Electrochemistry

Chapter 19

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Electrochemical processes are oxidation-reduction reactions in which:

- the energy released by a spontaneous reaction is converted to electricity or
- electrical energy is used to cause a nonspontaneous reaction to occur

$$\overset{0}{2Mg}\,(s) + \overset{0}{O_2}\,(g) \longrightarrow 2\overset{2+}{Mg}\overset{2-}{O}\,(s)$$

$2Mg \longrightarrow 2Mg^{2+} + 4e^-$ ***Oxidation*** half-reaction (lose e^-)

$O_2 + 4e^- \longrightarrow 2O^{2-}$ ***Reduction*** half-reaction (gain e^-)

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Oxidation number

The charge the atom would have in a molecule (or an ionic compound) if electrons were completely transferred.

1. Free elements (uncombined state) have an oxidation number of zero.

   Na, Be, K, Pb, H_2, O_2, P_4 = 0

2. In monatomic ions, the oxidation number is equal to the charge on the ion.

   Li^+, Li = +1; Fe^{3+}, Fe = +3; O^{2-}, O = -2

3. The oxidation number of oxygen *is* **usually** –2. In H_2O_2 and O_2^{2-} it is –1.

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4. The oxidation number of hydrogen is +1 *except* when it is bonded to metals in binary compounds. In these cases, its oxidation number is –1.

5. Group IA metals are +1, IIA metals are +2 and fluorine is always –1.

6. The sum of the oxidation numbers of all the atoms in a molecule or ion is equal to the charge on the molecule or ion.

Identify the oxidation numbers of all the atoms in HCO_3^- ?

HCO_3^-

O = –2 H = +1

3x(–2) + 1 + ? = –1

C = +4

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Balancing Redox Equations

The oxidation of Fe^{2+} to Fe^{3+} by $Cr_2O_7^{2-}$ in acid solution?

1. Write the unbalanced equation for the reaction ion ionic form.

   $$Fe^{2+} + Cr_2O_7^{2-} \longrightarrow Fe^{3+} + Cr^{3+}$$

2. Separate the equation into two half-reactions.

   Oxidation: $\overset{+2}{Fe^{2+}} \longrightarrow \overset{+3}{Fe^{3+}}$

   Reduction: $\overset{+6}{Cr_2}O_7^{2-} \longrightarrow \overset{+3}{Cr^{3+}}$

3. Balance the atoms other than O and H in each half-reaction.

   $$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+}$$

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Balancing Redox Equations

4. For reactions in acid, add H_2O to balance O atoms and H^+ to balance H atoms.

   $$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$$
   $$14H^+ + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$$

5. Add electrons to one side of each half-reaction to balance the charges on the half-reaction.

   $$Fe^{2+} \longrightarrow Fe^{3+} + 1e^-$$
   $$6e^- + 14H^+ + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$$

6. If necessary, equalize the number of electrons in the two half-reactions by multiplying the half-reactions by appropriate coefficients.

   $$6Fe^{2+} \longrightarrow 6Fe^{3+} + 6e^-$$
   $$6e^- + 14H^+ + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$$

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Balancing Redox Equations

7. Add the two half-reactions together and balance the final equation by inspection. **The number of electrons on both sides must cancel.**

Oxidation: $6Fe^{2+} \longrightarrow 6Fe^{3+} + \cancel{6e^-}$

Reduction: $\cancel{6e^-} + 14H^+ + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$

$14H^+ + Cr_2O_7^{2-} + 6Fe^{2+} \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$

8. Verify that the number of atoms and the charges are balanced.

$14x1 – 2 + 6 \times 2 = 24 = 6 \times 3 + 2 \times 3$

9. For reactions in basic solutions, add OH^- to **both sides** of the equation for every H^+ that appears in the final equation.

