### Vocabulary

- Electrochemistry: the study of the interchange of chemical and electrical energy
  - Redox reaction: a transfer of electrons from the reducing agent to the oxidizing agent
- Oxidation: a loss of electrons (an increase in the oxidation number)
- Reduction: a gain of electrons (a decrease in the oxidation number)
- Half-reactions: a redox reaction broken in to two parts, one half with the oxidation and the other with the reduction
- Salt bridge: the connection between the two solutions
- Galvanic cell: device in which chemical energy is changed to electrical energy
- Anode: the electrode at which oxidation occurs (an-ox)
- Cathode: the electrode at which reduction occurs (red-cat)
- Cell potential, (E<sub>cell</sub>): potential difference between the oxidation and reduction
- Volt: the unit of electrical potential (J/C)
- Standard hydrogen electrode: a platinum electrodes in contact with 1M H<sup>+</sup> ions bathed by H<sub>2</sub> gas at 1 atm
- Standard reduction potentials, E°: likelihood for the reduction to occur with all solutes at 1M or 1 atm
- Concentration cell: cell with both electrodes having identical components but at different concentrations
- Nernst equation: converts cells that are at nonstandard conditions to standard conditions  $E = E^{\circ} - \frac{RT}{nF} \ln(Q)$
- Glass electrode: contains a reference solution of dilute hydrochloric acid in contact with a thin glass membrane
- Lead storage battery: lead serves as the anode and lead coated with lead dioxide serves as the cathode
- Electrolytic cell: an apparatus that uses electrical energy to produce chemical change for nonspontaneous cells
- Electrolysis: forcing a current through a cell to produce a chemical change ; used for nonpontaneous cells
- Ampere: measure of current in coulombs per second (C/s). Often used to help convert the number of electrons flowing (current) to the rate of reaction in time

### **Description of Cells**

### Galvanic Cells:



Note that a porous frit or disc may substitute for the salt bridge

#### **Electron Flow, Spontaneity and Electrolysis**

- 1<sup>st</sup> Electrons flow in the spontaneous direction.
- $2^{nd}$  For a spontaneous cell, electrons will flow from the anode to the cathode as illustrated.
- $3^{rd}$  For a nonspontaneous cell, a power source [with a voltage greater than the electrochemical potential,  $E_{cell}$ ]
- 4<sup>th</sup> Nonspontaneous cells are electrolytic cells, electrolysis reactions.
   The calculations typically involve reducing/oxidizing a mass, g, in a time, s or with a current, Amp (C/s). To do the calculations set up a series of conversions between the given and wanted using the three conversion

factors: 
$$\frac{g}{mol}$$
  $\frac{96485C}{mol e^-}$   $\frac{C}{s}$ 

See p 868 example problem 17.9.

### **Calculating Electrochemical Potential of a Cell**

- 1) Write two  $\frac{1}{2}$  reactions written as reductions
- 2) Compare E's-the reaction with the highest E is reduced, the other is oxidized
- 3) Flip the oxidized reaction, or change the sign of E
- 4) Balance/add the reaction
- 5)  $E_{rxn} = E_{reduced} + E_{oxidized}$ 
  - \* If E > 0, the reaction is spontaneous
  - \* If E < 0, the reaction is nonspontaneous

This is because	$\Delta G = -nFE_{rxn}$	where	n = the number of moles of electrons, F = Faraday's constant, 96485 C/mol, $E_{rxn}$ = electrochemical potential	
and for a reaction to be spontaneous: nonspontaneous		us	$\Delta G = < 0$ , so $\Delta G = > 0$ , so	E > 0 E < 0

Note : The preceding notes are for nonstandard conditions ( E and  $\Delta G$  ). For standard conditions ( E<sup>o</sup> and  $\Delta G^o$  ) the same concepts apply.

### The Nernst Equation:

The Nernst equation is used to relate a cell's electrochemical potential, E, that is not at standard conditions (1 atm. 25 °C, 1 M solutions) with an electrochemical potential that is at standard conditions,  $E^{\circ}$ .

$$E = E^{\circ} - \frac{RT}{nF} \ln(Q)$$

where E = cell potential under nonstandard conditions

 $E^{\circ}$  = cell potential under standard conditions

R = 8.314 VC/mol K

F = 96485 C/mol

T = temperature

N = number of moles of electrons

Q = the reaction quotient ( use initial concentrations and is Q = [prod] / [react] )

\*As the concentration of the products of a redox reaction increases, the potential voltage decreases; and as the concentration of the reactants in a redox reaction increases, the potential voltage increases.

$$E^{\circ} = \frac{RT}{nF} \ln K$$
, K is the equilibrium constant

\*If  $E^{o}$  is positive, then K is greater than 1 and the forward reaction is favored. If  $E^{o}$  is negative, then K is less than 1 and the reverse reaction is favored.

