# Lecture Notes FF: Electrochemistry

# 1) Demo: Space Shuttle Fuels

Central engine

$$2H_2 + O_2 \rightarrow 2 H_2O$$

Side engines

 $3Mg + KClO_3 \rightarrow 3MgO + KCl$ 

(actual shuttle reaction is between Al and  $NH_4ClO_4$ )

# 2) Zn rod in $Cu^{+2}$ solution

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



# 3) Voltaic (Galvanic) Cell



- anode: site at which oxidation occurs

cathode: site at which reduction occurs

## 4) Electrolytic cell

Uses an external power source to cause cell to operate in the direction opposite to the spontaneous direction.



#### Concept

If you have fillings, biting on a piece of aluminum foil can cause an unpleasant sensation. This is because the following electrochemical cell is set up in your mouth:



Al foil: Al  $\rightarrow$  Al<sup>+3</sup> + 3 e<sup>-</sup> Occurs on the lower surface

Filling: Ag/Sn/Hg alloy allows:  $O_2$ + 4 H<sub>3</sub>O<sup>+</sup> + 2 e<sup>-</sup>  $\rightarrow$  6 H<sub>2</sub>O to occur on the upper surface Current activates the tooth's nerve.

Which of the following is true:

a) The Al foil is the cathode and the filling is the anode.

b) The Al foil is the anode and the filling is the cathode.

What is acting as the salt bridge?

#### 5) Faraday's laws

The charge on an electron is  $1.6021773 \times 10^{-19} \text{ C}$ 

One mole of electrons has a total charge of: ( $6.022137 \times 10^{23}$  electrons/mol) ( $1.6021773 \times 10^{-19}$  C/electron) = 96,485.31 C/mol = Faraday constant (F)

current = charge / unit time

1 amp (A) = 1 Coulomb/ sec

### Problem

Using a current of 4.75A, how long does it take to plate 1.50g of Cu onto a sculpture, from a CuSO<sub>4</sub> solution?

### 6) Standard cell potential and Gibbs free energy

$$\Delta G^{o} = -n F E^{0}_{cell}$$



#### Problem

A voltaic cell is constructed for the following reaction:

Pb(s) + 2 Ag<sup>+</sup> → Pb<sup>+2</sup> + 2 Ag (s) with  $[Ag^+] = [Pb^{+2}] = 1$  M, and T=25°C. The cell is found to have a voltage of 0.93V. What is  $\Delta G^\circ$  and K for this reaction?

## 7) Standard electrode (half-cell) potentials

$Zn^{+2} + 2e^{-} \rightarrow Zn(s)$	$E_{half-cell}^0 = -0.7628$
$Cu^{+2} + 2e^{-} \rightarrow Cu(s)$	$E_{half-cell}^0 = 0.158$

 $\begin{array}{ccc} \operatorname{Zn}^{+2} + 2 & \operatorname{e}^{-} \rightarrow \operatorname{Zn}(s) \\ \operatorname{Cu}(s) & \rightarrow & \operatorname{Cu}^{+2} + 2 & \operatorname{e}^{-} \end{array}$ 

 $\begin{array}{ccc} \operatorname{Zn}(s) & \rightarrow & \operatorname{Zn}^{+2} + 2 \ e^{-} \\ \operatorname{Cu}^{+2} + 2 \ e^{-} \end{array} \rightarrow \operatorname{Cu}(s) \end{array}$ 

Reference:

$$2 H_3O^+ + 2e^- \rightarrow H_{2(g)} + 2 H_2O_{(l)} \qquad E^0_{\text{half-cell}} = 0.0$$

Analogy to weak acids:

$HA_1 + H_2O - HA_2 + $			K <sub>1</sub> K <sub>2</sub>		
$HA_1 + H_2O - A_2 + H_3O + H$			K <sub>1</sub> 1/K <sub>2</sub>		
$HA_1 +$	$A_2 \rightarrow$	$A_1^{-} +$		$HA_2$	$K_1/K_2$

#### Problem

What is the standard cell potential for the cell formed by coupling a  $MnO_2/Mn^{+2}$  electrode to a  $NO/NO_3^{-1}$  electrode (in 1M acidic solution).



