# CHEM 116 Redox and Intro to Electrochemistry

Lecture 21 Prof. Sevian



## Today's agenda

- Click in on the quiz
  - Note that no time will be given to finish the quiz during class, but we will go over the solution after you click in
- Big picture of electrochemistry
  - Redox reactions and oxidation numbers (review)
  - Charge flow in electrochemical cells and diagramming a cell
  - Using the mathematical model to predict current and voltage under standard and non-standard conditions

#### Announcements

- Please welcome our visitors today from East Boston High School
- Exam 3
- Final exam has been scheduled for Tuesday, Dec 16, 3:00pm in S-1-006

# Please click in your answer to this clicker question (quiz)

A buffer is prepared by adding 0.150 mol NaH<sub>2</sub>PO<sub>4</sub> and 0.200 mol Na<sub>2</sub>HPO<sub>4</sub> to 1.00 L of water. The acid dissociation equilibrium reaction is

 $H_2PO_4^- + H_2O \leftrightarrows HPO_4^{2-} + H_3O^+$ 

For  $H_2PO_4^-$ , the acid equilibrium constant is  $K_a = 6.23 \times 10^{-8}$ What is the pH of the resulting buffer solution?

(A) Between 2 and 4

(B) Between 4 and 6

(C) Between 6 and 8

(D) Between 8 and 10

(E) Between 10 and 12

#### Why we are not going to cover solubility equilibrium

• Solubility equilibrium reactions all look like variations on this:

 $(\mathbf{M}^{+})(\mathbf{L}^{-})(s) \stackrel{t}{\hookrightarrow} \mathbf{M}^{+}(aq) + \mathbf{L}^{-}(aq)$ with  $K_{sn} = [\mathbf{M}^{+}][\mathbf{L}^{-}]$ 

- The mathematical calculations are easy. For example, if 0.0050 mol/L of the salt ML is the maximum amount of ML that can dissolve in water, then it produces 0.0050 moles of M<sup>+</sup> and 0.0050 moles of L<sup>-</sup>, so  $K_{sp} = (0.0050)^2$
- The problem is that there is always a lot more going on in the solution than a simple dissociation of the salt:
  - M<sup>+</sup> or L<sup>-</sup> could be a weak acid or weak base, and would hydrolyze
  - The dissociated ions from the salt can be re-attracted to each other and form complicated complexes
  - If the salt has a formula other than ML (e.g., CaCl<sub>2</sub>), partially dissociated ions can form (such as CaCl<sup>+</sup>)
  - The M<sup>+</sup> ions often form complexes with water molecules which then undergo other acid-base equilibrium reactions
- So the mathematical calculations are nearly always very far off from experimentally
  observed values, and they are so far off that they don't even serve as good
  approximations for comparing salts to each other, so chemists do not use these
  calculations in real life.
- We are running out of time in the semester, and something has to be cut, so this is a good choice.
- Any solubility equilibrium problems that appear on the final exam will be considered extra credit if you get them "correct"

### Electrochemistry overview

- What you need to know (mostly boils down to vocabulary)
  - How to recognize an electron transfer (redox) reaction
  - Oxidation vs. reduction
    - Loss of electrons is oxidation, gain of electrons is reduction (LEO the lion says GER)
    - Reduction is moving (oxidation number) down on a number line, oxidation is up
  - Agent means "that which causes"
- What you need to be able to do
  - Assign oxidation numbers to elements to figure out which species contain elements that are changing
  - Balance redox rxns in neutral, acid, and base solutions
  - Diagram an electrochemical cell and indicate direction of flow of negative charge through the system
  - Read and write electrochemical cell notation
  - Use reduction potentials to predict cell voltage under standard conditions
  - Use the Nernst equation to predict cell voltage at non-standard conditions

### Examples of non-redox vs. redox reactions

- Non-redox reactions
  - <u>http://www.jce.divched.org/JCESoft/CCA/samples/cca4CdNO.html</u>
  - http://www.jce.divched.org/JCESoft/CCA/samples/cca4CuNO.html

#### Redox reactions

- http://www.jce.divched.org/JCESoft/CCA/samples/cca4Na\_acid.html
- http://www.jce.divched.org/JCESoft/CCA/samples/cca7thermite.html
- http://www.jce.divched.org/JCESoft/CCA/samples/cca3glycerin.html

What differences do you notice?

