

# Announcements

- Quiz 6 scores posted
- Next week's surprise quizzes
  - Tues-oxidation number and breaking down redox processes
  - Thurs-balancing redox processes
- Tues summary
  - Oxidation numbers can be readily assigned for **most compounds**
  - $OA_1 + RA_2 \rightleftharpoons RA_1 + OA_2$
  - $OA \Rightarrow RA$  is a \_\_\_\_\_
  - $RA$  to  $OA$  is a \_\_\_\_\_

So You Thought Oxidation Numbers were simple



Assignment of oxidation states to the above requires (in general) a correct Lewis structure.

$\text{ON} = \text{Valences } e^- \text{ s} - (\text{LP } e^- \text{ s} + \text{assigned electrons})$

assigned electrons - All bonding electrons are assigned to the element with the greater electronegativity. Electrons in homonuclear bonds are split

# What's what

- Where in the periodic table would you expect to find the oxidizing agents? Where are the reducing agents?
- In the absence of some “extra” process, what will necessarily happen on a planet over the millions of years? Why has gold been so valuable Through the ages?
- What are examples of “extra” processes and what is the ultimate extra process?

# Two Examples

- $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + \text{Fe}(\text{s}) \rightleftharpoons \text{Cr}^{3+}(\text{aq}) + \text{Fe}^{2+}(\text{aq})$  (acid)
- Separate the reaction into two half reactions:
  - $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) \rightleftharpoons \text{Cr}^{3+}(\text{aq})$
  - $\text{Fe}(\text{s}) \rightleftharpoons \text{Fe}^{2+}(\text{aq})$
- Mass balance each half reaction without concern for oxygen or hydrogen
  - $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) \rightleftharpoons 2\text{Cr}^{3+}(\text{aq})$
  - $\text{Fe}(\text{s}) \rightleftharpoons \text{Fe}^{2+}(\text{aq})$
- Complete mass balance for H and O, based upon nature of the medium
  - $14\text{H}^+(\text{aq}) + \text{Cr}_2\text{O}_7^{2-}(\text{aq}) \rightleftharpoons 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}$
  - $\text{Fe}(\text{s}) \rightleftharpoons \text{Fe}^{2+}(\text{aq})$
- Charge balance each half reaction by adding the appropriate number of electrons
  - $6\text{e}^- + 14\text{H}^+(\text{aq}) + \text{Cr}_2\text{O}_7^{2-}(\text{aq}) \rightleftharpoons 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}$
- Combine the half reactions in a manner that achieves e- balance
  - $6\text{e}^- + 14\text{H}^+(\text{aq}) + \text{Cr}_2\text{O}_7^{2-}(\text{aq}) \rightleftharpoons 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}$  (x1)
  - $\text{Fe}(\text{s}) \rightleftharpoons \text{Fe}^{2+}(\text{aq}) + 2\text{e}^-$  (x3)
- Combine the half reactions and “clean up” as necessary
  - $14\text{H}^+(\text{aq}) + \text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 3\text{Fe}(\text{s}) \rightleftharpoons 2\text{Cr}^{3+}(\text{aq}) + 3\text{Fe}^{2+}(\text{aq}) + 7\text{H}_2\text{O}$

