## Announcements

- Marks on now on WebCT



Again, the cell potential does not tell you the rate of the chemical reaction. Battery makers for automobiles aim for the largest number of Cold Cranking Amps, a measure of how many Coulombs per second can be produced

➢To recharge the battery, the products of the discharge needs to be converted back to starting materials (electrolytic cell)

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

Anode $E^o_{ox}$ = -1.69 V $PbSO_4(s) + 2H_2O \rightarrow PbO_2(s) + 4H^+ 2e^- + SO_4^{2-}$

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

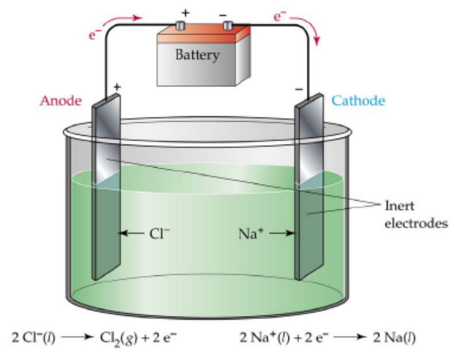
➢Note that in recharge mode (electrolytic cell) the anode and cathode have switched places!
Nonetheless, the anode is always the electrode where oxidation occurs

➢$E^o_{cell}$ -2V, which indicates the reaction is not spontaneous (expected).
Therefore to recharge we must apply an external voltage of at least 2 V to force this undesirable reaction to occur.
When a redox reaction is driven by electricity, it is called **electrolysis**

➢Recharging batteries is just one example of electrolysis but the principle is the same

**Example:**
Industrial electrolysis of molten (not aqueous) NaCl to generate Na(s) + $Cl_2$(g)

A battery or power source drives the reaction. A small amount of $CaCl_2$ is also added to lower the melting point




Anode: $2Cl^-(\ell) \rightarrow Cl_2(g) + 2e^-$

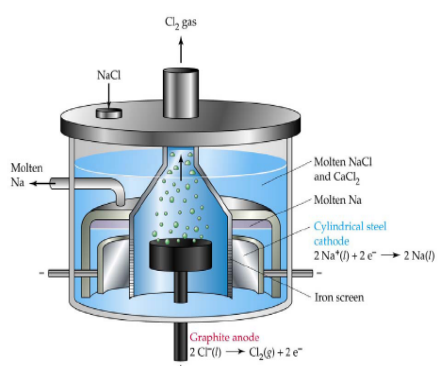
Cathode: $2Na^+(\ell) + 2e^- \rightarrow 2Na(\ell)$



**Challenge for you:**
Calculate the minimum external voltage needed for this electrolysis

**Industrial problem:**
How do you keep $Cl_2$(g) from reacting with the Na(s) product?

The solution is a cell design that incorporates an inverted funnel to isolate the chlorine gas product (≡ Downs electrolysis cell)



**Another question:**
Why use molten NaCl? Why not simply use NaCl dissolved in water?

Electrolysis of NaCl in water results in the same oxidation of $Cl^-$ to $Cl_2$, but $H_2O$ is reduced much more readily than $Na^+$

Anode: $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$

Possible cathode reactions:

$2Na^+(aq) + 2e^- \rightarrow 2Na(s)$ $\quad E^o_{red} = -2.71$ V

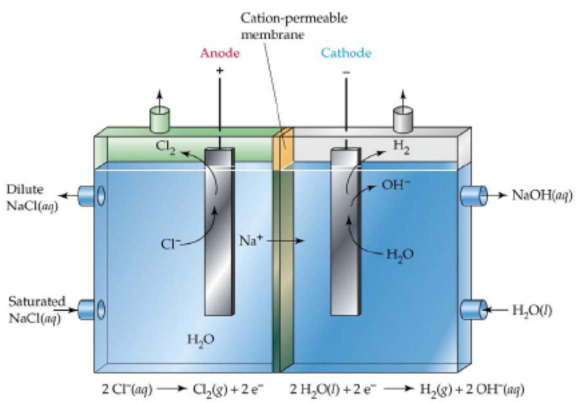
$2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-$ $\quad E^o_{red} = -0.83$ V

$\therefore$ reduction of water is much more favourable

$\therefore$ No Na(s) is formed but that is not so bad because $Cl_2$, $H_2$, and NaOH are industrially important. Therefore, the electrolysis of salt water is important



Electrolysis cell for this purpose:



# 4. Quantitative Analysis

In redox reactions, electrons are formed or consumed in stoichiometric ratios. The amount of electrons can be measured by moles or by charge (Coulombs)

1 mole $e^-$ = 96480 Coulombs (≡ Faraday's constant)

However, physicists, electricians, and engineers usually measure electric current instead of electrons

