ELECTROCHEMISTRY PRACTICE

This worksheet should help you identify how we use electrochemistry to understand chemical reactions. It is intended for you to work through it in order. *(Don't skip ahead.)*

Suppose you want to make a galvanic cell that you can use as a battery. In this battery, the two half reactions are:

$Ni^{2+}_{(aq)} \rightarrow Ni_{(s)}$ E° = -0.23 V

$Fe_2O_{3\,(s)} \rightarrow Fe^{2+}_{\cancel{(s)}aq}$ E° = 0.77 V

In order for the reaction to be spontaneous, what is the cathode? What is the anode? Show the $E°_{cell}$ calculation for how you determined this.

For the reaction to be spontaneous $E°_{cell}$ must be positive.

$E°_{cell} = E_{cath} - E_{anode}$

If Ni cathode −0.23V
Fe anode +0.77V

$E°_{cell} = -0.23\,V - 0.77\,V$
$= -1.00\,V$

nonspontaneous

If Fe cathode +0.77 V
Ni anode −0.23V

$E°_{cell} = 0.77\,V - -0.23\,V$
$= +1.00\,V$

Spontaneous! Therefore Fe_2O_3 is cathode & Ni is anode.

What compound is being oxidized? What is being reduced?

If Fe_2O_3 is the cathode it is being reduced to Fe^{2+}

If Ni is the anode it is being oxidized to Ni^{2+}

$Fe_2O_{3(s)} + Ni_{(s)} \rightarrow Fe^{2+}_{(aq)} + Ni^{2+}_{(aq)}$

What is the balanced redox reaction for the battery? (in basic conditions)

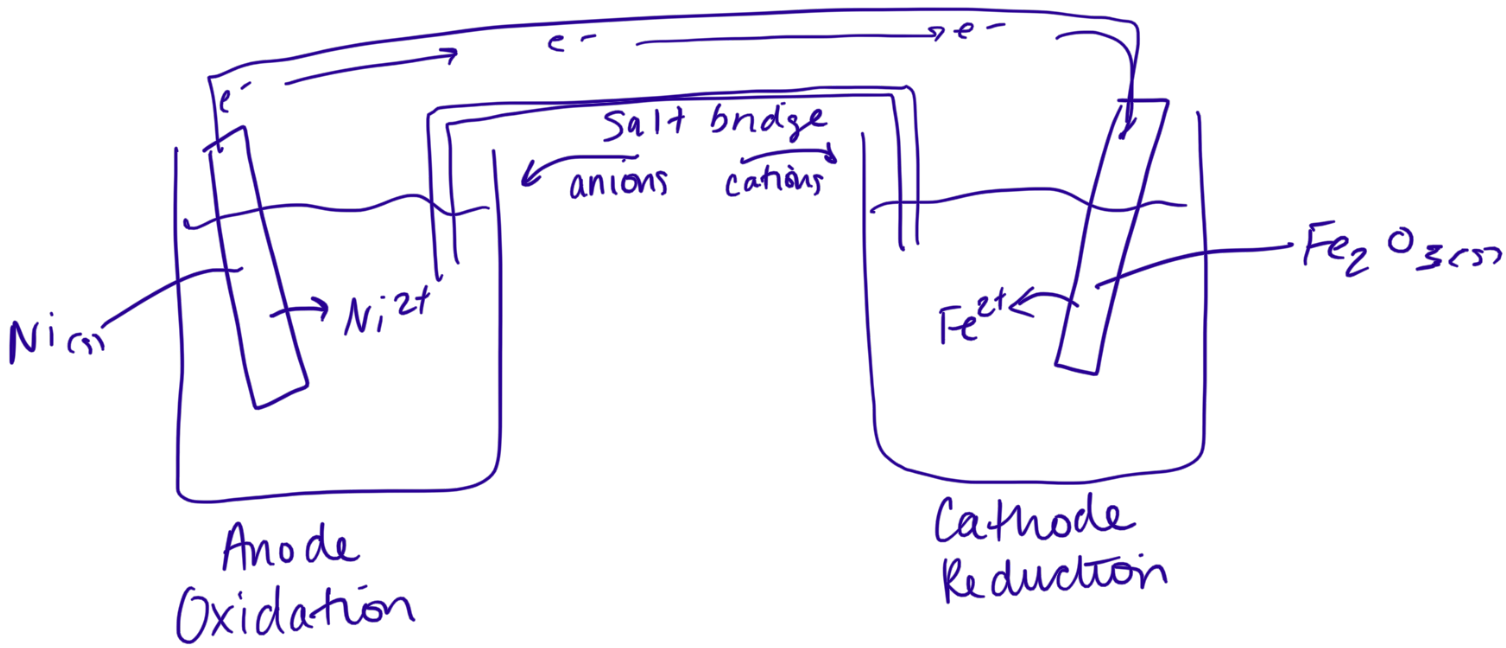
$6OH^- \; 6H^+ + Fe_2O_3 \rightarrow 2Fe^{2+} + 3H_2O + 6OH^-$

