

Admin:

**Repeat: Test #2 scheduled as indicated in syllabus: week 8, Fri Aug 10 NOT Aug 13.**

Last time:

- 1) balancing redox reactions
- 2) electrochemical potential

Today:

- 0) Redox potential
- 1) Redox titration
- 2) electrochemical cells: Galvanic Cells
- 3) Group Quiz (extra credit)

Lecture:

0) **practice:** Consider  
 $E^\circ_{\text{AuCl}_4^-/\text{Au}} = 1.00\text{V}$  and  $E^\circ_{\text{O}_2/\text{H}_2\text{O}} = 1.23\text{V}$   
what are the half reactions?

Balance them

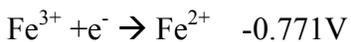
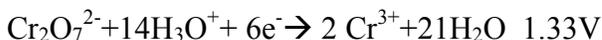
What is the spontaneous redox reaction between these 2 redox couples?

What is the  $\Delta E^\circ = ?$   $\Delta G^\circ = ?$

## 2) Redox titrations.

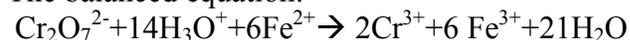
Consider titration of  $\text{Fe}^{2+}$  with  $\text{CrO}_4^{2-}$

The half reactions are: (from table)



So we see that indeed,  $\text{Fe}^{2+}$  can be oxidized by  $\text{Cr}_2\text{O}_7^{2-}$ .

The balanced equation:



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Remember that at equivalence point, the

# eq = # eq

#mol  $\text{Cr}_2\text{O}_7^{2-} \times 6 = \text{#mol Fe}^{2+}$

for solution titrations:

$$6M_{\text{Cr}_2\text{O}_7}V_{\text{Cr}_2\text{O}_7} = M_{\text{Fe}}V_{\text{Fe}}$$

3) How much work can the galvanic cell do?  
(assuming standard conditions)

$$W_{\text{max}} = \Delta G^\circ_{\text{rxn}} = -nFE^\circ_{\text{rxn}}$$

Where F = Faraday's constant  
= 96,500 coulombs/ mole electrons  
=  $9.65 \times 10^4 \text{C/mol}$

n = # electrons transferred.

Note that 1 Joule = 1 coul-volt

4) **Problem:**

25.0 mLs of  $\text{FeSO}_4$  solution requires 20.0 mLs  
of 0.150 M potassium dichromate,  $\text{K}_2\text{Cr}_2\text{O}_7$ .  
What is the concentration of the  $\text{FeSO}_4$   
solution?

$$6 \times M_{\text{Cr}}V_{\text{Cr}} = M_{\text{Fe}}V_{\text{Fe}} \Rightarrow M_{\text{Fe}} = 6M_{\text{Cr}}V_{\text{Cr}}/V_{\text{Fe}}$$

$$= 6(0.150)(20.0)/25.0 = .900(4/5) = 0.720 \text{M Fe}^{2+}$$

8) What is the  $E^\circ$  and  $\Delta G^\circ$  for the above  
reaction?

$$E^\circ = 1.33 - (-.771) = 2.10 \text{ V}$$

$$\begin{aligned} \Delta G^\circ &= - (6)(96500 \text{C/mol})(2.10 \text{V}) \\ &= - 1.22 \times 10^6 \text{ CV/mol} (= \text{J/mol}) \\ &= - 1.22 \times 10^3 \text{ kJ/mol} \end{aligned}$$

5) **Electrochemical Cells:**

2 types:

- Voltaic** Cells or Galvanic Cells (spontaneous)
- Electrolytic** cells (nonspontaneous)

## A) Voltaic Cells

Write a possible redox reaction based on the following half rxns.

1	$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$	+0.34V
2	$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Zn}(\text{s})$	-0.76

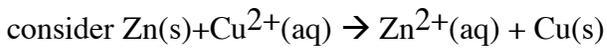
One has to be reduced, the other oxidized, so  
Reverse #2 and add to #1 :



1.10 V is the redox potential?

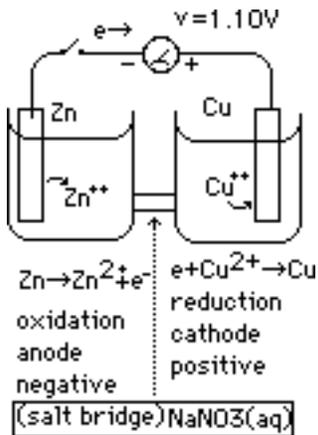
$$E^\circ_{\text{Cu}^{2+}/\text{Cu}} - E^\circ_{\text{Zn}^{2+}/\text{Zn}} = .34 + .76 = 1.10\text{V}$$

voltaic cells:

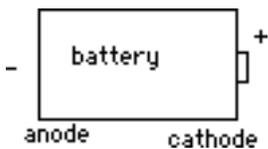


Zn supplies e and Cu(II) ion accepts electrons.  
What if we can force the e to go thru wire?

Consider the daniell cell and explain it.



Analogous to battery



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Group Quiz

Consider the following standard reduction potentials:

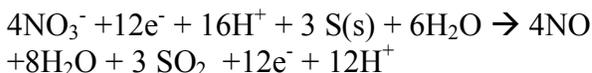
$$E^{\circ}_{\text{SO}_2/\text{S}} = 0.45 \text{ V} \quad \text{and} \quad E^{\circ}_{\text{NO}_3^-/\text{NO}} = 0.955$$

- Write each reduction half reaction and balance each one (acidic conditions).
- Write the balanced spontaneous redox reaction involving these two(2) redox couples.
- Determine the reductant and oxidant.
- Determine the reaction's standard redox potential for the spontaneous.
- Determine the maximum work this reaction can do.

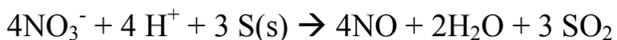
Key:

- (1)  $\text{SO}_2 + 4\text{e}^- + 4\text{H}^+ \rightarrow \text{S}(\text{s}) + 2\text{H}_2\text{O} \quad .45\text{V}$   
(2)  $\text{NO}_3^- + 3\text{e}^- + 4\text{H}^+ \rightarrow \text{NO} + 2\text{H}_2\text{O} \quad .955\text{V}$

- b) reverse (1) and multiply it by 3  
multiply (2) by 4 and add to the reversed (1)



cancelling redundant species:



- c) oxidant =  $\text{NO}_3^-$  ; reductant =  $\text{S}(\text{s})$

d)  $E^{\circ} = (.955 - .45) = +.505$

e)  $W_{\text{max}} = \Delta G^{\circ} = -nFE^{\circ}$   
 $= (-12)(96500 \text{C/mol})(.505 \text{V})$   
 $= -585,000 \text{ J} = -585 \text{ kJ/mol}$