Chem 103 lecture 7a Outline:

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(4) Redox reactions (READ CHAPTER 5 SECTIONS 3 , 4 (and 5)).

Definitions: **reduction**: loss of electrons **Oxidation**: gain of electrons

Here's a mnemonic: **O**xidation = **L**oss of e^-'s **R**eduction = **G**ain of e^-'s. "**OiL RiG**"

Example: Na(s) + ½ Cl(g) → NaCl(s)

Na loses an electron to become a cation: Na^+ and Cl gains an electron to become an anion, Cl^- . The complete ionic compound product is Na^+Cl^- or just NaCl.

This can be viewed as occuring in two *half reactions*:

Oxidation half-reaction: Na - - -> $Na^+ + e^-$ this is <u>oxidation</u>. (Na lost an electron)
Reduction half reaction: ½ Cl + e^- - - > Cl^- <u>reduction</u> (Cl gains an electron)

We call this an <u>oxidation-reduction</u> reaction, or *redox* reaction for short.

In the Na + Cl_2 reaction, which one is oxidized? **Na** Which is reduced? **Cl_2**
Which one is the **oxidizing agent** (or **oxidant**)? **Cl_2**
Which one is the **reducing agent** (or **reductant**)? **Na**
(Remember that the oxiding and reducing agents are both *reactants*. Don't look for the oxidants and reductants among the products).

(5) Oxidation numbers (**ON**) : Know how to determine the oxidation number of elements involved in a reaction.

Rules for oxidation numbers (ON): (5.4)
a) all monatomic ions: the charge is the ON
e.g. Na^+: ON = 1 ; Cl^- : ON = -1

b) elements in elemental form: ON = 0
e.g. O_2 : ON = 0; S_8 : ON = 0

c) usually: O = -2, H =+1
e.g. H_2O: ON of O =-2; ON of H =+1

also: other common ON's: F : -1,
other halides except when bound to O or F

know exceptions: NaH; ON of H = -1
H_2O_2: ON of O = -1

d) sum of ON's = overall charge of a polyatomic ion

Examples: Get the ON's all atoms in the following:
e.g. $HClO_2$ $KMnO_4$

6) Recognizing a Redox Reaction:

Is the ff a redox rxn?

Example 1: $Zn + HCl \dashrightarrow ZnCl_2 + H_2$

a) yes   b) no

The oxidation # of Zn in $ZnCl_2$ is:

a) 0   b) +1   c) +2   d) -2   e) -1

oxidizing agent = gets reduced
reducing agent=gets oxidize

what is the oxidizing agent in the above reaction?   (choose one)

a) Zn   b) HCl   c) $ZnCl_2$ d) H_2

half reactions:

oxidation: $Zn \rightarrow Zn^{2+} + 2e^-$

reduction: $2H^+ + 2e^- \rightarrow H_2$

Example 2:

$C_2H_6 + H_2 \rightarrow 2\ CH_4$

What are the oxidation #'s?

$$\begin{array}{llllll} C_2 & H_6 & + H_2 & \rightarrow & 2\ C & H_4 \\ -3 & +1 & 0 & & -4 & +1 \end{array}$$

C is reduced and H is oxidized.

We usually say "*ethane* is reduced" not just the *carbon* of ethane.

Note: in organic chemistry (and biochemistry too) easier to count H's and O's.

Element /change	Gain	Loss	#e's transf'd
Oxygen,O	Oxid'n	Red'n	2
Hydrogen, H	Red'n	Oxid'n	1

Example 3: Alcoholic fermentation step in yeast

acetaldehyde → ethanol (unbalanced half rxn)

CH_3CHO → CH_3CH_2OH
(acetaldehyde) (ethanol)
Is acetaldehyde oxidized or reduced?

Count the O's : no change in O
Count the H's: gain of 2 H's
So reduced with gain of 2 e's.

What is the reducing agent?
It's not given in the above equation.

7) Balancing redox reactions.

a) determine the Oxidation No's
b) write the 2 half rxns
c) balance the H's and O's.check charges
d) add the 2 half rxns so e's cancel out.

Example:

Oxalate reacts with permanganate to form CO_2 and manganese (II) ions.

$C_2O_4^{2-} + MnO_4^- \rightarrow CO_2 + Mn^{2+}$

a) determine ON's:

$$C_2O_4^{2-} + MnO_4^- \rightarrow CO_2 + Mn^{2+}$$

First: -2 -2 -2 +2

2^{nd}: +3 +7 +4

b) write the half rxns:

Oxidation:

#1 $C_2O_4^{2-} \rightarrow 2\ CO_2 + 2e^-$

+3 +4

Reduction:

#2 $5e^- + MnO_4^- \rightarrow Mn^{2+}$

+7 +2

c) balance the H's and O's.check charges

Oxidation : already balanced

Reduction:

#2 $8H^+ + 5e^- + MnO_4^- \rightarrow Mn^{2+} + 4H_2O$

+7 +2

1st: add 4 H_2O on the right to balance the O's
2nd: add 8 H^+'s on the left to balance the H's

balanced!

d) add the 2 half rxns so e's cancel out.