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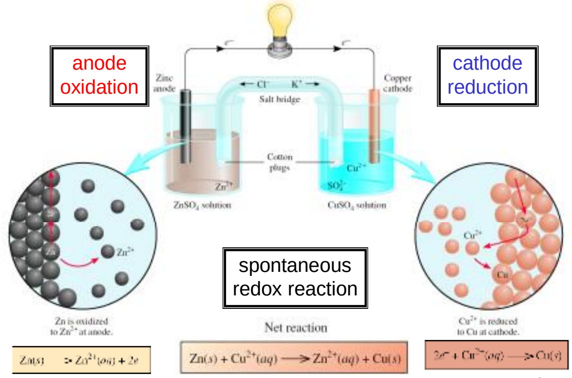
Galvanic Cells



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Galvanic Cells

The difference in electrical potential between the anode and cathode is called:

- ***cell voltage***
- ***electromotive force (emf)***
- ***cell potential***

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

$[Cu^{2+}] = 1\ M$ and $[Zn^{2+}] = 1\ M$

Cell Diagram

phase boundary

$Zn\ (s)\ |\ Zn^{2+}\ (1\ M)\ ||\ Cu^{2+}\ (1\ M)\ |\ Cu\ (s)$

anode salt bridge cathode

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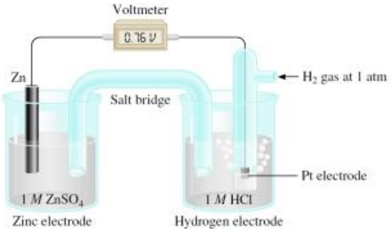
Standard Reduction Potentials



$Zn\ (s)\ |\ Zn^{2+}\ (1\ M)\ ||\ H^+\ (1\ M)\ |\ H_2\ (1\ atm)\ |\ Pt\ (s)$

Anode (oxidation): $Zn\ (s) \longrightarrow Zn^{2+}\ (1\ M) + 2e^-$

Cathode (reduction): $2e^- + 2H^+\ (1\ M) \longrightarrow H_2\ (1\ atm)$

$Zn\ (s) + 2H^+\ (1\ M) \longrightarrow Zn^{2+} + H_2\ (1\ atm)$

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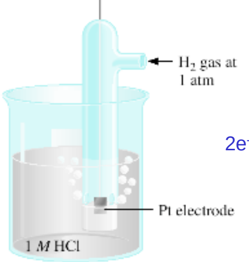
Standard Reduction Potentials

Standard reduction potential (E^0) is the voltage associated with a **reduction reaction** at an electrode when all solutes are 1 *M* and all gases are at 1 atm.



Reduction Reaction

$2e^- + 2H^+\ (1\ M) \longrightarrow H_2\ (1\ atm)$

$E^0 = 0$ V

Standard hydrogen electrode (SHE)

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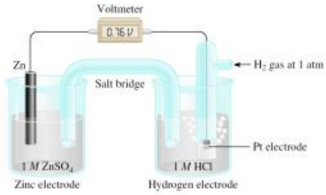
Standard Reduction Potentials

$E^0_{cell} = 0.76$ V



Standard emf (E^0_{cell})

$E^0_{cell} = E^0_{cathode} - E^0_{anode}$

$Zn\ (s)\ |\ Zn^{2+}\ (1\ M)\ ||\ H^+\ (1\ M)\ |\ H_2\ (1\ atm)\ |\ Pt\ (s)$

$E^0_{cell} = E^0_{H^+/H_2} - E^0_{Zn^{2+}/Zn}$

$0.76\ V = 0 - E^0_{Zn^{2+}/Zn}$

$E^0_{Zn^{2+}/Zn} = -0.76$ V

$Zn^{2+}\ (1\ M) + 2e^- \longrightarrow Zn \quad E^0 = -0.76$ V

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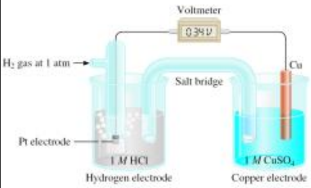
Standard Reduction Potentials