1 ampere (A) = 1 Coulomb per second

Thus, it is possible to express A in terms of electrons:

1 mole $e^-$ = 96480 V

$1.036 \times 10^{-5}$ mol $e^-$ = 1 C

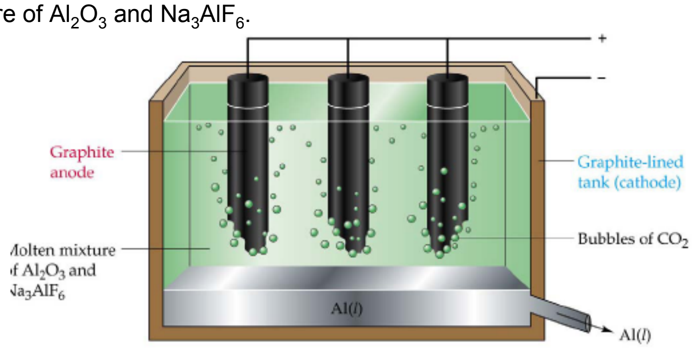
$6.240 \times 10^{18}$ $e^-$ = 1 C (using Avogadro number)
that is; 1 A = $6.240 \times 10^{18}$ $e^-$ per second



**Take home exercise:**
Calculate how many electrons go through your toaster if it draws 10 A of electricity for 4 minutes.

Since redox reactions are stoichiometric it should be possible to calculate how much electric current and what length of time is necessary for a particular reaction

**Example:**
Aluminium smelters in Canada electrolytically produce Al metal using a molten mixture of $Al_2O_3$ and $Na_3AlF_6$.



Cathode: $Al^{3+} + 3e^- \rightarrow Al(\ell)$

Anode: $C(s) + 2O^{2-} \rightarrow CO_2(g) + 4e^-$

The production of 1 mole Al requires 3 mole $e^-$,
so it is possible to calculate the Coulombs needed and $CO_2$ emissions (knowing the voltage):

Current: 1 A = 1 C $s^{-1}$ Voltage: 1 V = 1 J $C^{-1}$

Power: 1 W (Watt) = 1 J $s^{-1}$ Energy: 1 J = power x time = V x C

Process is energy intensive and environmentally unfriendly.



**Example based on #20 of the November 2006 exam.**
In the silver button cell which generates 1.50 V,
the overall cell reaction is $Zn(s) + Ag_2O(s) + H_2O(\ell) \rightarrow Zn(OH)_2\ (s) + 2Ag(s)$

Suppose that a small cell of this type contains 0.200 g $Ag_2O$ which is the (expensive) limiting reagent. Assuming the cell provides a current of $1.00 \times 10^{-6}$ A, how many hours could the cell operate?

The number of moles of $Ag_2O$ = 0.2/MM = 231.8 $gmol^{-1}$
=0.00086 mol.

Balanced reduction half reaction: $Ag_2O + 2H^+ + 2e^- \rightarrow 2Ag + H_2O$

∴ reducing one $Ag_2O$ requires 2 $e^-$s, the reaction requires 2 x 0.00086 mol =0.00172 mol $e^-$

∴ The number moles of electrons consumed = 0.00172 mol x 96490 C $mol^{-1}$ = 165.96 C

∴ $t = 165.96C/10^{-6}$ A = $1.66 \times 10^{8}$ s = $4.61 \times 10^{4}$ hr = answer E.

# Thermochemistry

C020



## ENERGY

When molecules react, there are energy changes, and energy can be released or consumed

Energy can appear and be measured as either:
**Work**: the ability to move a mass through a distance
or
**Heat**: increased molecular velocities, usually measured as temperature

The SI unit of energy is the joule, J

Note: 4.184 J = 1 calorie
Not to be confused with 1 Calorie = 1000 calories

**Specific Heat**

defined as the amount of heat required "to raise 1 gram of a substance 1 degree K; units: $Jg^{-1}K^{-1}$

Examples

| | |
|---|---|
| Water | Specific Heat = 4.184 $Jg^{-1}K^{-1}$ |
| Fe | Specific Heat = 0.451 $Jg^{-1}K^{-1}$ |
| Glass | Specific Heat = 0.84 $Jg^{-1}K^{-1}$ |

$\therefore$ By knowing the specific heat of a substance one can calculate the amount of heat required to raise a substance from one temperature to a higher one

Related to specific heats is a substance's heat capacity, C where the amount of material;
that is the mass is not factored in. Units = $JK^{-1}$

$\therefore$ The heat capacity is the amount of energy required to raise the system by 1 K.

For example, $C(H_2O) = 4.184\ JK^{-1}$

Heat capacity C = mass x specific heat



## Heat changes due to Phase Changes

Heat energy may be used not only to change the temperature of a system but also to cause phase changes at constant temperature

These are called **latent heats**