

## Info

- On Thursday's surprise quiz you will be asked to balance two redox equations-one in basic and one in acidic media
- Exam 1 keys will be available Thursday

- $\text{H}_2\text{SO}_4 + \text{CH}_3\text{NH}_2 \rightleftharpoons \text{SO}_2 + \text{CH}_3\text{NO}_2$
- $\text{H}_2\text{SO}_4 \rightleftharpoons \text{SO}_2$ 
  - $\text{H}_2\text{SO}_4 \rightleftharpoons \text{SO}_2 + 2\text{H}^+$
  - $4\text{H}^+ + \text{H}_2\text{SO}_4 \rightleftharpoons \text{SO}_2 + 2\text{H}_2\text{O} + 2\text{H}^+$
  - $2\text{e}^- + 4\text{H}^+ + \text{H}_2\text{SO}_4 \rightleftharpoons \text{SO}_2 + 2\text{H}_2\text{O} + 2\text{H}^+$
- $\text{CH}_3\text{NH}_2 \rightleftharpoons \text{CH}_3\text{NO}_2$ 
  - $\text{CH}_3\text{NH}_2 \rightleftharpoons \text{CH}_3\text{NO}_2 + 2\text{H}^+$
  - $2\text{H}_2\text{O} + \text{CH}_3\text{NH}_2 \rightleftharpoons \text{CH}_3\text{NO}_2 + 6\text{H}^+ + 6\text{e}^-$
- Combining:
  - $2\text{e}^- + 4\text{H}^+ + \text{H}_2\text{SO}_4 \rightleftharpoons \text{SO}_2 + 2\text{H}_2\text{O} + 2\text{H}^+ \text{ (x3)}$
  - $2\text{H}_2\text{O} + \text{CH}_3\text{NH}_2 \rightleftharpoons \text{CH}_3\text{NO}_2 + 6\text{H}^+ + 6\text{e}^- \text{ (x1)}$
- $2\text{H}_2\text{O} + \text{CH}_3\text{NH}_2 + 12\text{H}^+ + 3\text{H}_2\text{SO}_4 \rightleftharpoons 3\text{SO}_2 + 6\text{H}_2\text{O} + 6\text{H}^+ + \text{CH}_3\text{NO}_2 + 6\text{H}^+$
- Cleanup:
- $\text{CH}_3\text{NH}_2 + 3\text{H}_2\text{SO}_4 \rightleftharpoons 3\text{SO}_2 + 4\text{H}_2\text{O} + \text{CH}_3\text{NO}_2$

## Standard Half Potentials

- Since any redox process can be viewed as follows
  - $OA_1 \Rightarrow RA_1 \quad E_1$
  - $RA_2 \Rightarrow OA_2 \quad E_2$
  - $OA_1 + RA_2 \Rightarrow RA_1 + OA_2 \quad E_{\text{rxn}} = E_1 + E_2$
- 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  $2H^+ + 2e^- \rightleftharpoons H_2(g) \quad E^\circ_{1/2} = 0.00V$
- standard conditions require that all  $[ ]_s = 1.00M$  and all pressures = 1.00atm

## Using the Std Reduction Potentials

- The electrochemical series arranges half reactions as reductions in order of decreasing potential. Thus, the species shown on the reactant side of the reactions are all oxidizing agents. Those on the product are the reducing agents
- Any reactant will oxidize all species below it, on the product side. Be certain to look at the product side for the actual species being oxidized.
- Likewise, any species on the product side will reduce everything above it on the reactant side.
- 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.

- Use of the EC Series has both a qualitative and quantitative aspect. In many cases, the qualitative aspect is sufficient, for, as will be seen, nearly any positive potential ensures complete reaction. Each of the following assumes standard conditions.
- Will  $\text{Ag}^+$  oxidize  $\text{Pb(s)}$ 
  - what is  $E^\circ$  for this reaction
- Will  $\text{Zn}$  reduce  $\text{Al}^{3+}$ 
  - what is  $E^\circ$  for this reaction
- Will  $\text{Cl}_2$  be reduced by  $\text{Fe}^{2+}$ 
  - what is  $E^\circ$  for this reaction
- Will  $\text{NO}$  be oxidized by  $\text{Pb}^{2+}$ 
  - what is  $E^\circ$  for this reaction

## Basic Redox Vocabulary

- Write reactions for each of the following:
- oxidation of metallic nickel by  $\text{BiO}^+$
- reduction of  $\text{Zn}^{2+}$  by hydroxide ion
- reaction of  $\text{Fe}^{2+}$  with  $\text{Hg}^{2+}$
- reaction of  $\text{Cd}^{2+}$  with  $\text{NO}_2$
- $\text{AgI}$  acting as an oxidizing agent toward  $\text{Sn}^{2+}$
- What's wrong with
- The oxidation of  $\text{Cr}$  by  $\text{Cl}^-$
- The reduction of  $\text{Co}^{2+}$  by  $\text{Ag}^+$