# 8) Table of standard half-cell potentials Concept

Which is the stronger oxidizing agent: a) Br<sub>2</sub> b) Cl<sub>2</sub>

Which is the stronger reducing agent: a) Br b) Cl

#### 9) Reactivity of metals with acid and water

Which metals will react with acid to give off hydrogen gas?

 $2 H_3O^+ + 2e^- \rightarrow H_{2(g)} + 2 H_2O_{(l)} \qquad E^0_{\text{half-cell}} = 0.0$ 

Which of the following metals will react with water to give off hydrogen gas?

 $2H_2O + 2e^- \rightarrow H_{2(g)} + 2OH^ E^0_{half-cell} = -0.8277$ a) Cd b) Ca c) Fe d) Cu

### 10) The effects of concentration on cell potential (Nernst eq.)

$$\Delta G = \Delta G^{\circ} + RT \ln Q \qquad \qquad \Delta G^{\circ} = -n F E_{cell}^{0}$$

### Which of the following is true when Q < 1:

a)  $E_{cell} < E_{cell}^{0}$  b)  $E_{cell} = E_{cell}^{0}$  c)  $E_{cell} > E_{cell}^{0}$  d)  $E_{cell} = 0$ 

Which of the following is true when Q = 1:

a)  $E_{cell} < E_{cell}^{0}$  b)  $E_{cell} = E_{cell}^{0}$  c)  $E_{cell} > E_{cell}^{0}$  d)  $E_{cell} = 0$ 

Which of the following is true when Q < K:

a)  $E_{cell} < E_{cell}^{0}$  b)  $E_{cell} = E_{cell}^{0}$  c)  $E_{cell} > E_{cell}^{0}$  d)  $E_{cell} = 0$ 

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### Problem

What is the potential for the following cell:



### 11)Concentration cells

What is the potential for the following cell:





In mitochondria, the synthesis of ATP is driven by a proton gradient across the Inner Mitochondrial membrane. The pH inside the membrane is 1.4 units higher than the pH outside the membrane. What is the contribution of this concentration gradient to the membrane potential?

#### Concept

Which of the following is the strongest oxidizing agent: a)  $Fe^{+3}$  b)  $Br_2$  c)  $Cu^{+2}$ 

What effect would each of the following have on the cell potential,  $E_{cell}$ 

Increasing the temperature of the concentration cell on the previous page: a)  $E_{cell}$  awould increase b)  $E_{cell}$  would decrease c)no effect

Increasing the concentration of an active ion in the anode compartment:

a)  $E_{cell}$  would increase b)  $E_{cell}$  would decrease c) no effect

Increasing the concentration of an active ion in the cathode compartment: a) E<sub>cell</sub> would increase b) E<sub>cell</sub> would decrease c)no effect

# 12)Car battery



Consists of alternating grids of spongy lead (Pb) and PbO<sub>2</sub>, immersed in 4.5M  $H_2SO_4$ . Fiberglass sheets between the grids prevent shorting.

The relevant half-reactions are:

PbO<sub>2</sub> (s) + SO<sub>4</sub><sup>-2</sup> + 4 H<sub>3</sub>O<sup>+</sup> + 2e<sup>-</sup> → PbSO<sub>4</sub> (s) + 6 H<sub>2</sub>O 
$$E^{\circ}=1.685V$$
  
PbSO<sub>4</sub> (s) + 2e<sup>-</sup> → Pb (s) + SO<sub>4</sub><sup>-2</sup>  $E^{\circ}=-0.356V$ 

When the battery is being used to provide power (i.e. as a voltaic cell), which set of plates are the anode?

a) Pb b) PbO<sub>2</sub>

Which set of plates is the positive terminal? a) Pb b) PbO<sub>2</sub>

What is the standard-cell potential for the battery?

When the battery is being charged (i.e. as an electrolytic cell), what is happening at the cathode and the anode?

Which battery acid has the higher pH? a) that in a fully-charged battery

b) that in a fully-discharged battery