

## ELECTROCHEMISTRY PROBLEMS KEY

1.  $\text{MnO}_4^- (\text{aq}) + 8\text{H}^+ (\text{aq}) + 5\text{Fe}^{2+} (\text{aq}) \rightarrow \text{Mn}^{2+} (\text{aq}) + 5\text{Fe}^{3+} (\text{aq}) + 4\text{H}_2\text{O} (\text{l})$
- a) What is the oxidation number for Mn in  $\text{MnO}_4^- (\text{aq})$ ? +7
- b) What is oxidized?  $\text{Fe}^{2+}$                       c) What is reduced? Mn in  $\text{MnO}_4^-$
- d) What is the oxidizing agent?  $\text{MnO}_4^-$                       e) What is the reducing agent?  $\text{Fe}^{2+}$
2. Based on their  $E^\circ_{\text{red}}$  values, determine the best oxidizing agent, best reducing agent, worst oxidizing agent, and worst reducing agent.

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

best oxidizing agent                       **$\text{Co}^{2+}$  (most +  $E^\circ_{\text{red}}$  = easiest to reduce)**

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

worst oxidizing agent                       **$\text{Mn}^{2+}$  (most -  $E^\circ_{\text{red}}$  = hardest to reduce)**

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

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

A. Cd with  $\text{Mn}^{2+}$     B. Co with  $\text{Cd}^{2+}$     C. Mn with Co    **D. Mn with  $\text{Cd}^{2+}$**     E. Co with  $\text{Mn}^{2+}$

**+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  $E^\circ_{\text{cell}}$  for each one.

a) Fe(s) and Ni(s)

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

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

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

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

b) Cu(s) and Ag(s)

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

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

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

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

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

Half-reaction	$E^\circ_{\text{red}}$
$\text{Au}^{3+} + 3\text{e}^- \rightarrow \text{Au} (\text{s})$	1.50 V
$\text{Br}_2 (\text{l}) + 2\text{e}^- \rightarrow 2\text{Br}^- (\text{aq})$	1.07 V
$\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb} (\text{s})$	-0.13 V
$\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni} (\text{s})$	-0.25 V

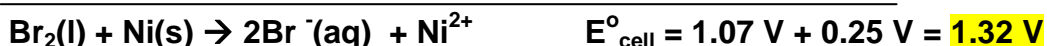
a) What will  $E^\circ_{\text{cell}}$  be if Ni(s) reacts with  $\text{Au}^{3+}$ ?  $\text{Au}^{+3}$  is reduced and Ni is oxidized!



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

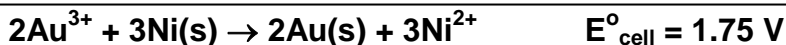
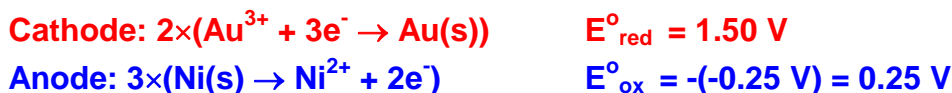


c) Calculate  $E^\circ_{\text{cell}}$  for the following cell: Ni(s) | Ni<sup>2+</sup>(aq) || Br<sub>2</sub>(l), Br<sup>-</sup>(aq) | Pt(s)



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

6. Calculate  $\Delta G^\circ$  for the Ni(s) + Au<sup>3+</sup> reaction in problem 5a.



$n = 6 \text{ mol e}^-$  transferred from anode to cathode

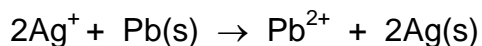
$$\Delta G^\circ = -nFE^\circ = -(6 \text{ mol e}^-) \left( \frac{96500 \text{ J}}{\text{V} \cdot \text{mol e}^-} \right) (1.75 \text{ V}) \quad \Delta G^\circ = -1.01 \times 10^6 \text{ J} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = -1.01 \times 10^3 \text{ kJ}$$

7. Calculate K at 25°C for the Ni(s) + Br<sub>2</sub>(l) reaction in problem 5c.

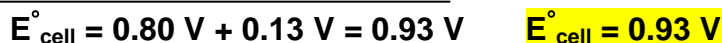
From 4c,  $E^\circ_{\text{cell}} = 1.32 \text{ V}$ ,  $n = 2$

$$E^\circ = \frac{0.0592 \text{ V}}{n} \log K \quad \text{Rearrange: } K = 10^{\left( \frac{nE^\circ}{0.0592 \text{ V}} \right)} \quad K = 10^{\left( \frac{2 \times 1.32 \text{ V}}{0.0592 \text{ V}} \right)} \quad K = 3.93 \times 10^{44}$$

8. A galvanic cell utilizes the following reaction:



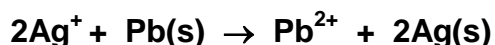
a) Write the half reactions for the cell and calculate  $E^\circ_{\text{cell}}$ . (Refer to table 19.1)



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



c) Calculate the cell potential,  $E_{\text{cell}}$ , if  $[\text{Pb}(\text{NO}_3)_2] = 0.88 \text{ M}$  and  $[\text{Ag}(\text{NO}_3)] = 0.14 \text{ M}$ .

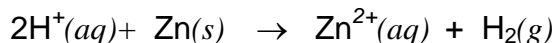


$$E^\circ_{\text{cell}} = 0.93 \text{ V}, n = 2 \quad Q = \frac{[\text{Pb}^{2+}]}{[\text{Ag}^+]^2} = \frac{(0.88)}{(0.14)^2} \quad Q = 44.9$$

$$E = E^\circ - (0.0592 \text{ V}/n) \log Q \Rightarrow E = 0.93 \text{ V} - (0.0592 \text{ V}/2) \times \log 44.9$$

$$E = 0.93 \text{ V} - (0.0296 \text{ V})(1.65) = 0.93 - 0.049 = 0.88 \text{ V} \quad \mathbf{E = 0.88 \text{ V}}$$

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



a) Calculate  $E^\circ_{\text{cell}}$ . (Look up  $E^\circ$  values).



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

b) Calculate  $E_{\text{cell}}$  when  $[\text{Zn}^{2+}] = 0.050 \text{ M}$ ,  $P_{\text{H}_2} = 0.25 \text{ atm}$ , and  $[\text{H}^+] = 1.0 \times 10^{-4} \text{ M}$ .

$$E = E^\circ - \frac{0.0592 \text{ V}}{n} \log Q \quad n = 2; \quad Q = \frac{[\text{Zn}^{2+}]P_{\text{H}_2}}{[\text{H}^+]^2}$$

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

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

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

10. How many grams of Cu can be collected in 1.00 hour by a current of 1.62 A from a  $\text{CuSO}_4$  solution?



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

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

11. A current of 2.00 amps is passed through a solution of  $\text{Pb}(\text{NO}_3)_2$  until 6.35 grams of Pb metal has been deposited. How many seconds did the current flow?



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