Chem 103 Lecture 19 PS 158 7715

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

Last time:
0) Redox potential
1) Redox titration
2) Group Quiz (extra credit)

Today:
0) The group quiz
1) Electrochemical Cells: Galvanic cells
2) Applications: Batteries

Lecture:

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0) Group Quiz (SKIP THIS-REFER TO WEBSITE POSTING OF LECTURE 18)
Consider the following standard reduction potentials:
$E°_{SO2/S}$ =0.45 V and $E°_{NO3-/NO}$=0.955
a) Write each reduction half reaction and balance each one (acidic conditions).
b) Write the balanced spontaneous redox reaction involving these two(2) redox couples. c) Determine the reductant and oxidant.
d) Determine the reaction's standard redox potential for the spontaneous.
e) Determine the maximum work this reaction can do.

Key:
a) (1) SO_2 $+4e^- + 4H^+ \rightarrow S(s) + 2H_2O$ .45V
(2) $NO_3^- +3e^- + 4H^+ \rightarrow NO +2H_2O$ .955V

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

$4NO_3^- +12e^- + 16H^+ + 3\ S(s) + 6H_2O \rightarrow 4NO +8H_2O + 3\ SO_2\ +12e^- + 12H^+$
cancelling redundant species: $4NO_3^- + 4\ H^+ + 3\ S(s) \rightarrow 4NO + 2H_2O + 3\ SO_2$

c) oxidant = NO_3^- ; reductant = S(s)
d) E° = (.955-.45)= +.505
e) $W_{max} = \Delta G° = -nFE° =(-12)(96500C/mol)(.505V)$ = 585,000 J = 585 kJ/mol

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1) Electrochemical Cells:
2 types:
a) **Voltaic** Cells or **Galvanic** Cells (spontaneous)
b) **Electrolytic** cells (nonspontaneous)

A) Voltaic (Galvanic) Cells
=these generate potential spontaneously

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

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

One has to be reduced, the other oxidized, so
Reverse #2 and add to #1 : The spontaneous reaction is given by:

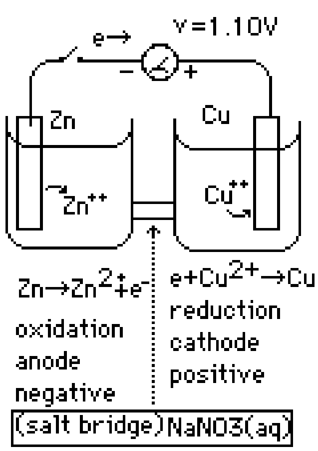
(1) –(2): $Cu^{2+} + Zn \rightarrow Cu + Zn^{2+}$ .34+.76=1.10V

1.10 V is the reaction (redox) potential? $E°_{Cu2+/Cu} - E°_{Zn2+/Zn} = .34+.76=1.10V$

voltaic cells: consider $Zn(s)+Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

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.



B) Brief intro to Electrolytic Cells

- nonspontaneous
-runs only if a higher external E is applied.
-doesn't need salt bridge
-oxidation = anode = *positive*
-reduction = reduction = *negative*

typical measurements:

q, charge = current x F = it   mol e = it/F   mol substance = it/nF
current, i=flow of e = i = in amperes (C/s)

F = 96500 C/mol

If the reaction transfers 2e's   Example: $Cu^{2+} + Zn \rightarrow Cu + Zn^{2+}$

How many moles and grams of Cu are plated after 2.0 hr electrolysis at 15 A and E_{appl} –2.0 V

Mol Cu = it/nF = $\frac{15A(120s)}{(2)(96500)}$ = 9.3×10^{-3} mol

grams Cu plated = $(9.3 \times 10^{-4})(63.5)$=0.59 g Cu

Suppose we reverse the Daniell Cell:

We can force the "plating" the Zn and dissolving Cu , by applying E_{appl} of greater magnitude than 1.10 V in reverse direction
(say magnitude is 2.0 V. We write: E_{appl} = - 2.0V.)

Draw the electrolytic cell:

Typical calculation:

Example:

Electrolysis of water: Overall $2\ H_2O \rightarrow 2\ H_2 + O_2$

Oxidation: $2\ H_2O \rightarrow O_2 + 4H^+ + 4e^-$

Reduction: $4\ H_2O + 4e^- \rightarrow 2H_2 + 4\ OH^-$

$2H^+ + H_2O + 2e^- \rightarrow H_2 + H_2O$
or $4H^+ + \cancel{2H_2O} + 4e^- \rightarrow 2H_2 + \cancel{2H_2O}$

But there are few H^+'s in pure water. so, realistically, we use basic conditions:

Add 4 OH^- to both sides:

$4\ H_2O + 4e^- \rightarrow 2H_2 + 4\ OH^-$

Analogous to battery

$E_{Cell} = E_{cath} – E_{anode} = +$

$= E_{+} - E_{-}$

(here the E’s are reduction potentials*)

OK?

An electrochemical cell involving Cu and Zn.
Half cell(Cu^{2+}/Cu) vs Half cell (Zn^{2+}/Zn) has potential $E_{Cu2+/Cu} – E_{Zn2+/Zn}$.

If the concentration of Zn and Cu are as given above, the expected potential will be 0.98 V

OK how about if we have Half cell(Ag^{+}/Ag) vs Half cell (Zn^{2+}/Zn) has potential $E_{Ag+/Ag} – E_{Zn2+/Zn}$ = 0.80 V –(-.76)=+1.56 V (+ correction)

What about Half cell(Ag^{+}/Ag) vs Half cell (Cu^{2+}/Cu): i.e. an Ag-Cu cell.

$E_{cell} = E°_{Ag} – E°_{Cu} =$

We substitute the cell potentials:
$(E_{Ag} – E_{Zn}) –(E_{cu} – E_{Zn}) =$

(It’s like saying:
10 = X-Y
4 =U-Y
What is X-U?

X-U = W-Z = 10-4 = 6

Why? W-Z=X-Y-(U-Y)=X-Y-U+Y=X-U

$E_{Ag} – E_{Cu}$ = 1.56- 1.10 V =0.46 V