- $\text{Cr}^{3+}(\text{aq}) + \text{MnO}_2(\text{s}) \rightleftharpoons \text{Mn}^{2+}(\text{aq}) + \text{CrO}_4^{2-}(\text{aq})$  (basic)
- half reactions:
  - $\text{Cr}^{3+}(\text{aq}) \rightleftharpoons \text{CrO}_4^{2-}(\text{aq})$
  - $\text{MnO}_2(\text{s}) \rightleftharpoons \text{Mn}^{2+}(\text{aq})$
- both half reactions are already mass balanced except for O, so go directly to that step(basic solution)
  - $8\text{OH}^-(\text{aq}) + \text{Cr}^{3+}(\text{aq}) \rightleftharpoons \text{CrO}_4^{2-}(\text{aq}) + 4\text{H}_2\text{O}$
  - $2\text{H}_2\text{O} + \text{MnO}_2(\text{s}) \rightleftharpoons \text{Mn}^{2+}(\text{aq}) + 4\text{OH}^-(\text{aq})$
- add electrons
  - $8\text{OH}^-(\text{aq}) + \text{Cr}^{3+}(\text{aq}) \rightleftharpoons \text{CrO}_4^{2-}(\text{aq}) + 4\text{H}_2\text{O} + 3\text{e}^-$
  - $2\text{e}^- + 2\text{H}_2\text{O} + \text{MnO}_2(\text{s}) \rightleftharpoons \text{Mn}^{2+}(\text{aq}) + 4\text{OH}^-(\text{aq})$
- common factor is 6
  - $8\text{OH}^-(\text{aq}) + \text{Cr}^{3+}(\text{aq}) \rightleftharpoons \text{CrO}_4^{2-}(\text{aq}) + 4\text{H}_2\text{O} + 3\text{e}^-$  (x2)
  - $2\text{e}^- + 2\text{H}_2\text{O} + \text{MnO}_2(\text{s}) \rightleftharpoons \text{Mn}^{2+}(\text{aq}) + 4\text{OH}^-(\text{aq})$  (x3)
  - $16\text{OH}^-(\text{aq}) + 2\text{Cr}^{3+}(\text{aq}) + 6\text{H}_2\text{O} + 3\text{MnO}_2(\text{s}) \rightleftharpoons 2\text{CrO}_4^{2-}(\text{aq}) + 8\text{H}_2\text{O} + 3\text{Mn}^{2+}(\text{aq}) + 12\text{OH}^-(\text{aq})$
  - this reaction is “cleaned up” by removing 12 OH<sup>-</sup> and 6 H<sub>2</sub>O from each side, yielding the following final result
  - $4\text{OH}^-(\text{aq}) + 2\text{Cr}^{3+}(\text{aq}) + 3\text{MnO}_2(\text{s}) \rightleftharpoons 2\text{CrO}_4^{2-}(\text{aq}) + 2\text{H}_2\text{O} + 3\text{Mn}^{2+}(\text{aq})$

- $\text{ClO}_4^- + \text{NO}_2 \Rightarrow \text{Cl}^- + \text{NO}_3^-$  (acid)
- same as above in base
- $\text{MnO}_2 + \text{Sb} \Rightarrow \text{Mn}^{2+} + \text{Sb}_2\text{O}_3$  (base)
- same as above in acid
- $\text{Cl}_2 \Leftrightarrow \text{Cl}^- + \text{ClO}_3^-$  (base)
- $\text{H}_2\text{SO}_4 + \text{CH}_3\text{NH}_2 \Leftrightarrow \text{SO}_2 + \text{CH}_3\text{NO}_2$

# Electrochemical Potential

- The measure of the tendency for the electron transfer is the electrochemical potential(E), measured in volts.
- The determination of E is relatively straightforward. One sets up a voltaic cell(see Fig 18.2-p 765)
  - the two half reactions are isolated (separate beakers)
  - a salt bridge and external circuit are added. The salt bridge permits movement of ions between the two half cells and the external circuit carries the current. The electrode which is the **site of oxidation is the anode**, the **site of reduction is the cathode**.
  - The potential is measured using a voltmeter. If the measured potential is +, the reaction is spontaneous. A voltaic cell which is spontaneous is termed galvanic. The potential of a redox process is a state function.
- A very critical point is that the measured potential for the overall reaction is the sum of the potentials for the two half reactions-who's responsible for that?
- One other note-reversing the reaction reverses the sign of the potential.
- A few notes on electrical terms-note these are clearly interrelated
  - volt-unit of electrical pressure-1.00volt is the potential required to produce a current of 1.00amps against a resistance of 1.00ohms
  - Coulomb-unit of charge-dimensionless unit of charge= $6.24 \times 10^{18}$ -the amount of charge when a current of 1 ampere flows for 1 second
  - ampere-current 1coulomb/second
  - Faraday-1 mole of electrons 96,500coulombs=1 Faraday

