ELECTROCHEMISTRY

3. **Schematic Cell representation:**

Oxidation || Reduction

$Cu^\circ|$ $Cu^{2+}(aq)$ || $Ag^+(aq)|$ Ag° (s)

Ag° | AgBr(sat'd) , $Br^-(0.04M)$ || $H^+(1.00 \times 10^{-4})$ | H_2 (0.90 atm), Pt

Voltaic Cells:
(also known as galvanic cells)
Danielle cell: John Daniell invented the first battery to generate electricity

$Cu(s)+ Zn^{2+}$ ---> $Zn(s) + Cu^{2+}$

2 rxns: $Cu^\circ \rightarrow Cu^{2+} +2e^-$ $Zn^{2+} +2e^- \rightarrow Zn^\circ$

oxidation 1/2 rxn   reduction 1/2 rxn
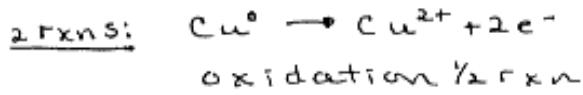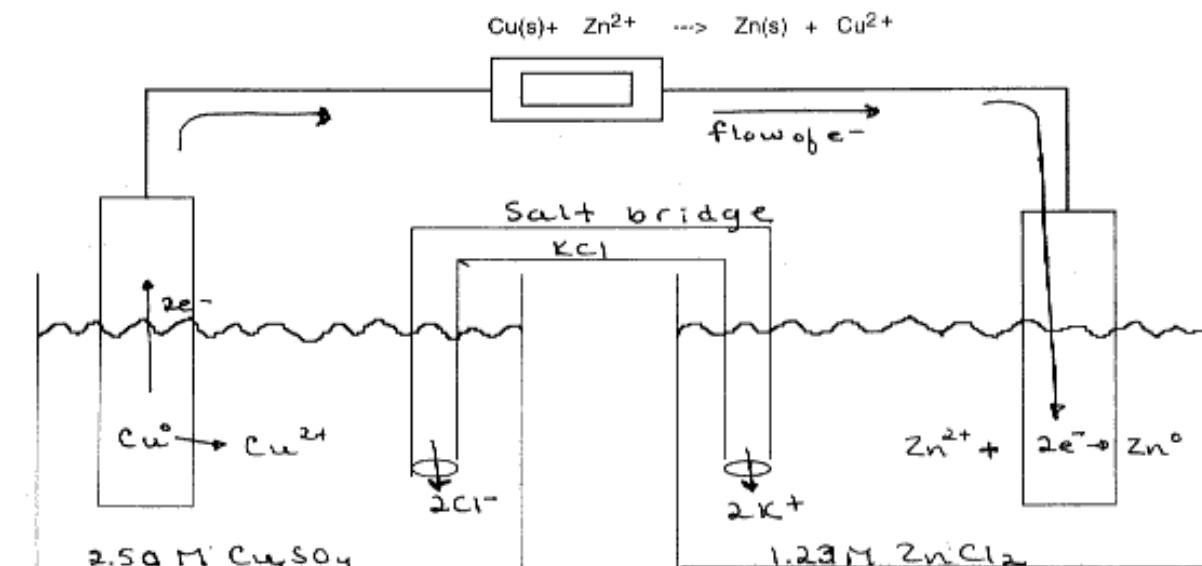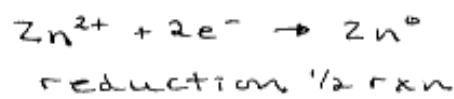
Anode   Cathode