$Ni \rightarrow Ni^{2+} + \cancel{2e^-}$

$\cancel{2e^-} + 3H_2O + Fe_2O_3 \rightarrow 2Fe^{2+} + 6OH^-$

$3H_2O + Fe_2O_{3(s)} + Ni_{(s)} \rightarrow 2Fe^{2+}_{(aq)} + Ni^{2+}_{(aq)} + 6OH^-$

Draw a diagram of the cell and write the shorthand cell notation.



$Ni_{(s)} | Ni^{2+}_{(aq)} || Fe_2O_{3(s)} | Fe^{2+}_{(aq)}$

What is the value of ΔG° for the reaction?

$E^\circ_{cell} = 1.00\,V$

$\Delta G^\circ = -nFE_{cell}$

$\Delta G^\circ = -(2\,\frac{mol}{e^-})(96{,}485\,\frac{C}{mol\,e^-})(1.00\,J/C)$

$\Delta G^\circ = -192970\,J \rightarrow -192.97\,kJ$

What is the value of K for the reaction?

$E_{cell} = \frac{0.0592V}{n} \log K$

$1.00V = \frac{0.0592\,V}{2} \log K \qquad K = 6.08 \times 10^{33}$

Considering Le Chatelier's principle, when you make the battery should you have high or low Fe^{2+} and Ni^{2+} concentrations? Why?

Looking at the reaction from page 1...

$$3H_2O_{(l)} + Fe_2O_{3(s)} + Ni_{(s)} \rightarrow 2Fe^{2+}_{(aq)} + Ni^{2+}_{(aq)} + 6OH^-_{(aq)}$$

Both Fe^{2+} and Ni^{2+} appear on the products side of the reaction. Thus the lower these concentrations are the smaller the value of Q will be, and according to Le Chatelier's, a decrease in product concentration causes a shift forward.

Now check your hypothesis. Solve for Q, E_{cell}, and ΔG for the following two scenarios:

we really should include OH^- here... but we don't have pH

Scenario A: $[Ni^{2+}]$ = 0.250 M $[Fe^{2+}]$ = 0.250 M
Scenario B: $[Ni^{2+}]$ = 1.3 M $[Fe^{2+}]$ = 1.3 M

$$Q = [Fe^{2+}]^2[Ni^{2+}]$$

Which scenario will yield a better, longer lasting battery?

A

$$Q = (0.250)^2(0.250)$$
$$Q = 0.01563$$
$$E_{cell} = 1.00\,V - \frac{0.0592\,V}{2}\log(0.01563)$$
$$E_{cell} = 1.053\,V$$
$$\Delta G = -(2)(96485)(1.053)$$
$$\Delta G = -203197\ J$$
$$= -203.197\ kJ$$

B

$$Q = (1.3)^2(1.3)$$
$$Q = 2.197$$
$$E_{cell} = 1.00\,V - \frac{0.0592\,V}{2}\log(2.197)$$
$$E_{cell} = 0.990\,V$$
$$\Delta G = -(2)(96485)(0.990)$$
$$= -191040\ J$$
$$= -191.04\ kJ$$

As the reaction proceeds, what will happen to the mass of the Ni electrode? What will happen to the mass of the Fe_2O_3 electrode?

Both the Ni electrode and the Fe_2O_3 electrodes are on the reactants side, so as the reaction proceeds they will dissolve turning into ions and losing mass.