# Fall out from the November Term Test



- •At least one student was not allowed to use a non-legal calculator. Be aware: The **only** calculator allowed in C020 is the Sharp EL-510R(B)
- •There were reports of students talking before the TAs released you from the test. As we can not control the conversation in the future this will be taken as cheating. Listen to the proctors.
- •Too many people did not fill out which exam code.

  This meant a lot of work to find out what it was. Please be more careful.
- •Some people did not fill out their student number correctly.
- •It doesn't matter which lecture section you attend but you must write with the one you're registered in!

# **Section 006**



Average = 75.1% Standard Deviation = 17.8%

## **Distribution**

A+: 24%

A: 22%

B: 18%

C: 16%

D: 11%

F: 9%

Individual marks should be up soon on Owl WebCT

This is the week of November 5-9, 2007

Group 1: Lab on Redox

Group 2: Tutorial on Atoms & Periodicity

#### **Example:**

Calculate E<sub>cell</sub> for the voltaic cell: I-| I<sub>2</sub> || Fe<sup>3+</sup> | Fe<sup>2+</sup>

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

From the table we find:

$$2Fe^{3+}(aq) + 2e^{-} \rightarrow 2Fe^{2+}(aq)$$
  $E^{o}_{red} = +0.77 \text{ V}$   $I_{2}(s) + 2e^{-} \rightarrow 2I^{-}(aq)$   $E^{o}_{red} = +0.53 \text{ V}$ 

#### 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,  $2I^- \rightarrow I_2 + 2e^- E^0_{0x} = -0.53V$ 

Therefore 
$$E_{\text{cell}}^{\circ} = E_{\text{red}}^{\circ} + E_{\text{ox}}^{\circ} = +0.77 + (-0.53) = +0.24 \text{ V}$$

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:

$$Zn^{2+}(aq) + 2e^{-} \rightarrow Zn(s)$$
  $E_{red}^{o} = -0.76 \text{ V}$ 

$$Fe^{2+}(aq) + 2e^{-} \rightarrow Fe(s)$$
  $E_{red}^{\circ} = -0.45V$ 

The reaction shows Fe being oxidized so turn it around:

$$Fe \rightarrow Fe^{2+} + 2e^{-}$$
  $E_{ox}^{o} = +0.45 \text{ V}$ 

Therefore, 
$$E_{cell}^{\circ} = E_{red}^{\circ} + E_{ox}^{\circ} = -0.76 + 0.45 = -0.31 \text{ V}$$

Since  $E_{cell}^{\circ}$  < 0, the reaction will **NOT** spontaneous occur as written.

The backwards reaction will in fact take place

### **Corollary:**

Fe<sup>2+</sup> is a better oxidizing agent than  $Zn^{2+}$ , so Fe<sup>2+</sup> 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<sup>3+</sup>(aq)||Br<sub>2</sub>( $\ell$ )|Br(aq)|Pt(s)

- a) Write out the half reactions and a balanced redox equation.
- b) Determine Eo<sub>cell</sub>
  - a) From table of standard reduction potentials:

$$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$$
  $E^o_{red} = -1.68V$   
But this is an oxidation as written in cell notation above Therefore:  $Al(s) \rightarrow Al^{3+}(aq) + 3e^ E^o_{ox} = +1.68V$  x2

$$Br_2(\ell) + 2e^- \rightarrow 2Br^-(aq)$$
  $E_{red}^0 = +1.08V$  x3

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

b) 
$$E_{cell}^{o} = E_{red}^{o} + E_{ox}^{o}$$
  
= 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<sup>+</sup> The cell equation will therefore be: metal | metal ion || H<sup>+</sup>|H<sub>2</sub>

From the table:

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$$\Rightarrow$$
 Au<sup>+</sup>(aq) + e<sup>-</sup>  $\rightarrow$  Au(s)  $E^{o}_{red} = +1.5 \text{ V}$   
 $\Rightarrow$  Ag<sup>+</sup>(aq) + e<sup>-</sup>  $\rightarrow$  Ag(s)  $E^{o}_{red} = +0.80 \text{ V}$   
 $\Rightarrow$  2H<sup>+</sup>(aq) + 2e<sup>-</sup>  $\rightarrow$  H<sub>2</sub>(g)  $E^{o}_{red} = 0.00 \text{ V}$   
 $\Rightarrow$  Fe<sup>2+</sup>(aq) + 2e<sup>-</sup>  $\rightarrow$  Fe(s)  $E^{o}_{red} = -0.45 \text{ V}$ 

The only metal H<sup>+</sup> 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<sup>+</sup>(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<sup>+</sup>(aq) + e<sup>-</sup> → Ag(s), need 0.0926 mol of e<sup>-</sup>

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

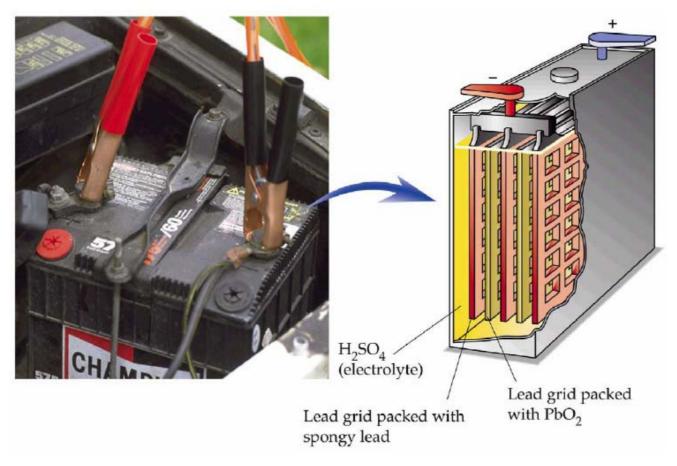
$$t = 17885 s = 298.1 min = 4.96 hr.$$

# 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<sub>2</sub> plates

As a voltaic cell the following reactions are taking place:

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

Cathode: 
$$E_{red}^{\circ}$$
 = +1.69 V PbO<sub>2</sub>(s) + H<sup>+</sup> + 2e<sup>-</sup>  $\rightarrow$  PbSO<sub>4</sub>(s) + 2H<sub>2</sub>O

Cell notation: Pb| PbSO<sub>4</sub> || PbO<sub>2</sub> | PbSO<sub>4</sub>

 $E_{cell}^{o}$  = ~ +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<sub>2</sub>SO<sub>4</sub> 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.
- $\triangleright PbSO_4(s)$  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