# Cell Notation

- As was noted earlier, galvanic cells normally consist of two distinct regions, one housing the oxidation half and the other the reduction half. There is a simplified notation form that allows one to represent the cell easily( text p 768).
- The oxidation is written on the left and the reduction on the right. starting with the anode and ending with the cathode
- phase boundaries represented with single vertical lines “|”
- the physical separation between the two half cells is a double vertical line “||” if it’s a salt bridge and with a single broken vertical line, “:”, if it’s a liquid junction
- within each half cell, the species are written in a reactant-product order, separated by commas if they are in the same phase. Acid/base components should be included
- The electrode material may be actively participating in the redox chemistry (active electrode) or merely providing surface for the electron transfer (passive or inert electrode, usually graphite or Pt)
- Represent the following as galvanic cells(assume the reactions are spontaneous as written)
- $\text{Tl(s)} + \text{Cd}^{2+} \rightleftharpoons \text{Tl}^{+} + \text{Cd(s)}$
- $\text{Pb(s)} + \text{MnO}_4^{-} \rightleftharpoons \text{Pb}^{2+} + \text{Mn}^{2+} \text{ (acid)}$
- $\text{O}_2\text{(g)} + \text{Sn}^{2+} \rightleftharpoons \text{H}_2\text{O} + \text{Sn}^{4+}$

# Practical Galvanic Cells-batteries

- Batteries represent the most common application of the electrochemical cell. The first batteries were relatively simple devices but represented an enormous step forward in the initial efforts towards the practical use of electricity.
- Primary cells-designed to provide current one time
- Secondary-rechargeable
- Fuel cells-reactants continuously fed to the electrodes



# Potential, Free Energy and Equilibrium

- Logic requires that if the potential is an unambiguous measure of spontaneity, it must be “relatable” to the other indicators of spontaneity,  $\Delta G$  and  $K$ .
- Before proceeding, it should be noted that  $E$  should be viewed as representing the “per electron” potential. In order to scale it up to a “per reaction” value, it needs to be multiplied by the number of moles of electrons in the balanced reaction, normally represented as “ $n$ ”. In general, you do not have to balance the reaction to get  $n$ , as the half reactions are in the EC Series.
- $\Delta G = -nFE$  ( $F = 96.5 \text{ kJ/V}\cdot\text{mol}$ ). If one uses the standard potential  $E^\circ$ , then the result is the standard free energy.

$$\ln K = \frac{nFE^\circ}{RT}$$

- at  $25^\circ\text{C}$   $\ln K = nE^\circ / 0.0257$
- A key observation, hopefully obvious from the above equations, is that relatively small potentials lead to very large (or very small) values for  $\Delta G$  and  $K$ .
- In utilizing the above, one does not need to balance the redox equation, but care must be taken in determining the values for  $E^\circ$  and  $n$ .

# Summary-the key equations

- $\Delta G^{\circ} = -RT \ln K$ 
  - T in deg K
  - $R = .008314 \text{ KJ/K}$
- $\Delta G = -nFE$ 
  - n is the number of electrons transferred in the balanced redox eqn
  - $F = 96.5 \text{ KJ/V}$
- $\Delta G^{\circ} = -nFE^{\circ}$
- $K = e^{-\Delta G^{\circ}/RT}$ 
  - T in deg K
  - $R = .008314 \text{ KJ/K}$
- at  $25^{\circ}\text{C}$   $\ln K = nE^{\circ}/0.0257$  or  $\log K = 16.9nE^{\circ}$ 
  - n as above

- A reaction has an equilibrium constant of  $2.28 \times 10^{-15}$  at 478K. What is the standard free energy change in KJ/mole?
- $\Delta G = -RT \ln K$                        $\ln(2.28 \times 10^{-15}) = -33.7$   
 $\Delta G = -0.008314 \times 478 \times -33.7 = 134 \text{ KJ}$
- A reaction has a standard free energy change of -191KJ/mole at 380K. What is the equilibrium constant ?
- $K = e^{-\Delta G/RT}$   
 $K = e^{-191 / (0.008314 \times 380)} = 1.8 \times 10^{26}$

- $\text{Ag}^+ + \text{S}_2\text{O}_3^{2-} \Rightarrow \text{Ag} + \text{SO}_3^{2-} \quad E^\circ = 1.38\text{V}$
- $\text{Ag}^+ + 1\text{e}^- \Rightarrow \text{Ag}$
- $\text{S}_2\text{O}_3^{2-} \Rightarrow \text{SO}_3^{2-} + 4\text{e}^-$
- $n = 4$
- $\ln K = (n * E^\circ) / .0257 = (4 * 1.38) / .0257 = 215$
- $K = e^{215} = 2.36 * 10^{93}$
- $\Delta G^\circ = -nFE^\circ = -4 * 96.5 * 1.38 = -532\text{KJ}$

- $I_3^- + Fe^{2+} \Rightarrow I^- + Fe^{3+} \quad E^{\circ} = -0.226V$
- $I_3^- + 2e^- \Rightarrow I^-$   
 $Fe^{2+} \Rightarrow Fe^{3+} + 1e^-$
- $n=2$
- $\ln K = (n * E^{\circ}) / .0257 = (2 * -0.226) / .0257 = -17.6$   
 $K = e^{-17.6} = 2.27 * 10^{-8}$
- $\Delta G^{\circ} = -nFE^{\circ} = -2 * 96.5 * -0.226 = 43.6KJ$