Announcements

- Marks on now on WebCT

Example:

Calculate E^o_{cell} for the voltaic cell: $I^-| I_2 || Fe^{3+} | Fe^{2+}$

$$2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(s)$$

From the table we find:

$2Fe^{3+}(aq) + 2e^- \rightarrow 2Fe^{2+}(aq)$ $\quad E^o_{red} = +0.77$ V

$I_2(s) + 2e^- \rightarrow 2I^-(aq)$ $\quad E^o_{red} = +0.53$ V

Note: NEVER multiply the voltage by the coefficients of the balanced equation!!!
This is because the voltage is related to the energy of a mole of electrons transferred

The more positive reaction will go as written.
The other reaction must be reversed to be an oxidation;
that is, $2I^- \rightarrow I_2 + 2e^-$ $\quad E^o_{ox} = -0.53$V

Therefore $E^o_{cell} = E^o_{red} + E^o_{ox} = +0.77 + (-0.53) = +0.24$ V

The reaction will proceed spontaneously, as written

Note: a voltaic cell based on the reverse reaction will **not** work as there the cell potential would be -0.24 V

Example:
Determine if the following reaction is spontaneous

$$Zn^{2+}(aq) + Fe(s) \rightarrow Zn(s) + Fe^{2+}(aq)$$

This can be written as: $Fe(s)|\ Fe^{2+}(aq)\ ||\ Zn^{2+}(aq)|Zn(s)$

From the table we find:
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$ $\quad E^o_{red} = -0.76$ V

$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$ $\quad E^o_{red} = -0.45$V

The reaction shows Fe being oxidized so turn it around:

$$Fe \rightarrow Fe^{2+} + 2e^- \qquad E^o_{ox} = +0.45 \text{ V}$$

Therefore, $E^o_{cell} = E^o_{red} + E^o_{ox} = -0.76 + 0.45 = -0.31$ V

Since $E^o_{cell} < 0$, the reaction will **NOT** spontaneous occur as written.

The backwards reaction will in fact take place

Corollary:
Fe^{2+} is a better oxidizing agent than Zn^{2+}, so Fe^{2+} can oxidize Zn.
Recall that the species with the most positive E^o_{red} is the strongest oxidizing agent (likes to be reduced the most).

Example: related to question 3 from tutorial questions on electrochemistry.

Given the following voltaic cell: $Al(s)|Al^{3+}(aq)||Br_2(\ell)|Br(aq)|Pt(s)$

a) Write out the half reactions and a balanced redox equation.

b) Determine E^o_{cell}

a) From table of standard reduction potentials:

$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$ $\quad E^o_{red} = -1.68V$

But this is an oxidation as written in cell notation above

Therefore: $Al(s) \rightarrow Al^{3+}(aq) + 3e^-$ $\quad E^o_{ox} = +1.68V$ x2

$Br_2(\ell) + 2e^- \rightarrow 2Br^-(aq)$ $\quad E^o_{red} = +1.08V$ x3

$2Al(s) + 3Br_2(\ell) \rightarrow 2Al^{3+}(aq) + 6Br^-(aq)$

b) $E^o_{cell} = E^o_{red} + E^o_{ox}$

$= 1.68V + 1.08V$

$= 2.76V$

Example:
A student makes three pieces of jewelry, each from a different type of metal: Fe, Ag, and Au. The student places them in 1M acid. Which one(s) will be resistant to acid?

The items that are **not** resistant to acid will most likely dissolve; that is, the metal will oxidize to its aqueous ion

The only likely reduction is the reduction of H^+
The cell equation will therefore be: metal | metal ion || $H^+|H_2$

From the table:

- $Au^+(aq) + e^- \rightarrow Au(s)$ $E^o_{red} = +1.5$ V
- $Ag^+(aq) + e^- \rightarrow Ag(s)$ $E^o_{red} = +0.80$ V
- $2H^+(aq) + 2e^- \rightarrow H_2(g)$ $E^0_{red} = 0.00$V
- $Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$ $E^o_{red} = -0.45$ V

The only metal H^+ can oxidize is Fe.
Thus, the items made of Au and Ag are resistant to acid!

Realize that the value of E^o_{cell} only predicts if a reaction is spontaneous or not.
Spontaneity is governed by equilibrium constants.
It says nothing about the rate of the chemical reaction
(or how many e-s can be delivered per second… related to current; units = amperes, A

Example: Q6 from the tutorial manual on electrochemistry
A silverplating process requires the deposition of 10g of the metal.
If a current of 0.5 A is passed through a solution of $Ag^+(aq)$, how long will this take?

Current, I = charge (Q in Coulombs)/time (in seconds)

10 g Ag is 10 g/107.9 g mol^{-1} = 0.0926 mol.

Since the reduction reaction is $Ag^+(aq) + e^- \rightarrow Ag(s)$, need 0.0926 mol of e^-

1 mole of electrons = 96,490 C.
Therefore, 0.0926 mol = 0.0926 x 96490 = 8942.5 C.

$\therefore$ 0.5 A = 8942.5 C/t

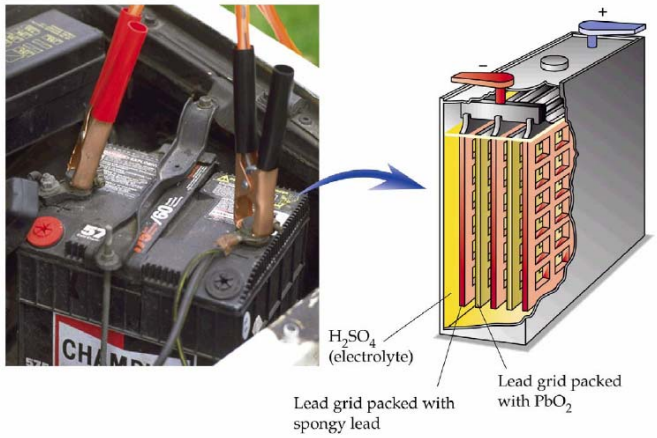
t = 17885 s = 298.1 min = 4.96 hr.

3. Reversibility: Electrolytic Cells

In voltaic cells chemical energy was converted into electricity spontaneously;
for example, using a battery

However, often we want to do the reverse:
use electrical energy to force a non-spontaneous reaction;
for example, recharge a battery.
In this context where electrical energy is applied, we have an **electrolytic cell**.

Consider the lead-acid battery which can be used in both voltaic- and electrolytic modes (discharge and recharge)



There are separate Pb and PbO_2 plates

As a voltaic cell the following reactions are taking place:

Anode: E^o_{ox} = +0.36 V $Pb(s) + SO_4^{2-} \rightarrow PbSO_4(s) + 2e^-$

Cathode: E^o_{red} = +1.69 V $PbO_2(s) + H^+ + 2e^- \rightarrow PbSO_4(s) + 2H_2O$

Cell notation: $Pb|\ PbSO_4\ ||\ PbO_2\ |\ PbSO_4$

E^o_{cell} = ~ +2V and six of these are connected in series to provide a car battery of +12 V

Interesting notes:

➢As a car battery discharges, the level of H_2SO_4 decreases, as does the density of the electrolyte.
Some batteries have a green “eye” that lets you estimate this condition…
when the electrolyte is dense the eye floats up and appears green.

➢$PbSO_4(s)$ coats the cathode as the battery discharges.
Thus the more discharged the battery is, the thicker the coating, and the less contact with the electrolyte.
If you have a dead battery and wait a few minutes, you can crank your engine again
…the electrolyte needs time to diffuse through the coating