(−) electrode   (+) electrode

Redox rxn: $Cu^\circ + Zn^{2+} \rightarrow Zn^\circ + Cu^{2+}$

Cell schematic: $Cu^\circ| Cu^{2+}(2.50 M) || Zn^{2+}(1.23 M) | Zn^\circ$
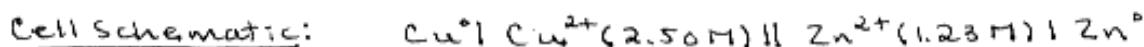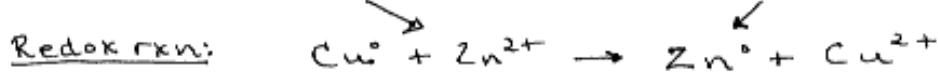
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EXAMPLES
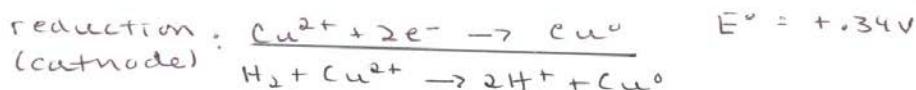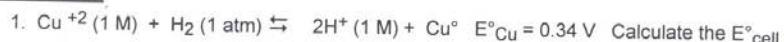
1. Cu^{+2} (1 M) + H_2 (1 atm) $\rightleftarrows$ $2H^+$ (1 M) + Cu° E°_{Cu} = 0.34 V   Calculate the E°_{cell}

oxidation: $H_2 \longrightarrow 2e^- + 2H^+$ $E^\circ = \emptyset V$
(Anode)

reduction: $\underline{Cu^{2+} + 2e^- \rightarrow Cu^\circ}$ $E^\circ = +.34 V$
(cathode): $H_2 + Cu^{2+} \rightarrow 2H^+ + Cu^\circ$

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

$= +.34 V - \emptyset V = +.34 V$

2. $2H^+$(1M) + Zn° $\rightleftarrows$ Zn^{2+}(1M) + H_2 (1 atm) E°_{cell} = + 0.76 V   Calculate E°_{Zn}

oxidation: $Zn^\circ \rightarrow Zn^{2+} + 2e^-$ $E^\circ = x$
(Anode)

reduction: $2H^+ + 2e^- \rightarrow H_2$ $E^\circ = \emptyset$
(cathode)

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

$+.76 V = \emptyset - x$

$E^\circ_{anode} = x = -.76 V$
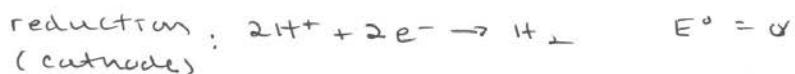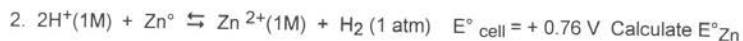
3. Calculate the $E°_{cell}$ for the following:

$$Zn° (s) + Ni^{2+}(1 M) \rightleftarrows Zn^{2+} (1 M) + Ni°(s)$$

Oxidation; $Zn° \longrightarrow Zn^{2+} + 2e^-$; $E° = -.763 V$
anode

reduction; $Ni^{2+} + 2e^- \longrightarrow Ni°$, : $E° = -.250 V$
cathode

$$Zn° + Ni^{2+} \longrightarrow Zn^{2+} + Ni°$$
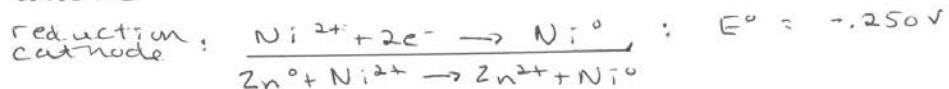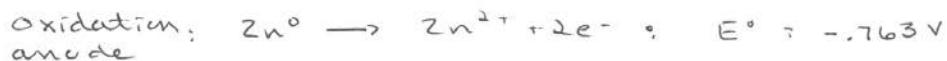
$E°_{cell} = E°cathode - E°anode$

$\quad = -.250 V - (-.763V) = 1.013 V$

I. Standard Reduction Potential Table
A listing of common reduction half-reactions
1. The more positive the E°, the higher the tendency the species will undergo reduction.