$E^0_{cell} = 0.34$ V



$E^0_{cell} = E^0_{cathode} - E^0_{anode}$

$E^0_{cell} = E^0_{Cu^{2+}/Cu} - E^0_{H^+/H_2}$

$0.34 = E^0_{Cu^{2+}/Cu} - 0$

$E^0_{Cu^{2+}/Cu} = 0.34$ V

Pt (*s*) | H_2 (1 *atm*) | H^+ (1 *M*) || Cu^{2+} (1 *M*) | Cu (*s*)

Anode (oxidation): H_2 (1 *atm*) ⟶ $2H^+$ (1 *M*) + $2e^-$

Cathode (reduction): $2e^-$ + Cu^{2+} (1 *M*) ⟶ Cu (s)

H_2 (1 *atm*) + Cu^{2+} (1 *M*) ⟶ Cu (*s*) + $2H^+$ (1 *M*)

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- E^0 is for the reaction as written
- The more positive E^0 the greater the tendency for the substance to be reduced
- The half-cell reactions are reversible
- The sign of E^0 changes when the reaction is reversed
- Changing the stoichiometric coefficients of a half-cell reaction ***does not*** change the value of E^0

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What is the standard emf of an electrochemical cell made of a Cd electrode in a 1.0 *M* $Cd(NO_3)_2$ solution and a Cr electrode in a 1.0 *M* $Cr(NO_3)_3$ solution?

Cd^{2+} (*aq*) + $2e^-$ ⟶ Cd (*s*) $E^0 = -0.40$ V   Cd is the stronger oxidizer

Cr^{3+} (*aq*) + $3e^-$ ⟶ Cr (*s*) $E^0 = -0.74$ V   Cd will oxidize Cr

Anode (oxidation): Cr (s) ⟶ Cr^{3+} (1 *M*) + $3e^-$ x 2

Cathode (reduction): $2e^-$ + Cd^{2+} (1 *M*) ⟶ Cd (s) x 3

2Cr (*s*) + $3Cd^{2+}$ (1 *M*) ⟶ 3Cd (*s*) + $2Cr^{3+}$ (1 *M*)

$E^0_{cell} = E^0_{cathode} - E^0_{anode}$

$E^0_{cell} = -0.40 - (-0.74)$

$E^0_{cell} = 0.34$ V

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Spontaneity of Redox Reactions

$\Delta G = -nFE_{cell}$ *n* = number of moles of electrons in reaction

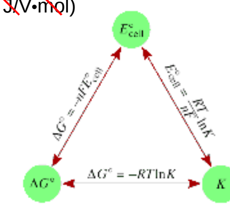
$\Delta G^0 = -nFE^0_{cell}$ $F = 96{,}500 \frac{J}{V \cdot mol} = 96{,}500$ C/mol

$\Delta G^0 = -RT \ln K = -nFE^0_{cell}$

$$E^0_{cell} = \frac{RT}{nF} \ln K = \frac{(8.314\ J/K \cdot mol)(298\ K)}{n\ (96{,}500\ J/V \cdot mol)} \ln K$$

$$E^0_{cell} = \frac{0.0257\ V}{n} \ln K$$

$$E^0_{cell} = \frac{0.0592\ V}{n} \log K$$



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Spontaneity of Redox Reactions

TABLE 19.2 Relationships Among ΔG°, *K*, and E°_{cell}

ΔG°	*K*	E°_{cell}	Reaction Under Standard-State Conditions
Negative	>1	Positive	Favors formation of products.
0	=1	0	Reactants and products are equally favored.
Positive	<1	Negative	Favors formation of reactants.