## Standard Half Potentials

- Since any redox process can be viewed as follows
  - $OA_1 \Rightarrow RA_1 \quad E_1$
  - $RA_2 \Rightarrow OA_2 \quad E_2$
  - $OA_1 + RA_2 \Rightarrow RA_1 + OA_2 \quad E_{rxn} = E_1 + E_2$
- This underscores two issues:
- the usefulness in knowing the potential for a half reaction
- the impossibility of measuring the potential of a half reaction
- I think this is called a conundrum-what to do?
- cheat-SHE
- standard conditions require that all  $[ ]_s = 1.00M$  and all pressures = 1.00atm



$\text{F}_2(\text{g}) + 2\text{e}^- \Rightarrow 2\text{F}^-$	+2.87V
$\text{Ce}^{4+}(\text{aq}) + \text{e}^- \Rightarrow \text{Ce}^{3+}(\text{aq})$	+1.61V
$\text{MnO}_4^- (\text{aq}) + 8\text{H}^+ + 5\text{e}^- \Rightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$	+1.51V
$\text{Cl}_2(\text{g}) + 2\text{e}^- \Rightarrow 2\text{Cl}^-(\text{aq})$	+1.36V
$\text{O}_2(\text{g}) + 4\text{H}^+ \Rightarrow 2\text{H}_2\text{O}(\text{l})$	+1.23V
$\text{NO}_3^-(\text{aq}) + 4\text{H}^+(\text{aq}) + 3\text{e}^- \Rightarrow \text{NO}(\text{g}) + 2\text{H}_2\text{O}(\text{l})$	+0.96V
$\text{Ag}^+(\text{aq}) + \text{e}^- \Rightarrow \text{Ag}(\text{s})$	+0.80V
$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \Rightarrow \text{Fe}^{2+}(\text{aq})$	+0.77V
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \Rightarrow \text{Cu}(\text{s})$	+0.34V
$2\text{H}^+(\text{aq}) + 2\text{e}^- \Rightarrow \text{H}_2(\text{g})$	0.00V
$\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \Rightarrow \text{Pb}(\text{s})$	-0.13V
$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \Rightarrow \text{Fe}(\text{s})$	-0.44V
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \Rightarrow \text{Zn}(\text{s})$	-0.76V
$2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \Rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$	-0.83V
$\text{Fe}^{3+}(\text{aq}) + 3\text{e}^- \Rightarrow \text{Fe}(\text{s})$	-0.44V
$\text{Al}^{3+}(\text{aq}) + 3\text{e}^- \Rightarrow \text{Al}(\text{s})$	-1.66V
$\text{Li}^+(\text{aq}) + \text{e}^- \Rightarrow \text{Li}(\text{s})$	-3.05V

## Using the Std Reduction Potentials

- The electrochemical series arranges half reactions as reductions in order of decreasing potential. Thus, the species shown on the left side of the reactions are all oxidizing agents.
- Any species will oxidize all species below it. Be certain to look at the product side for the actual species being oxidized.
- You determine the overall potential by taking the difference between the two potentials-this process may seem very awkward at first.
  - $E_{\text{cell}} = E_{\text{red}} + E_{\text{ox}}$
  - since, for the process which is occurring as an oxidation:  $E_{\text{ox}} = -E_{\text{red}}$
  - $E_{\text{cell}} = E_{\text{red}} - E_{\text{red(ox)}}$
  - key check-if the oxidizing agent is above the reducing agent the potential will be positive

- Will  $\text{Ag}^+$  oxidize  $\text{Co(s)}$ 
  - what is  $E^\circ$  for this reaction
- Will  $\text{I}^-$  reduce  $\text{Sn}^{4+}$ 
  - what is  $E^\circ$  for this reaction
- Will  $\text{Br}_2$  oxidize  $\text{Fe(s)}$ 
  - what is  $E^\circ$  for this reaction
- Will  $\text{BiO}^+$  oxidize  $\text{Au}^+$  to  $\text{Au}^{3+}$ 
  - what is  $E^\circ$  for this reaction