CH 302 – Unit 4 Review 1

INTRODUCTION TO ELECTROCHEMISTRY, THE STANDARD CELL

Electrochemistry Definitions

1. **Redox Reaction**: a chemical reaction that involves the transfer of electrons from one species to another, resulting in a change in oxidation state. A redox reaction involves one species undergoing reduction and another undergoing oxidation.
2. **Reduction**: a species gains electrons, resulting in a lower oxidation state
3. **Oxidation**: a species loses electrons, resulting in a higher oxidation state
4. **Oxidizing Agent:** the species that drives the oxidation of another species in a redox reaction ; the oxidizing agent is always the species undergoing reduction
5. **Reducing Agent:** the species that drives the reduction of another species in a redox reaction ; the reducing agent is always the species undergoing oxidation

$$3Cu^{2+} + 2Al \rightarrow 3Cu + 2Al^{3+}$$

$$Cu^{2+} + 2e^{-} \rightarrow Cu$$

$$Al \rightarrow Al^{3+} + 3e^{-}$$

LEO says GER
OIL RIG

Balanced Reaction in Base

$$Cr_{(s)} + ClO_4^-{}_{(aq)} \rightarrow Cr(OH)_{3\,(s)} + ClO_3^-{}_{(aq)}$$

balance in base

$$Cr_{(s)} \longrightarrow Cr(OH)_3$$

2) balance H w/ H+

1) balance O with H2O

$$Cr_{(s)} + 3H_2O \rightarrow Cr(OH)_3 + 3H^+$$

$$+3OH^- \qquad\qquad +3OH^-$$

3) Add OH-

$$Cr_{(s)} + 3H_2O + 3OH^- \rightarrow Cr(OH)_3 + 3H_2O$$

4) balance charge

$$2\times\left(Cr_{(s)} + 3\cancel{H_2O} + 3OH^- \rightarrow Cr(OH)_3 + 3\cancel{H_2O} + 3e^-\right)$$

$$ClO_4^- \rightarrow ClO_3^-$$

$$2H^+ + ClO_4^- \rightarrow ClO_3^- + H_2O$$

OH

$$\cancel{2}H_2O + ClO_4^- \rightarrow ClO_3^- + \cancel{H_2O} + 2OH^-$$

$$\left(2e^- + H_2O + ClO_4^- \rightarrow ClO_3^- + 2OH^-\right)\times 3$$

$$2Cr_{(s)} + \cancel{6OH^-} + \cancel{6e^-} + 3H_2O + 3ClO_4^-$$

$$\rightarrow 2Cr(OH)_3 + \cancel{6e^-} + 3ClO_3^- + \cancel{6OH^-}$$

$$\boxed{2Cr_{(s)} + 3H_2O + 3ClO_4^- \rightarrow 2Cr(OH)_3 + 3ClO_3^-}$$

Electrochemical Potential

- **Electrical Cell Potential (ε°_{cell})**: the voltage associated with the redox reaction occurring in an electrochemical cell

$$\varepsilon^\circ_{cell} = \varepsilon^\circ_{cathode} - \varepsilon^\circ_{anode}$$

in this equation, both ε° values are reduction potentials read from a table

- This can also be written in the following way:

$$\varepsilon^\circ_{cell} = \varepsilon^\circ_{reduction} + \varepsilon^\circ_{oxidation}$$

**However, this equation uses the reduction potential plus the oxidation potential.

This means that you will not be able to directly use the data from a reduction potential chart.**

Question

Which of the following species will reduce Cu^{2+} but not Pb^{2+}?

