ELECTROCHEMISTRY PROBLEMS KEY

1. $MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(l)$
   a) What is the oxidation number for Mn in $MnO_4^-(aq)$? **+7**
   b) What is oxidized? **Fe^{2+}** c) What is reduced? **Mn in MnO_4^-**
   d) What is the oxidizing agent? **MnO_4^-** e) What is the reducing agent? **Fe^{2+}**

2. Based on their E^o_{red} values, determine the best oxidizing agent, best reducing agent, worst oxidizing agent, and worst reducing agent.

Half-reaction	E°_{red}
$Co^{2+}(aq) + 2e^- \rightarrow Co(s)$	-0.28 V
$Mn^{2+}(aq) + 2e^- \rightarrow Mn(s)$	-1.18 V
$Cd^{2+}(aq) + 2e^- \rightarrow Cd(s)$	-0.40 V

best oxidizing agent **Co^{2+}** (most + E°_{red} = easiest to reduce)

best reducing agent **$Mn(s)$ (easiest to oxidize; has most + E^o_{ox})**

worst oxidizing agent **Mn^{2+}** (most - E°_{red} = hardest to reduce)

worst reducing agent **$Co(s)$ (hardest to oxidize; has most - E^o_{ox})**

3. Which of the following will react spontaneously? Need + V! Change sign for ox!

A. Cd with Mn^{2+}	B. Co with Cd^{2+}	C. Mn with Co	**D. Mn with Cd^{2+}**	E. Co with Mn^{2+}
+0.40 +(-1.18)= **-**	+.28 +(-.40)= **-**	NR	+1.18 +(-.40) = +	+.28+(-1.18) = **-**

4. If we were to make a Galvanic cell from the following metals, which would act as the anode and which as the cathode? Refer to table 19.1. Write the half-cell reactions and the overall balanced reaction for each cell. Calculate E^o_{cell} for each one.

   a) Fe(s) and Ni(s)

$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$ $E^o_{red} = -0.44$ V Reverse anode!

Cat $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$ **$E^o_{red} = -0.25$ V = more + is cathode**

An $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$ **$E^o_{ox} = -(-0.44\text{ V}) = 0.44$ V**

$Ni^{2+}(aq) + Fe(s) \rightarrow Ni(s) + Fe^{2+}(aq)$ $E^o_{cell} = -0.25\text{V} + 0.44\text{ V} =$ 0.19 V

   b) Cu(s) and Ag(s)

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $E^o_{red} = 0.34$ V Reverse anode!

Cat $(Ag^+(aq) + e^- \rightarrow Ag(s)) \times 2$ **$E^o_{red} = 0.80$ V = more + is cathode**

An $(Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-) \times 1$ **$E^o_{ox} = -(0.34\text{ V})$**

$2Ag^+(aq) + Cu(s) \rightarrow 2Ag(s) + Cu^{2+}(aq)$ $E^o_{cell} = 0.80\text{ V} - 0.34\text{ V} =$ 0.46 V

5. Use the information in the table below to answer the following questions

Half-reaction	E°_{red}
$Au^{3+} + 3e^- \rightarrow Au(s)$	1.50 V
$Br_2(l) + 2e^- \rightarrow 2Br^-(aq)$	1.07 V
$Pb^{2+} + 2e^- \rightarrow Pb(s)$	-0.13 V
$Ni^{2+} + 2e^- \rightarrow Ni(s)$	-0.25 V

a) What will E^o_{cell} be if Ni(s) reacts with Au^{3+}? Au^{+3} is reduced and Ni is oxidized!

Red Cat: $2\times(Au^{3+} + 3e^- \rightarrow Au(s))$ $E^o_{red} = 1.50$ V
An Ox: $3\times(Ni(s) \rightarrow Ni^{2+} + 2e^-)$ $E^o_{ox} = -(-0.25$ V) Change sign!

$2Au^{3+} + 3Ni(s) \rightarrow 2Au(s) + 3Ni^{2+}$ $E^o_{cell} = 1.50$ V + 0.25 V = 1.75 V

b) What will E^o_{cell} be if Pb^{2+} reacts with Br^-? Pb^{+2} is reduced and Br^- is oxidized!

Red Cat: $Pb^{2+} + 2e^- \rightarrow Pb(s)$ $E^o_{red} = -0.13$ V
An Ox: $2Br^-(aq) \rightarrow Br_2(l) + 2e^-$ $E^o_{ox} = -(1.07$ V) Change sign!

$Pb^{2+} + 2Br^-(aq) \rightarrow Pb(s) + Br_2(l)$ $E^o_{cell} = -0.13$ V – 1.07 V = -1.20 V

c) Calculate E^o_{cell} for the following cell: Ni(s) | Ni^{2+}(aq) || Br_2(l), Br^-(aq) | Pt(s)

An Ox: $Ni(s) \rightarrow Ni^{2+} + 2e^-$ $E^o_{ox} = -(-0.25$ V) Change sign!
Red Cat: $Br_2(l) + 2e^- \rightarrow 2Br^-(aq)$ $E^o_{red} = 1.07$ V

$Br_2(l) + Ni(s) \rightarrow 2Br^-(aq) + Ni^{2+}$ $E^o_{cell} = 1.07$ V + 0.25 V = 1.32 V

d) Which of the reactions given in parts a-c are spontaneous? **+V for a & c**

6. Calculate ΔG^o for the Ni(s) + Au^{3+} reaction in problem 5a.

Cathode: $2\times(Au^{3+} + 3e^- \rightarrow Au(s))$ $E^o_{red} = 1.50$ V
Anode: $3\times(Ni(s) \rightarrow Ni^{2+} + 2e^-)$ $E^o_{ox} = -(-0.25$ V) = 0.25 V

