Electrochemistry

Ease of reactions

$H_2 \rightarrow 2H^+ + 2e$ (oxidation)

$2e + 2H^+ \rightarrow H_2$ (reduction)

$Mg \rightarrow Mg^{2+} + 2e$ (This reaction is easier to accomplish than the reaction below.)

$H_2 \rightarrow 2H^+ + 2e$ (This reaction loses electrons easier than the reaction below.)

$Ag \rightarrow Ag^+ + e$

$Zn^{2+} + 2e \rightarrow Zn$ -.76 volts Both written as reduction reaction, so rewrite one

$Cu^{2+} + 2e \rightarrow Cu$ .34 volts

$Cu \rightarrow Cu^{2+} + 2e$ -.34 v Reversing this electrode defeats the purpose because

adding algebraically gives a neg. emf, so we reverse the

Zn electrode.

$$
\begin{array}{ll}
Zn \rightarrow Zn^{2+} + 2e & .76v \\
Cu^{2+} \rightarrow Cu + 2e & .34v \\
\hline
Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu & 1.1v
\end{array}
$$

Same as single displacement reaction.

$Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$

ionic: $Zn + Cu^{2+} + SO_4^{2-} \rightarrow Zn^{2+} + SO_4^{2-} + Cu$

net ionic: $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

Conventional Cell Reaction

Write anode first, then cathode:

anode || cathode

For anode write electrode first, then electrolyte. For cathode write electrolyte first, then electrode.

$Zn; Zn^{2+} || Cu^{2+}; Cu$

$Cu^{2+} + 2e \rightarrow Cu$ .34 v Cannot add because both are written as reduction.

$Cl_2 + 2e \rightarrow 2Cl^-$ 1.36 v Need to reverse the Cu electrode.

$Cu \rightarrow Cu^{2+} + 2e$	-.34v
$Cl_2 + 2e \rightarrow 2Cl^-$	1.36 v
$Cu + Cl_2 \rightarrow 2Cl^- + Cu^{2+}$	1.02 v

anode || cathode

$Cu; Cu^{2+} || Cl^-; Cl_2; Pt$ (Note if cathode was anode write: $Pt; Cl_2; Cl^-$. Notice the use of Pt with gaseous electrodes.)

Given the following reaction, is this a spontaneous reaction?

$Au + Zn^{2+} \rightarrow Au^{3+} + Zn$

The emf values for these half cell reactions are taking place:

$$
\begin{array}{ll}
Zn^{2+} + 2e \rightarrow Zn & -.76 \\
Au \rightarrow Au^{3+} + 3e & -1.50 \\
\hline
Au + Zn^{2+} \rightarrow Au + Zn & -2.26
\end{array}
$$

Gives a neg. emf so cell is not spontaneous.

It will be a spontaneous cell if Zn is the anode and Au is the cathode.

1 F = 96,500 coul = 6.02 x 10^{23} e's   coul = (amps)(sec)

1 F = 1 g H   Eq. wt of hydrogen

1 F = 35.5 g Cl   Eq. wt of chlorine

1 F = 8 g ox.   Eq. wt of oxygen

1 F $\rightarrow$ 11.2 L of H_2 at STP

11.2 L of Cl_2 at STP

5.6 L of ox. at STP

1 mol of ox. = 32 g ox. = 22.4 L of ox. at STP

1 F = 8 g ox. = 5.6 L of ox. at STP

Calculate the weight of gold ion Au^{3+} deposited by a 2 amp current that passes through the Au^{3+} cell for 1 hr 20 min 4 sec (4804 sec).

96,500 coul = Eq. wt of anything

coul = amp x sec 96,500 coul = 65.7 g Au

coul = 2 x 4804 2 x 4804 coul = x

$$\frac{(2 \times 4804)\ \text{coul} \times 65.7\ \text{g Au}}{96{,}500\ \text{coul}} = 6.54\ \text{g Au}$$

Calculate the weight of gold and weight of silver deposited by a 2 amp current that passes through the cell for 1 hr 20 min 4 sec.

2 amp	1 hr 20 min 4 sec	Au^{3+}	6 54 g Au
	2 x 4804	Ag^{+}	10.75

$$\left.\begin{array}{l} 96{,}500 \text{ coul} = \frac{197}{3} \text{ g Au} \\ 2 \times 4804 \text{ coul} = x \end{array}\right\} \qquad \frac{2 \times 4804 \times 197}{96{,}500 \times 3} = 6.5 \text{ g Au}$$

The different masses of elements deposited at the cathode is in ratio of their equivalent weights.