a. Fe^{2+}

b. H_2

c. Zn

d. Fe^{3+}

e. H^+

Cl_2	+	$2e^-$	$\rightleftharpoons$	$2Cl^-$	+1.36 V
Ag^+	+	$1e^-$	$\rightleftharpoons$	Ag	+0.80 V
Fe^{3+}	+	$1e^-$	$\rightleftharpoons$	Fe^{2+}	+0.77 V
Cu^{2+}	+	$2e^-$	$\rightleftharpoons$	Cu	+0.34 V
$2H^+$	**+**	**$2e^-$**	$\rightleftharpoons$	**H_2**	**0.00 V**
Fe^{3+}	+	$3e^-$	$\rightleftharpoons$	Fe	−0.04 V
Pb^{2+}	+	$2e^-$	$\rightleftharpoons$	Pb	−0.13 V
Fe^{2+}	+	$2e^-$	$\rightleftharpoons$	Fe	−0.44 V
Zn^{2+}	+	$2e^-$	$\rightleftharpoons$	Zn	−0.76 V
Al^{3+}	+	$3e^-$	$\rightleftharpoons$	Al	−1.66 V

increasing strength as an reducing agent

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Ag^+	+	$1e^-$	$\rightleftharpoons$	Ag	+0.80 V
Fe^{3+}	+	$1e^-$	$\rightleftharpoons$	Fe^{2+}	+0.77 V
Cu^{2+}	+	$2e^-$	$\rightleftharpoons$	Cu	+0.34 V
$2H^+$	**+**	**$2e^-$**	$\rightleftharpoons$	**H_2**	**0.00 V**
Fe^{3+}	+	$3e^-$	$\rightleftharpoons$	Fe	−0.04 V
Pb^{2+}	+	$2e^-$	$\rightleftharpoons$	Pb	−0.13 V
Fe^{2+}	+	$2e^-$	$\rightleftharpoons$	Fe	−0.44 V
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increasing strength as an reducing agent

Question

What is the standard cell potential of the strongest battery that could be made using these half-reactions?

$Br_2 + 2e^- \longrightarrow 2Br^-$ $\quad E° = +1.07$

$Fe^{3+} + 3e^- \longrightarrow Fe$ $\quad E° = -0.04$

$Co^{3+} + e^- \longrightarrow Co^{2+}$ $\quad E° = +1.80$

$Zn^{2+} + 2e^- \longrightarrow Zn$ $\quad E° = -0.76$

Hint: look for the strongest reducing agent and the strongest oxidizing agent

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$Zn^{2+} + 2e^- \longrightarrow Zn$ $\quad E° = -0.76$

Answer:
$Zn \mid Zn^{2+} \parallel Co^{3+} \mid Co^{2+}$

Electrochemical Cell Definitions

1. **Cathode**: the site of reduction (Red Cat) ; takes in electrons from the wire
2. **Anode**: the site of oxidation (An Ox) ; gives electrons to the wire
3. **Voltaic Cell (Galvanic Cell)**: an electrochemical cell with a positive standard cell potential ; the redox reaction of the cell occurs without an external power source (spontaneous)
4. **Electrolytic Cell:** an electrochemical cell with a negative standard cell potential ; the redox reaction of the cell relies on an external power source (non-spontaneous)
5. Shorthand Notation:

anode|anodic solution ||cathodic solution | cathode

inert metal | anode reactant | anode product ||cathode reactant | cathode product | inert metal

The Electrochemical Cell

Using the following half-reactions, show the voltaic and electrolytic cells that can be created:

$$Cu^{2+} + 2e^{-} \rightarrow Cu\ (0.34V)$$

$$Al^{3+} + 3e^{-} \rightarrow Al\ (-1.66V)$$

$$\varepsilon°_{cell} = \varepsilon°_{cathode} - \varepsilon°_{anode}$$

Galvanic Voltage: **2.00V** = (0.34V) – (-1.66V) ; **Al | Al^{3+} || Cu^{2+} | Cu**

Electrolytic Voltage: **-2.00V** = (-1.66V) – (0.34V) ; **Cu | Cu^{2+} || Al^{3+} | Al**

The Electrochemical Cell Summary

	voltaic cells	electrolytic cells
free energy, ΔG	negative (–)	positive (+)
potential, *E*	positive (+)	negative (–)
push/pull of electrons	from the chemical reactions of the two half-reactions	from an external electrical power source
anode	negative (–)	positive (+)
cathode	positive (+)	negative (–)

In all electrochemical cells, the electrons travel from the site of oxidation (anode) to the site of reduction (cathode). The main difference is that voltaic cells are spontaneous cells, **where the redox reaction drives the current**. In an electrolytic cell, the redox reaction is non-spontaneous. **Therefore, the push/pull of current is driven by an external power source.**