Multiply #1 by 5 and #2 by 2 and combine:

$16H^+ + 5C_2O_4^{2-} + 2MnO_4^- \rightarrow 5CO_2 + 2Mn^{2+} + 8H_2O$

Balanced!

8) Electrochemical potential:
In general, metals placed in water tend to dissolve in the form of cations.

e.g. $Cu \rightarrow Cu^{2+} + 2e^-$ and $Zn \rightarrow Zn^{2+} + 2e^-$

the tendency to oxidize can be represented by the *oxidation potential*, $E°_{ox}$.

From Table 19.1, page 927)

Standard reduction potentials, $E°_{red}$
(the more + E° is, the more spont the half rxn)

Reduction half rxn	E°(Volts)
$F_2(g) + 2e^- \rightarrow 2\ F^-(aq)$	+2.87 V
$Cu^{+2}(aq) + 2e^- \rightarrow Cu(s)$	+0.34
$2H^+(aq) + 2e^- \rightarrow H_2(g)$	0.00
$Zn^{2+}(aq)\ ) + 2e^- \rightarrow Zn(s)$	-0.76
$Li^+(aq) + e^- \rightarrow Li(s)$	-3.05

a) Which is the most spontaneous reduction half rxn?

$F_2(g) + 2e^- \rightarrow 2\ F^-(aq)$
(i.e. the one with the most positive E°)

b) Which is the <u>least</u> spontaneous redn half rxn?

$Li^+(aq) + e^- \rightarrow Li(s)$
(i.e. the one with the most negative E°)

c) Which is most spont oxidation half rxn?

$Li(s) \rightarrow Li^+(aq) + e^-$

Li is the "most active" metal

d) Which is the strongest oxidizing agent?

$F_2(g)$ (i.e. the most spontaneously reduced)

e) Which is the strongest reducing agent?

Li(s) (i.e. the most spontaneously reduced)

f) What is the $E°_{red}$ for:

$$2\ F_2(g) + 4\ e^- \rightarrow 4\ F^-(aq)\ \ ?$$

$E°_{red}$ = +2.87 V (not 2(2.87 V)). Note that $E°_{red}$ is an intrinsic property not extrinsic. Doesn't depend on mass (like pressure or density).

g) What is the $E°_{oxid}$ for 3 Li(s)?

$3\ Li(s) \rightarrow 3\ Li^+(aq) + 3\ e^-$ $\quad E°_{oxid} = +3.05V$

h) 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 :

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

1.10 V is the redox potential?

$E°_{Cu2+/Cu} - E°_{Zn2+/Zn} = .34+.76=1.10V$

Electrochemical Cells:

2 types:
a) Voltaic Cells or Galvanic Cells (spontaneous)

b) Electrolysis cells (nonspontaneous)

Voltaic Cells

voltaic cells: One of the simplest is the Daniell Cell:
It uses: $Zn(s)+Cu^{2+}(aq)$ - - - > $Zn^{2+}(aq) + Cu(s)$ 1.1 Volt output.

Zn supplies e^- and Cu(II) ion accepts electrons.
What if we can force the e to go thru wire?
Draw the Daniell cell and explain it.

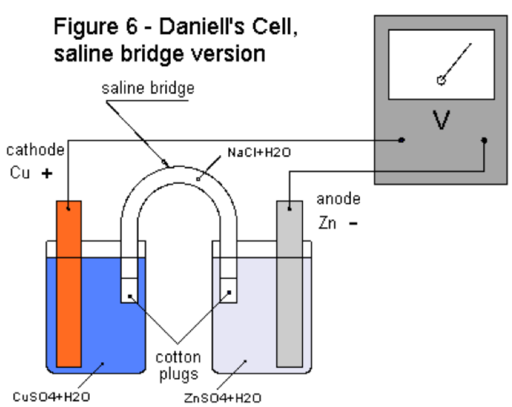

Figure 6 - Daniell's Cell, saline bridge version

this battery can be represented using the line diagram as:
$Cu(s)|CuSO_4(aq)||ZnSO_4(aq)(Zn(s)$

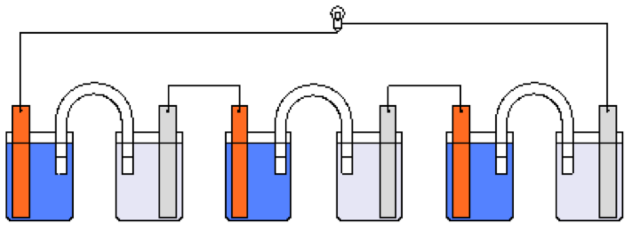

Figure 8 - Battery of three Daniell's Cells

This equivalent to 3 batteries in series