$\Delta G^0 = -RT \ln K = -nFE^0_{cell}$

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What is the equilibrium constant for the following reaction at 25⁰C? Fe^{2+} (*aq*) + 2Ag (*s*) ⇌ Fe (*s*) + $2Ag^+$ (*aq*)

$$E^0_{cell} = \frac{0.0257\ V}{n} \ln K$$

Oxidation: 2Ag ⟶ $2Ag^+$ + $2e^-$

Reduction: $2e^-$ + Fe^{2+} ⟶ Fe

n = 2

$E^0 = E^0_{Fe^{2+}/Fe} - E^0_{Ag^+/Ag}$

$E^0 = -0.44 - (0.80)$

$E^0 = -1.24$ V

$$K = e^{\left[\frac{E^0_{cell} \times n}{0.0257\ V}\right]} = e^{\left[\frac{-1.24\ V \times 2}{0.0257\ V}\right]}$$

$K = 1.23 \times 10^{-42}$

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The Effect of Concentration on Cell Emf

$\Delta G = \Delta G^0 + RT \ln Q$ $\quad \Delta G = -nFE \quad$ $\Delta G^0 = -nFE^0$

$-nFE = -nFE^0 + RT \ln Q$

Nernst equation

$$E = E^0 - \frac{RT}{nF} \ln Q$$

At 298 K

$$E = E^0 - \frac{0.0257\ \text{V}}{n} \ln Q \qquad E = E^0 - \frac{0.0592\ \text{V}}{n} \log Q$$

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Will the following reaction occur spontaneously at 25^0C if $[Fe^{2+}] = 0.60\ M$ and $[Cd^{2+}] = 0.010\ M$?

$$Fe^{2+}\ (aq) + Cd\ (s) \rightleftharpoons Fe\ (s) + Cd^{2+}\ (aq)$$

Oxidation: $Cd \longrightarrow Cd^{2+} + 2e^-$

Reduction: $2e^- + Fe^{2+} \longrightarrow 2Fe$

$n = 2$

$E^0 = E^0_{Fe^{2+}/Fe} - E^0_{Cd^{2+}/Cd}$

$E^0 = -0.44 - (-0.40)$

$E^0 = -0.04$ V

$$E = E^0 - \frac{0.0257\ \text{V}}{n} \ln Q$$

$$E = -0.04\ \text{V} - \frac{0.0257\ \text{V}}{2} \ln \frac{0.010}{0.60}$$

$E = 0.013$

$E > 0$ Spontaneous

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Concentration Cells

Galvanic cell from two half-cells composed of the *same* material but differing in ion concentrations.

$$Zn(s)\,|\,Zn^{2+}(0.10\ M)\,||\,Zn^{2+}(1.0\ M)\,|\,Zn(s)$$

Oxidation: $Zn(s) \longrightarrow Zn^{2+}(0.10\ M) + 2e^-$

Reduction: $Zn^{2+}(1.0\ M) + 2e^- \longrightarrow Zn(s)$

Overall: $Zn^{2+}(1.0\ M) \longrightarrow Zn^{2+}(0.10\ M)$

$$E = E^\circ - \frac{0.0257\ \text{V}}{2} \ln \frac{[Zn^{2+}]_{dil}}{[Zn^{2+}]_{conc}}$$

$$E = 0 - \frac{0.0257\ \text{V}}{2} \ln \frac{0.10}{1.0} = 0.0296\ \text{V}$$

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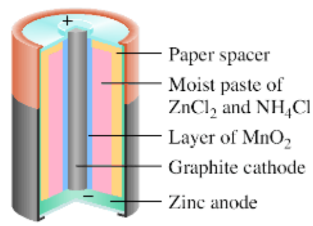
Batteries

Dry cell

Leclanché cell



Anode: $Zn\ (s) \longrightarrow Zn^{2+}\ (aq) + 2e^-$

Cathode: $2NH_4^+\ (aq) + 2MnO_2\ (s) + 2e^- \longrightarrow Mn_2O_3\ (s) + 2NH_3\ (aq) + H_2O\ (l)$