$2Au^{3+} + 3Ni(s) \rightarrow 2Au(s) + 3Ni^{2+}$ $E^o_{cell} = 1.75$ V

n = 6 mol e^- transferred from anode to cathode

$$\Delta G^\circ = -nFE^\circ = -\left(6\,mol\,e^-\right)\left(\frac{96500J}{V\cdot mol\,e^-}\right)(1.75V) \qquad \Delta G^\circ = -1.01\times10^6\,J\times\frac{1\,kJ}{1000J} = -1.01\times10^3\,kJ$$

7. Calculate K at 25°C for the Ni(s) + Br_2(l) reaction in problem 5c.

From 4c, **$E^o_{cell} = 1.32$ V, n = 2**

$$E^\circ = \frac{0.0592V}{n}\log K \quad \text{Rearrange: } K = 10^{\left(\frac{nE^\circ}{0.0592V}\right)} \quad K = 10^{\left(\frac{2\times1.32\ V}{0.0592\ V}\right)} \quad \mathbf{K = 3.93\times10^{44}}$$

8. A galvanic cell utilizes the following reaction:

$$2Ag^+ + Pb(s) \rightarrow Pb^{2+} + 2Ag(s)$$

a) Write the half reactions for the cell and calculate E^o_{cell}. (Refer to table 19.1)

Cat: $Ag^+(aq) + e- \rightarrow Ag(s)$ $E^\circ_{red} = 0.80$ V

An: $Pb(s) \rightarrow Pb^{+2}(aq) + 2e-$ $E^\circ_{ox} = -(-0.13)$ V = 0.13 V

$E^\circ_{cell} = 0.80$ V + 0.13 V = 0.93 V $E^\circ_{cell} = 0.93$ V

b) Write the short-hand notation of this reaction.

$Pb(s)|Pb^{+2}(aq)||Ag^+(aq)|Ag(s)$

c) Calculate the cell potential, E_{cell}, if $[Pb(NO_3)_2] = 0.88$ M and $[Ag(NO_3)] = 0.14$ M.

$2Ag^+ + Pb(s) \rightarrow Pb^{2+} + 2Ag(s)$

$E^o_{cell} = 0.93$ V, n = 2 $Q = \frac{[Pb^{2+}]}{[Ag^+]^2} = \frac{(0.88)}{(0.14)^2}$ **Q = 44.9**

$E = E^o - (0.0592\ V/n) \log Q \quad \Rightarrow \quad E = 0.93\ V - (0.0592\ V/2) \times \log 44.9$

$E = 0.93\ V - (0.0296\ V)(1.65) = 0.93 - 0.049 = 0.88\ V$ **E = 0.88 V**

9. A cell utilizes the following reaction and operates at 298 K:

$$2H^+(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + H_2(g)$$

a) Calculate E^o_{cell}. (Look up E° values).

Ox $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ $E^\circ_{ox} = -(-0.76\ V)$

Red $\mathbf{2e^- + 2H^+(aq) \rightarrow H_2(g)}$ $\mathbf{E^\circ_{red} = 0.00\ V}$

$\mathbf{E^\circ_{cell} = 0.76\ V}$

b) Calculate E_{cell} when $[Zn^{2+}] = 0.050$ M, $P_{H_2} = 0.25$ atm, and $[H^+] = 1.0 \times 10^{-4}$ M.

$$E = E^\circ - \frac{0.0592\,V}{n} \log Q \qquad n = 2;\ Q = \frac{[Zn^{2+}]P_{H_2}}{[H^+]^2}$$

$$E = 0.76\ V - \frac{0.0592\,V}{2} \log \frac{(0.050)(0.25)}{(1.0 \times 10^{-4})^2}$$

$$E = 0.76 - 0.0296(\log 1.25 \times 10^6)$$

$E = 0.76 - 0.0296(+6.10) = 0.76 - 0.18 = \mathbf{0.58\ V}$ $\mathbf{E_{cell} = 0.58\ V}$

10. How many grams of Cu can be collected in 1.00 hour by a current of 1.62 A from a $CuSO_4$ solution?

Reduction reaction: $\mathbf{Cu^{+2} + 2e^- \rightarrow Cu(s)}$

A = C/s so need to multiply amps x time in seconds to find charge (C).

$$1\text{hr} \times \frac{3600\text{s}}{1\text{hr}} \times \frac{1.62\ \text{C}}{\text{s}} \times \frac{1\ \text{mol}\ e^-}{96{,}500\ \text{C}} \times \frac{1\ \text{molCu}}{2\ \text{mol}\ e^-} \times \frac{63.5\ \text{g Cu}}{\text{mol Cu}} = \mathbf{1.92\ g\ Cu}$$

11. A current of 2.00 amps is passed through a solution of $Pb(NO_3)_2$ until 6.35 grams of Pb metal has been deposited. How many seconds did the current flow?

Reduction reaction: $Pb^{+2} + 2e^- \rightarrow Pb(s)$

$$6.35\text{g} \times \frac{\text{molPb}}{207.2\text{g}} \times \frac{2\text{mol}\ e^-}{1\ \text{mol Pb}} \times \frac{96500\ \text{C}}{1\ \text{mol}\ e^-} \times \frac{\text{s}}{2.00\text{C}} = \mathbf{2960\ s}$$