#### Redox rxns at the macroscopic level

- It is possible to separate the reaction into two parts that must occur simultaneously and where electrons (electricity) are generated in one part and used in the other part (and travel through a wire to get there)
- The following observables are always signals that a redox reaction is occurring:
  - Rusting of a metal reactant, production of a new metal
  - Combustion
  - Hydrogen ions (H<sup>+</sup>) or water is consumed and hydrogen gas is produced, or vice-versa
  - Hydroxide ions (OH<sup>-</sup>) are consumed and oxygen gas is produced
- The following observables are often (but not always) signals that a redox reaction is occurring:
  - Color change
  - Production of a gas
  - Hydrogen ions (H<sup>+</sup>) or hydroxide ions (OH<sup>-</sup>) catalyze the reaction

# Model of redox rxns at the particle level

- · Electrons are exchanged between one species and another
- One species is an electron donor, another species is an electron acceptor
- Therefore, one species must lose one or more electrons, the other species must gain one or more electrons
- A redox reaction can be broken into two halves: the electron donation (called oxidation) and the electron acceptance (called reduction)
- If these half-reactions are separated in space, electrons can be forced to flow through a wire
- If Q < K for the starting concentrations, then the reaction is product-favored and the reaction progresses toward products, generating electricity as it does

### **Redox Reactions and Electrochemistry**

#### Part I: Foundational

- Assigning oxidation numbers (oxidation numbers are part of the redox model)
- Balancing redox equations

#### Part II: Applied

- Diagramming electrochemical cells
- Facility with cell notation

Part III: Using the redox model to make mathematical predictions of properties

- Calculating cell potential at standard conditions
- Calculating cell potential at non-standard conditions
- Relating the amount of a substance oxidized or reduced to the electrical current and the time during which current is allowed to flow

## Recall: What are oxidation numbers?

- A charge (sometimes real, sometimes fake) that can be assigned to each atom in a compound
  - In charged particles (ions within ionic solid, ions dissolved in water), the charge is real
  - In molecules (which are neutral), atoms don't have real charges
- · Measures electron density that resides on the individual atom
  - Caveat: if the atom is in a molecule, and there is more than one of a particular kind of atom, in reality each one doesn't have the same electron density
- A model that provides an accounting method for explaining electron transfer in redox reactions

#### How to assign oxidation numbers (see pp. 848-849, and review pp. 60-65 and pp. 138-139)

- Oxidation numbers sum to zero if compound is neutral, and total charge on ion if not neutral
- Atoms in free, neutral elements have oxidation number zero (0)
   Zn (s), Ar (g), O<sub>2</sub> (g), S<sub>8</sub> (s), Ag (s), N<sub>2</sub> (g)
- Charged ions have oxidation number equal to their charges FeCl<sub>3</sub> (s), FeCl<sub>2</sub> (s), Na<sup>+</sup> (aq), Al<sup>3+</sup> (aq), AlBr<sub>3</sub> (s)
- Oxygen, when in a compound or ion, nearly always has oxidation number -2 (exception: peroxides)
   Al<sub>2</sub>O<sub>3</sub> (s), MgO (s), SO<sub>4</sub><sup>2-</sup> (aq), NO<sub>3</sub><sup>-</sup> (aq); Exceptions: H<sub>2</sub>O<sub>2</sub> (l), Na<sub>2</sub>O<sub>2</sub> (s)
- Hydrogen, when in a compound or ion, nearly always has oxidation number +1 (exception: hydrides)

HCl (1), H<sub>2</sub>SO<sub>3</sub> (aq), CH<sub>3</sub>COO<sup>-</sup> (aq); Exceptions: CaH<sub>2</sub> (s), NaH (s)