### **Example Problems**

1. Consider the galvanic cell based on the reaction  $Al^{3+} + Mg \rightarrow Al + Mg^{2+}$ 

The half reactions are

 $Al^{3+} + 3e^- \rightarrow Al$   $E^0 = -1.66V$  $Mg^{2+} + 2e^- \rightarrow Mg$   $E^0 = -2.37V$ 

Give the balanced cell reaction and calculate  $E^0$  for the cell.

(See work on page 845) **Solution:** 0.71 V

2. Using the data in Table 17.1, calculate the  $\Delta G$  for the reaction

$$Cu^{2+} + Fe \rightarrow Cu + Fe^{2+}$$

Is this reaction spontaneous?

(See work on page 850) **Solution:**  $\Delta G = -1.5 \times 10^5 J$ , spontaneous

.

3. Describe the cell based on the following half reactions

$$VO_{2}^{+} + 2H^{+} + e^{-} \rightarrow VO^{2+} + H_{2}O \qquad E^{0} = 1.00V$$

$$Zn^{2+} + 2e^{-} \rightarrow Zn \qquad E^{0} = -0.76V$$
where  $T = 25^{\circ}C$ 
 $[VO_{2}^{+}] = 2.0M$ 
 $[H^{+}] = 0.50M$ 
 $[VO^{2+}] = 1.0 \times 10^{-2}M$ 
 $[Zn^{2+}] = 1.0 \times 10^{-1}M$ 

(See work on page 855) **Solution:** 1.89V

work

3. Determine the cell potential for the rxn  $Al^{3+}(aq) + Mg(s) \rightarrow Al(s) + Mg^{2+}(aq)$ Half-Reactions:

$Al^{3+} + 3e^- \rightarrow Al$	$\varepsilon^{\circ} = -1.66 \text{ V}$
$Mg^{2+} + 2e^- \rightarrow Mg$	$\varepsilon^{\circ} = -2.37 \text{ V}$
$2 (Al^{3+} + 3e^{-} \rightarrow Al)$	$\varepsilon^{\circ} = -1.66 \text{ V}$
$3 (Mg \rightarrow Mg^{2+} + 2e^{-})$	$\varepsilon^{\circ} = 2.37 \text{ V}$
2+ / )	

 $2\overline{Al^{3+}(aq) + 3Mg(s)} \rightarrow 2Al(s) + 3Mg^{2+}(aq) \qquad \varepsilon^{\circ} = 0.71 \text{ V}$ 

4. Write the line notation for the cell, given:  $\begin{aligned} Ag^+ + e^- \to Ag \\ Fe^{3+} + e^- \to Fe^{2+} \end{aligned}$ 

*work* Line Notation:

$$Pt(s) | Fe^{2+}(aq), Fe^{3+}(aq) || Ag^{+}(aq) || Ag(s)$$

5. Determine the free energy of the cell that has the rxn:

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

 $Cu^{2+} + 2e^{-} \rightarrow Cu \qquad \qquad \varepsilon^{\circ} = 0.34 \text{ V}$  $Fe \rightarrow Fe^{2+} + 2e^{-} \qquad \qquad -\varepsilon^{\circ} = 0.44 \text{ V}$ 

$$Cu^{2+} + Fe \rightarrow Fe^{2+} + Cu$$
  $\varepsilon^{\circ} = 0.78 \text{ V}$ 

$$\Delta G^{\circ} = -nF\varepsilon^{\circ}$$
$$\Delta G^{\circ} = -(2mol)(96,485\frac{C}{mol})(0.78\frac{J}{C})$$
$$\Delta G^{\circ} = -1.5 \times 10^{5} \text{ J}$$

6. Determine the cell potential for the galvanic cell with the following half-reactions at 25 °C with the given concentrations:  $[Ag^+] = 1.0 \text{ M}$ ,  $[H_2O_2] = 2.0 \text{ M}$ ,  $[H^+] = 2.0 \text{ M}$ .

$$Ag^{+} + e^{-} \rightarrow Ag$$
$$H_{2}O_{2} + 2H^{+} + 2e^{-} \rightarrow 2H_{2}O$$

work

$$-2 (Ag^{+} + e^{-} \rightarrow Ag) \qquad -\varepsilon^{\circ} = 0.80 \text{ V}$$
$$H_2O_2 + 2H^{+} + 2e^{-} \rightarrow 2H_2O \qquad \varepsilon^{\circ} = 1.78 \text{ V}$$

$$2Ag + H_2O_2 + 2H^+ \rightarrow 2Ag^+ + 2H_2O \qquad \qquad \mathcal{E}^{\circ} = 0.98 \text{ V}$$

$$\begin{split} \varepsilon_{cell} &= \varepsilon_{cell}^{\circ} - \frac{RT}{nF} \ln(\frac{[Ag^{+}]^{2}}{[H^{+}]^{2}[H_{2}O_{2}]}) \\ \varepsilon_{cell} &= 0.98V - \frac{(8.314 \frac{J}{K \bullet mol})(298K)}{(2mol)(96485 \frac{C}{mol})} \ln(\frac{(1.0M)^{2}}{(2.0M)^{2}(2.0M)^{2}}) \\ \varepsilon_{cell} &= 1.01 \text{ V} \end{split}$$