Eq. wt of Au

$$\left.\begin{array}{l} 65.7 \text{ g} \approx 6.54 \text{ g Au deposited} \\ 108 \text{ eq. wt of Ag} \approx x \end{array}\right\} \qquad \frac{108 \times 6.54}{65.7} = 10.75 \text{ g Au deposited}$$

$$\left.\begin{array}{l} 65.7 \text{ g} \approx 6.54 \text{ g Au} \\ 1 \approx x \end{array}\right\} \qquad \frac{1 \times 6.54}{65.7} = .09 \text{ g H}$$

$$\begin{array}{l} 2 \text{ g } H_2 = 22.4 \text{ L} \\ .09 = x \end{array} \qquad \frac{.09 \times 22.4}{2}$$

A 2.5 amp current that passed through an unknown element for 30 min deposited .65 g of the element. Calculate the eq. wt of the unknown element.

$$\left.\begin{array}{r} 2.5 \times 30 \times 60 \text{ coul} = .65 \text{ g} \\ 96{,}500 \text{ coul} = x \end{array}\right. \qquad \frac{96{,}500 \times .65}{2.5 \times 30 \times 60} = 14.5 \text{ eq. wt}$$

Calculate the time it takes to deposit 3 g Ag by a 5 amp current that passes through a Ag ion solution.

$$\left.\begin{array}{r} 96{,}500 \text{ coul} = 108 \text{ g Ag} \\ x = 3 \text{g Ag} \end{array}\right. \qquad \frac{96{,}500 \text{ coul} \times 3 \text{g Ag}}{108 \text{g Ag}} = 2680.6 \text{ coul}$$

coul = amp x sec

2680.6 = (5)(sec)

$$\frac{2680.6}{5} = \text{sec}$$

Nernst Equation

$$E = E^0 - \frac{.06}{n} \log Q$$

Calculate the emf of a cell if the concentration of the Zn^{2+} is .003 M and Cu^{2+} is .1M.

$$\begin{array}{lll} Cu^{2+} + 2e \rightarrow Cu & & .34 \\ Zn \rightarrow Zn^{2+} + 2e & & .76 \\ \hline Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu & E^0 & 1.1v \end{array}$$

$$\begin{aligned} E &= 1.1 - \frac{.06}{2} \log \left[\frac{5 \times 10^{-3}}{.1} \right] \\ &= 1.1 + .04 \\ &= 1.14 \end{aligned}$$

$\Delta G = -nEF$

Balancing Reactions

$MnO_4^- + Cl^- \rightarrow Mn^{2+} + Cl_2$

1 2

$[(2)Cl^- \rightarrow Cl_2 \ (+ \ 2e)] \ 5$

5 4 3

$[(5e +) \ (8H^+ +) \ MnO_4^- \rightarrow Mn^{2+} \ (+ \ 4H_2O)] \ 2$

$10e + 16H^+ + 2MnO_4^- + 10Cl^- \rightarrow 2Mn^{2+} + 8H_2O + 5Cl_2 + 10e$

$NO_3^- + S^{2-} \rightarrow S + NO$

1

$[S^{2-} \rightarrow S\ (+\ 2e)]\ 3$

4 3 2

$[(3e\ +)\ (4H^+\ +)\ NO_3^- \rightarrow NO\ (+\ 2H_2O)]\ 2$

$8H^+ + 2NO_3^- + 3S^{2-} \rightarrow 2NO + 4H_2O + 3S$

$NO_2 \rightarrow NO_2^- + NO_3^-$ (Basic)

1

$(e\ +)\ NO_2 \rightarrow NO_2^-$ $2H_2O$

4 2 3 4 5

$(2OH^-\ +)\ (H_2O\ +)\ NO_2 \rightarrow NO_3^-\ (+\ 2H^+)\ (+\ 2OH^-)\ (+\ e)$

$2NO_2 + 2OH^- + H_2O \rightarrow NO_2^- + NO_3^- + 2H_2O$

$2NO_2 + 2OH^- \rightarrow NO_2^- + NO_3^- + H_2O$

gain 1e (red.)

+5 +4

$C + \mathbf{4}HNO_3 \rightarrow \mathbf{4}NO_2 + \mathbf{2}H_2O + CO_2$

0 +4

loss of 4e (ox.)

gain 1e (red.)

+5 +4

$\mathbf{3}HClO_3 \rightarrow HClO_4 + \mathbf{2}ClO_2 + H_2O$

+5 +7

loss of 2e (ox.)

gain 1e (red.)

+5 +4

$Cu + \mathbf{4}HNO_3 \rightarrow Cu(NO_3)_2 + \mathbf{2}H_2O + \mathbf{2}NO_2$

loss of 2e (ox.) 0 +2

2 mols HNO_3 ox. ag.

2 mols HNO_3 supply NO_3^- to Cu^{2+}

$[Cu \rightarrow Cu^{2+} + 2e]$ 1

$[2H^+ + NO_3^- \rightarrow NO_2 + H_2O]$ 2

$Cu + 4H^+ + 2NO_3^- \rightarrow Cu^{2+} + 2NO_2 + 2H_2O$

loss of 5e (ox.) -3 +2 loss of 5e (ox.) -3

+2

If use this,

$\mathbf{4}NH_3 + \mathbf{5}O_2 \rightarrow \mathbf{4}NO + \mathbf{6}H_2O$ $NH_3 + O_2 \rightarrow NO + H_2O$ hard time

0 -2 0 -2

balancing

4 gain 2e