# Practice with oxidation numbers

Identify oxidation numbers for each atom



#### **Balancing redox reactions**

- Inspection method
  - Same method for balancing reactions that you are already familiar with: conservation of matter
  - Example: balance the following reaction

 $\mathrm{Al}\,(s)\,+\,\mathrm{Cl}_{2}\,(g)\,\rightarrow\,\mathrm{AlCl}_{3}\,(s)$ 

- $2 \operatorname{Al}(s) + 3 \operatorname{Cl}_2(g) \rightarrow 2 \operatorname{AlCl}_3(s)$
- When the inspection method doesn't work, use SOHe<sup>-</sup>
  - When you have ions (e.g., a net ionic reaction) and it looks too complicated
  - When there are extra waters (H<sub>2</sub>O) on one or the other side of the reaction
  - Examples:

$$Cu (s) + NO_3^{-}(aq) \rightarrow Cu^{2+}(aq) + NO_2 (g)$$
  
Cd (s) + NiO<sub>2</sub> (s) + H<sub>2</sub>O (l)  $\rightarrow$  Cd(OH)<sub>2</sub> (s) + Ni(OH)<sub>2</sub> (s) (nicad)

#### SOHe<sup>-</sup> method of balancing redox equations

- Separate the redox reaction into reduction and oxidation halves, and then for each half:
- Species in the species that contains the element whose oxidation number is changing, balance that element
- Oxygen balance the oxygens by adding H<sub>2</sub>O on whichever side of the equation is missing oxygen
- Hydrogen balance the hydrogens by:
  - If acid solution, add H+ to one side
  - If basic solution, add OH<sup>-</sup> to one side and H<sub>2</sub>O to the other side, so H<sub>2</sub>O is added to side needing more H atoms
- Electrons balance the charge on both sides by adding electrons (e<sup>-</sup>) to whichever side requires negative charge

Now add the two half reactions together in such a way that the electrons cancel (least common multiple)

## Practice using SOHe<sup>-</sup> method

1.  $\operatorname{Cu}(s) + \operatorname{NO}_{3}(aq) \rightarrow \operatorname{Cu}^{2+}(aq) + \operatorname{NO}_{2}(g)$  in acid

### Practice using SOHe<sup>-</sup> method

2.  $\operatorname{Cd}(s) + \operatorname{NiO}_2(s) + \operatorname{H}_2\operatorname{O}(l) \rightarrow \operatorname{Cd}(\operatorname{OH})_2(s) + \operatorname{Ni}(\operatorname{OH})_2(s)$ in acid

# Review of vocabulary that applies to redox reactions

- Species = a reactant that contains an element whose oxidation number changes
  - On the reactant side, there must be one species that gets oxidized (oxidation number of an element in it goes up) <u>and</u> one species that gets reduced (oxidation number of an element in it goes down)
- Oxidation half-reaction: the reaction showing the species that gets oxidized, its product, and how many electrons get produced
- Reduction half-reaction: the reaction showing the species that gets reduced, its product, and how many electrons react in order for this to happen
- Species that gets oxidized is called the reducing agent because it causes the reduction half-reaction to occur
- Species that gets reduced is called the oxidizing agent because it causes the oxidation half-reaction to occur

#### **Electrochemical cells**

- Electrochemical, voltaic, galvanic = all mean the same thing
- Divide the half-reactions into separate cells (locations) so that electrons generated at the oxidation half-cell are forced to travel through a wire to get to the reduction half-cell
- http://www.chem.iastate.edu/group/Greenbowe/sections/proje ctfolder/flashfiles/electroChem/voltaicCellEMF.html
- What's the role of the salt bridge?
- Why do reactions occur in only one direction?
- How can you predict the voltage?



## Animation shown in class

# Key ideas so far about electrochem

- You must review ions and ionic charges
- You must be able to assign oxidation numbers to elements in a compound or ion
- Redox reactions are when oxidation numbers change during a reaction
  - One element (part or all of a "species") has its oxidation number increase (this is oxidation)
  - Another element (part or all of a "species") has its oxidation number decrease (this is reduction)
  - Both processes must occur, because redox is electron transfer
- Study the vocabulary