$Zn\ (s) + 2NH_4\ (aq) + 2MnO_2\ (s) \longrightarrow Zn^{2+}\ (aq) + 2NH_3\ (aq) + H_2O\ (l) + Mn_2O_3\ (s)$

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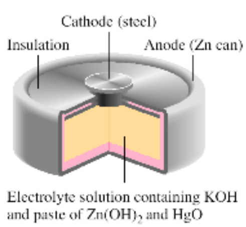
Batteries

Mercury Battery



Anode: $Zn(Hg) + 2OH^-\ (aq) \longrightarrow ZnO\ (s) + H_2O\ (l) + 2e^-$

Cathode: $HgO\ (s) + H_2O\ (l) + 2e^- \longrightarrow Hg\ (l) + 2OH^-\ (aq)$

$Zn(Hg) + HgO\ (s) \longrightarrow ZnO\ (s) + Hg\ (l)$

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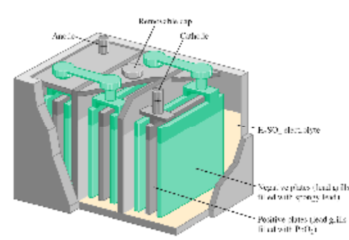
Batteries

Lead storage battery



Anode: $Pb\ (s) + SO_4^{2-}\ (aq) \longrightarrow PbSO_4\ (s) + 2e^-$

Cathode: $PbO_2\ (s) + 4H^+\ (aq) + SO_4^{2-}\ (aq) + 2e^- \longrightarrow PbSO_4\ (s) + 2H_2O\ (l)$

$Pb\ (s) + PbO_2\ (s) + 4H^+\ (aq) + 2SO_4^{2-}\ (aq) \longrightarrow 2PbSO_4\ (s) + 2H_2O\ (l)$

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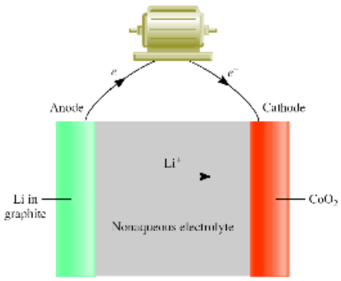
Batteries



$Li \longrightarrow Li^+ + e^-$ $\quad Li^+ + CoO_2 + e^- \longrightarrow LiCoO_2$

Solid State Lithium Battery

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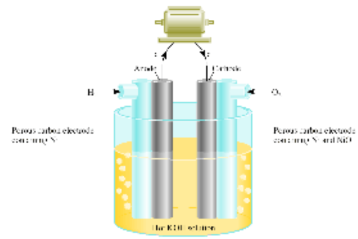
Batteries



A ***fuel cell*** is an electrochemical cell that requires a continuous supply of reactants to keep functioning

Anode: $2H_2\,(g) + 4OH^-\,(aq) \longrightarrow 4H_2O\,(l) + 4e^-$

Cathode: $O_2\,(g) + 2H_2O\,(l) + 4e^- \longrightarrow 4OH^-\,(aq)$

$2H_2\,(g) + O_2\,(g) \longrightarrow 2H_2O\,(l)$

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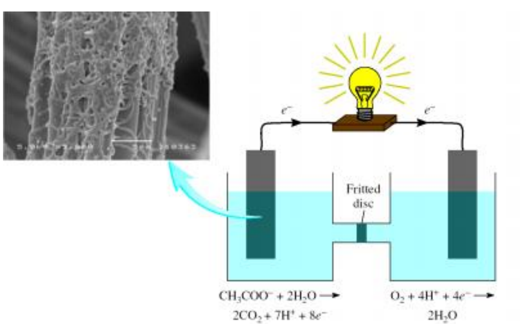
Chemistry In Action: Bacteria Power

$CH_3COO^- + 2O_2 + H^+ \longrightarrow 2CO_2 + 2H_2O$



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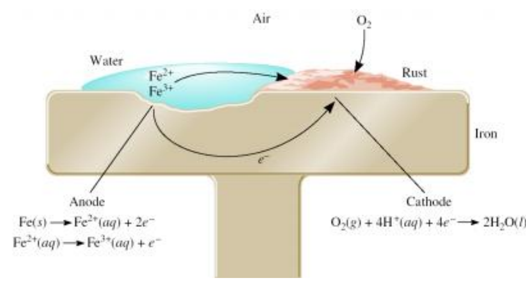
Corrosion

Corrosion is the term usually applied to *the deterioration of metals by an electrochemical process*.



