations are not 1 M for all ions? The Nernst Equation relates the cell potential to the concentrations of the ions.

$$E = E° - [RT/nF] \ \ln Q$$

Q is the reaction quotient, the ratio of product concentrations divided by reactant concentrations. Since this equation is a holdover from the days when $\log_{10}$ was easier to compute than natural log the equation became

$$E = E° - [RT/nF] \ 2.303 \log Q$$

Using R = 8.314 J/mole K, F = 96,500 coulombs /mole and T = 298 K (most reported data) the equation finally becomes

$$E = E° - [0.0592/n] \ \log Q$$

When equilibrium is reached E = 0 V and the reactions quotient Q equals the equilibrium constant K. This gives an expression relating the equilibrium constant to the E° of the cell.

$$\textbf{log K = n E°/0.0592}$$

Example:

Find the cell potential for the reaction of an iron strip with Cd^{+2} ion if the concentration of ferrous ion is 1.0 M and the concentration of the cadmium ion is 0.010 M.
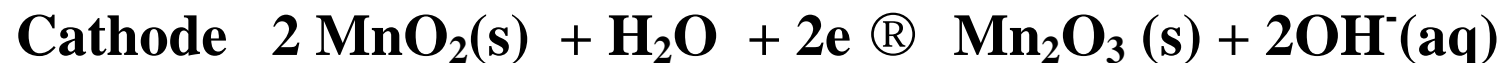
$$\textbf{Fe(s) + Cd}^{+2}\textbf{(aq)} \quad ® \quad \textbf{Fe}^{+2}\textbf{(aq) + Cd (s)}$$

H. Common Batteries

1. Dry Cell (1.5 V)

Anode $Zn \circledR Zn^{+2}(aq) + 2e$

Cathode $2NH_4^+ + 2e \circledR 2NH_3(g) + H_2(g)$

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

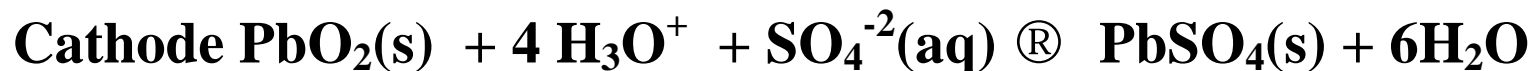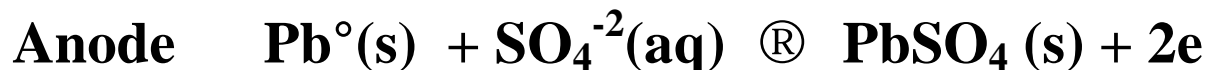### 2. Alkaline   (1.54 V)

Anode $Zn(s) + 2OH^-(aq) \circledR ZnO(aq) + H_2O + 2e$

Cathode $2 MnO_2(s) + H_2O + 2e \circledR Mn_2O_3(s) + 2OH^-(aq)$

no gases are formed

- no decline in voltage under high load

3. Lead storage (2.04V)

Anode $Pb°(s) + SO_4^{-2}(aq)$ ® $PbSO_4 (s) + 2e$

Cathode $PbO_2(s) + 4 H_3O^+ + SO_4^{-2}(aq)$ ® $PbSO_4(s) + 6H_2O$
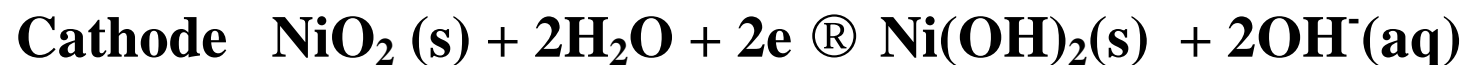
Net reaction

$Pb + PbO_2 + 2H_2SO_4$ ® $2PbSO_4 + 2H_2O$

These reactions are just a little different than the text.

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

4. Nickel/Cadmium (1.3 V)

Anode $Cd(s) + 2OH^-(aq)$ ® $Cd(OH)_2(s) + 2e$

Cathode $NiO_2 (s) + 2H_2O + 2e$ ® $Ni(OH)_2(s) + 2OH^-(aq)$

- 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

I. Fuel Cell

a special type of voltaic 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

anode $2H_2$ (g) + 4 OH- (aq)® 4 H_2O (l) + 4e

cathode O_2(g) + 2 H_2O (l) +4e ® 4OH⁻ (aq)

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

Anode $Fe(s) ® Fe^{+2} + 2e$
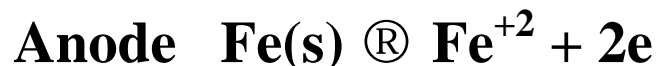
Cathode $O_2 (g) + 2 H_2O (l) + 4e ® 4OH^- (aq)$
This gives the net reaction
$2Fe(s) + O_2(g) + 2H_2O(l) ® 2Fe(OH)_2 (s)$
Further reaction with oxygen gives the red-brown hydrated iron (III) oxide - $Fe_2O_3 \cdot H_2O (s)$

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 baths to form a tight film of iron and chromium oxides on the surface.

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.

IV. Electrolysis

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

Cell	Electrode	Function	Polarity
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
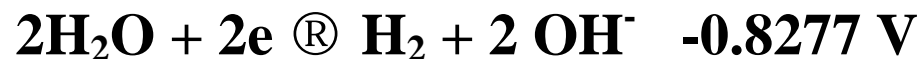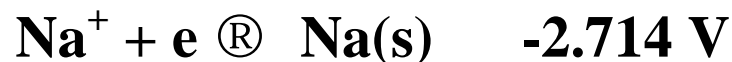

C. Predicting reactions

1. Molten NaBr

Anode (ox) $2 Br- \rightarrow Br_2 + 2e$ -1.09 V

Cathode (red) $Na^+ + e \rightarrow Na(s)$ -2.714 V

$$2Br^- + 2 Na^+ \rightarrow 2 Na + Br_2$$

A battery with a voltage of 3.8 V or greater must be used.

2. An aqueous solution of NaBr

Possible anode reactions

$2 Br- \rightarrow Br_2 + 2e$ -1.09 V

$6H_2O \rightarrow O_2 + 4H_3O^+ + 4 e$ -1.229 V

Possible cathode reactions

$Na^+ + e \rightarrow Na(s)$ -2.714 V

$2H_2O + 2e \rightarrow H_2 + 2 OH^-$ -0.8277 V

Choose the reactions that are the most positive to get

$$2 Br^- + 2H_2O \rightarrow Br_2 + H_2 + 2OH^-$$

D. Electrical Energy Use

- 1 mole of electrons (a Faraday) will give 1 equivalent of material in an electrolysis reaction
- 1 equiv = molar mass/ # of mole of e transferred
- 1 amp of current = 1 coulomb of charge/sec

These relationships give the following equation for the calculation of the mass (m) of material produced at an electrode

$$m = \frac{MIt}{nF}$$

m [=] g

M[=] g/mole

I[=]amps or coulombs/s

t[=] seconds

F[=] 96,500 coulombs/mole

n[=] no units, it is equal to the number of moles of electrons transferred in the half reaction

Examples

In a commercial operation of sodium by the electrolysis of NaCl the cell operates at 7.0 V and a current of 25×10^3 amps. How many g of sodium can be produced in 1 hour?

A current of 0.015 amps is passed through a solution of $Cu(NO_3)_2$ for 155 minutes. What mass of copper is deposited at the cathode?