2. The more negative the E°, the higher the tendency the species will undergo oxidation.

|	
$Au^{+3} + 3e^- \rightleftarrows Au°$	$E° = 1.50 V$
$Ag^+ + 1e^- \rightleftarrows Ag°$	$E° = .80 V$
$Fe^{+2} + 2e^- \rightleftarrows Fe°$	$E° = .77 V$
$Cu^{+2} + 2e^- \rightleftarrows Cu°$	$E° = .34 V$
$Zn^{+2} + 2e^- \rightleftarrows Zn°$	$E° = -.76 V$

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III. Cell Potential, E°, and Free Energy, G°.

G° and E° :

$$\Delta G°rxn = -nFE°$$

Problems:

1. Calculate the Δ G° for the following redox reaction:

   $Cu(s) + Zn^{2+}(aq) \leftrightarrows Cu^{2+}(aq) + Zn(s)$ E° = -1.10 V
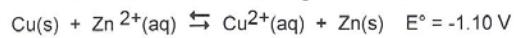
   $F = 9.6485 \times 10^4 \frac{J}{V\,mol}$

   $$\Delta G° = (2\,mol\,e^-)\left(9.6485 \times 10^4 \frac{J}{V\text{-}mol}\right)(-1.10V)$$

   $$= 212\ KJ$$

2. Given the following Δ G° values: I^- (aq) = - 51.7 kJ/mol

                                                                       Cl^- (aq) = -131.2 kJ/mol

   Calculate E° for the following reaction: $Cl_2 + 2\ I^-(aq) \overset{\leftarrow}{\underset{2e^-}{\rightarrow}} 2\ Cl^-(aq) + I_2$

   a. $\Delta G_{rxn} = 2\Delta G_{Cl^-} + \Delta G_{I_2} - \Delta G_{Cl_2} - 2\Delta G_{I^-}$

      $= 2(-131.2\ KJ) + \emptyset - \emptyset - 2(-51.7\ KJ)$

      $= -159.4\ KJ/mol$

   b. $\Delta G°_{rxn} = -nFE°$

      $-159.4 \times 10^3 \frac{J}{mol} = -(2\,mol\,e^-)\left(9.6485 \times 10^4 \frac{J}{V\,mol}\right)E°$

      $E° = 0.826V$ (spontaneous)

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E° and K: Equilibrium calculations:

When $E_{cell} = +$ the reaction proceeds spontaneously to the right. As the reaction proceeds the $E+_{cell}$ becomes smaller and smaller until eventually it reaches zero. An $E_{cell} = 0$ means that there is no net reaction occurring and that the cell has reached equilibrium. When $E_{cell} = 0$ The Q term in the Nernst equal equals to K (Q = K):

$$E = 0 = E° - \frac{0.0592}{n} \log K \qquad \text{Where K = equlibrium constant}$$

and

$$E° = \frac{0.0592}{n} \log K$$

Problems

1. Calculate the K_{eq} for the following reaction:

$$\overset{red}{\overbrace{Sn^{2+} + Cr^{2+}}} \rightleftharpoons Sn° + Cr^{3+}$$

a. oxidation: $2 Cr^{2+} \longrightarrow 2 Cr^{3+} + 2e^-$ $E° = -.408V$
(anode)
reduction: $Sn^{2+} + 2e^- \longrightarrow Sn°$ $E° = -.136V$
(cathode) $\overline{Sn^{2+} + 2 Cr^{2+} \rightleftharpoons 2 Cr^{3+} + Sn°}$

$E°_{cell} = -.136V - (-.408V) = +.276V$

b. $+.276V = \frac{.0592V}{2} \log K$ $K = 1.6 \times 10^4$
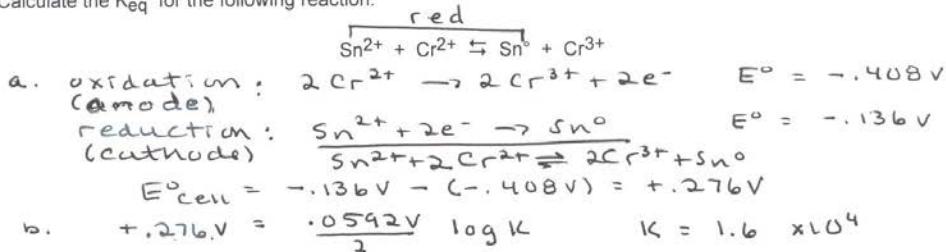
2. Calculate the Ksp of $ZnCO_3$ if:

$Zn^{2+} + 2e^- \rightleftharpoons Zn°$ $E° = -0.763$ $Ksp: ZnCO_3 \rightleftharpoons Zn^{2+} + CO_3^{2-}$
$ZnCO_3 + 2e^- \rightleftharpoons Zn° + CO_3^{2-}$ $E° = -1.055V$

a. oxidation: $Zn° \rightleftharpoons Zn^{2+} + 2e^-$ $\therefore E° = -.763V$
(anode)
reduction: $ZnCO_3 + 2e^- \rightleftharpoons Zn° + CO_3^{2-}$ $\therefore E° = -1.055V$
(cathode)
$E°_{cell} = -1.055V - (-.763V) = -.292V$

b. $E°_{cell} = \frac{0.0592V}{n} \log K$

$-.292V = \frac{0.0592V}{2} \log K$

$K = 1.26 \times 10^{-10}$

3. Calculate the equilibrium constant for: $2 Fe^{3+} + 2I^- \rightleftharpoons I_2 + Fe^{2+}$

a. oxidation: $2I^- \rightleftharpoons I_2 + 2e^-$ $\therefore E° = .536V$
(anode)
reduction: $2Fe^{3+} + 2e^- \rightleftharpoons 2Fe^{2+}$ $\therefore E° = .771V$
(cathode) $\overline{2Fe^{3+} + 2I^- \rightleftharpoons I_2 + 2Fe^{2+}}$

$E°_{cell} = E°_{cathode} - E°_{anode} = .771V - .536V = +.235V$

b. $E°_{cell} = \frac{0.0592V}{n} \log K$

$+.235V = \frac{0.0592V}{2} \log K$

$K = 8.69 \times 10^7$

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<u>E calculations:</u>

1. Calculate E for the following if the Cu(II) and Zn^{+2} solutions are both 0.50 M:

$$Cu^{2+} + Zn^\circ \leftrightarrows Zn^{2+} + Cu^\circ$$
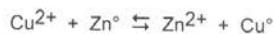
2. Determine the cell potential When the Ni(II) = 0.01M, Cl^- = 0.20 M and the Cl_2 = 1.0 atm

$$Ni + Cl_2 \leftrightarrows Ni^{2+} + 2 Cl^-$$
$$\underline{\quad +2e- \quad \uparrow}$$
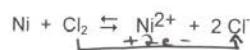
a. oxidation : $Ni^\circ \longrightarrow Ni^{2+} + 2e-$ $E^\circ = -.25$ V
(anode)

reduction : $Cl_2 + 2e^- \longrightarrow 2 Cl^-$ $E^\circ = 1.36$ V
(cathode)

$E^\circ cell = E^\circ cathode - E^\circ anode = 1.36 V - (-.25 V) = 1.61 V$

b. $E cell = E^\circ cell - \dfrac{0.0542}{n} \log \dfrac{[Cl^-]^2 [Ni^{2+}]}{P_{Cl_2}}$

$= 1.61 V - \dfrac{0.0542}{2} \log \dfrac{(.20)^2 (.01)}{(1.0)}$

$E cell = 1.71$ V

3. What is the E of the cell:
       anode   cathode

$\underline{Sn \mid Sn^{2+}(1.0 M)} \parallel Pb^{2+}(0.0010M) \mid Pb$

a. oxidation : $Sn^\circ \longrightarrow Sn^{2+} + 2e-$ $E^\circ = .126$ V
(anode)

reduction : $Pb^{2+} + 2e- \longrightarrow Pb^\circ$ $E^\circ = .136 V$
(cathode)