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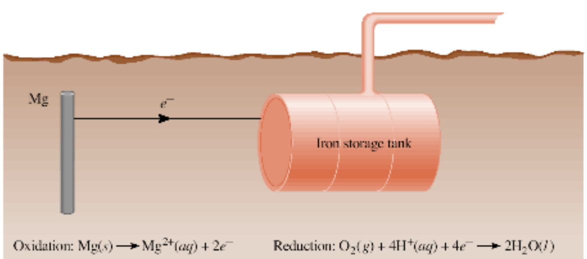
Cathodic Protection of an Iron Storage Tank



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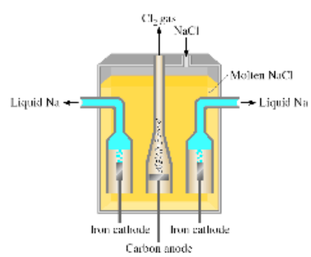
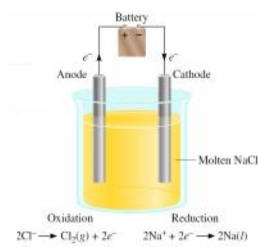
Electrolysis is the process in which electrical energy is used to cause a **nonspontaneous** chemical reaction to occur.

Electrolysis of molten NaCl





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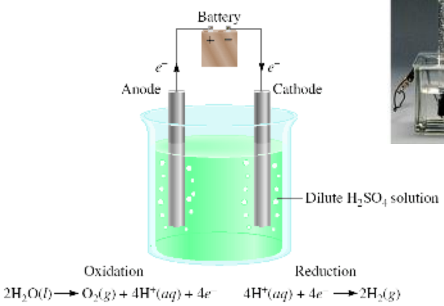
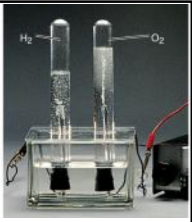
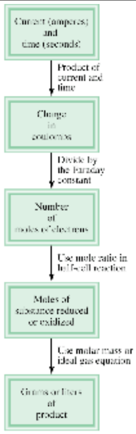
Electrolysis of Water







Electrolysis and Mass Changes

charge (C) = current (A) x time (s)

1 mol e^- = 96,500 C

How much Ca will be produced in an electrolytic cell of molten $CaCl_2$ if a current of 0.452 A is passed through the cell for 1.5 hours?

Anode: $2Cl^-(l) \longrightarrow Cl_2(g) + 2e^-$

Cathode: $Ca^{2+}(l) + 2e^- \longrightarrow Ca(s)$

$$Ca^{2+}(l) + 2Cl^-(l) \longrightarrow Ca(s) + Cl_2(g)$$

2 mole e^- = 1 mole Ca

$$\text{mol Ca} = 0.452\ \frac{\text{C}}{\text{s}} \times 1.5\ \text{hr} \times 3600\ \frac{\text{s}}{\text{hr}} \times \frac{1\ \text{mol}\ e^-}{96{,}500\ \text{C}} \times \frac{1\ \text{mol Ca}}{2\ \text{mol}\ e^-}$$

= 0.0126 mol Ca

= 0.50 g Ca

Chemistry In Action: Dental Filling Discomfort

Hg_2^{2+}/Ag_2Hg_3 0.85 V

Sn^{2+}/Ag_3Sn -0.05 V

Sn^{2+}/Ag_3Sn -0.05 V