$E^\circ cell = E^\circ cathode - E^\circ anode = .136 V - (-.126 V) = 0.010 V$

b. $E cell = E^\circ cell - \dfrac{0.0542}{n} \log \dfrac{[Sn^{2+}]}{[Pb^{2+}]}$

$= 0.010 V - \dfrac{0.0542}{2} \log \dfrac{(1.0)}{(.0010)}$

$= -0.079 V$

4. What is the pH in a cell in which Mg^{+2} = 1.00 M and pressure of H_2 = 1.00 atm, if the E of the cell = 2.099 V?

$$Mg (s) + 2 H^+ \leftrightarrows Mg^{2+} (aq) + H_2 (g) \quad E°_{cell} = 2.363 \text{ V}$$
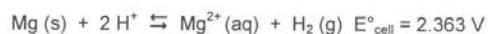
$$E_{cell} = E°_{cell} - \frac{0.0542}{n} \log \frac{[Mg^{2+}] P_{H_2}}{[H^+]^2}$$

$$2.099 = 2.363 V - \frac{0.0542}{2} \log \frac{(1.00)(1.00)}{[H^+]^2}$$

↓ using math!

$$[H^+] = 3.5 \times 10^{-5} M$$

$$pH = -\log 3.5 \times 10^{-5} = 4.46$$

5. ~~Calculate the equilibrium constant from electrode potentials at 25°C for the reaction.~~

$$~~2Fe^{3+} + 2I^- \leftrightarrows I_2 + 2Fe^{2+}~~$$

6. What is the potential of the cell represented by the following?

$$5Fe^{2+} + MnO_4^- + 8H_3O^+ \leftrightarrows 5Fe^{3+} + Mn^{2+} + 12H_2O$$

When the concentration of each of the solute species is 0.010M and at 25°C?

a. oxidation: (anode): $5 Fe^{2+} + 5e^- \longrightarrow 5 Fe^{3+}$ $\qquad E° = +.771 \text{ V}$

reduction: (cathode): $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4 H_2O$ $\qquad E° = +1.51 \text{ V}$

$$5Fe^{2+} + MnO_4^- + 8H^+ \longrightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$

$$E°_{cell} = E°_{cathode} - E°_{anode}$$

$$= 1.51 V - .771 V = .739 V$$
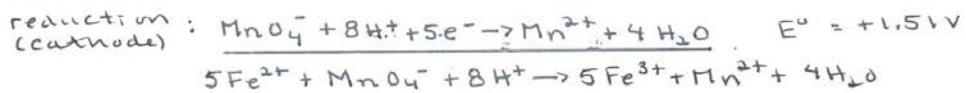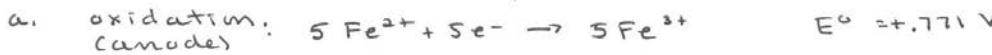
b. $$E = E° - \frac{0.0542}{n} \log \frac{[Fe^{3+}]^5 [Mn^{2+}]}{[Fe^{2+}]^5 [MnO_4^-][H^+]^8}$$

$$= .739 V - \frac{0.0542}{5} \log \frac{(.010)^5 (.010)}{(.010)^5 (.010)^8}$$

$$= 1.0 \times 10^{14} V$$

F. Concentration Cells

Since an electrode potential, E°, depends upon the concentration of the solutions used in the electrode, a cell may be constructed from two half-cells composed of the same materials but differing in concentration of ions. The spontaneous reaction occurs in the direction that tends to make the two ion concentrations equal. In the more concentrated half-cell the Cu(II) ions are reduced to form Zn in order to decrease the Cu(II) concentration. In the more dilute half-cell, more Cu(II) ion will be produced.

Ex.   Calculate the electrode potential for the following:

$Cu + Cu^{+2} (0.10M) \rightleftharpoons Cu^{2+} (0.010 M) + Cu$

a. $E° = \emptyset$ for a concentration cell

b. $E = E° - \dfrac{0.0592}{n} \log \dfrac{[Cu^{2+}]_{dil}}{[Cu^{2+}]_{conc}}$

$= \emptyset - \dfrac{0.0592}{2} \log \dfrac{(.010)}{(.10)}$

$= +0.030 \text{ V}$