5.111 Lecture Summary #24 **Wednesday, November 5, 2014**

Reading for Today: Sections 12.4-12.6 in 5th ed. (4th ed: 11.4-11.6) and 13.1-13.2
Reading Lecture #25: Sections 13.3-13.12 in 5th **(** 4th ed: 12.3-12.12)

Topics: Acid-Base Titrations
I. Titration of Weak Acid with Strong Base (Continued)
II. Introduction to Oxidation-Reduction (Redox) Reactions
III. Balancing Redox Reactions

I. TITRATION OF WEAK ACID WITH STRONG BASE CONTINUED

25.0 mL of 0.10 M HCOOH with 0.15 M NaOH ($K_a = 1.77 \times 10^{-4}$ for HCOOH)

3. $V = V_{eq}$ (Point S)
At the equivalence point, the amount of NaOH added is equal to the amount of HCOOH. The pH is not 7 as it is for a strong acid and a strong base.

The pH is ______ 7 when a weak acid is titrated with a strong base.

The pH depends on the properties of the ______________ formed during the neutralization process.

HCOOH and NaOH form $NaHCO_2$ and H_2O.

Na^+ has ______________________ on pH and

HCO_2^- is a ____________________.

Thus at the equivalence point, the pH is >7.

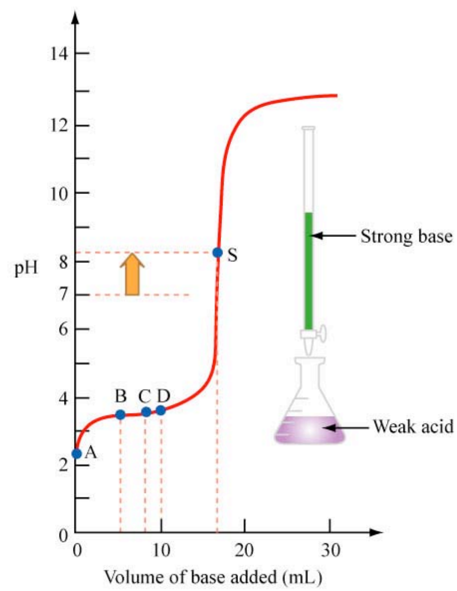


Figure by MIT OpenCourseWare.

Calculate the pH at the equivalence point

Calculate total volume at equivalence point

moles of HCOOH = 2.5×10^{-3} moles = moles of HCO_2^- formed = moles of OH^- added

$$2.5 \times 10^{-3} \text{ moles of } OH^- \times \frac{1L}{0.15 \text{ mol}} = 1.67 \times 10^{-2} \text{ L of NaOH added}$$

Total volume = 0.0250 L + 0.0167 L = 0.0417 L

Molarity of HCO_2^-
2.5×10^{-3} moles of HCO_2^- / (0.0417 L) = 0.0600 M HCO_2^-

HCO_2^- (aq) + H_2O (l) $\rightleftharpoons$ HCOOH (aq) + OH^- (aq)

	HCO_2^- (aq)	HCOOH (aq) +	OH^- (aq)
initial molarity	0.0600	0	0
change in molarity	-x	+x	+x
equilibrium molarity	0.0600 -x	+x	+ x

This is a ____________________ in water problem.
You can take it from here. Simplify if x is small compared to 0.0600 M.
Calculate x, which is equal to $[OH^-] = 1.83 \times 10^{-6}$ M. Then calculate pOH = 5.74.
From pOH, calculate pH. pH = 8.26 (which is >7)

4. $V > V_{eq}$ (Point E)

Beyond the equivalence point, NaOH is added to the solution of the conj. base HCO_2^-.

Since HCO_2^- does not give rise to much OH^- in solution (1.83×10^{-6} M), the pOH and pH are determined by the amount of _____________ NaOH.

This problem is similar to a strong base problem.

At 5.00 mL past the equivalence point

$0.00500 \text{ L} \times 0.15 \text{ M} = 7.5 \times 10^{-4}$ moles excess OH^-

7.5×10^{-4} moles OH^- / (_________________________L)
= 0.016 M OH^-

pOH = -log [0.016] = 1.79

pH = 12.21

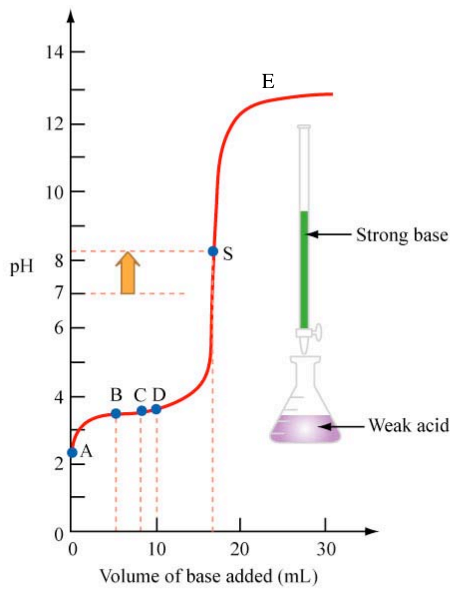
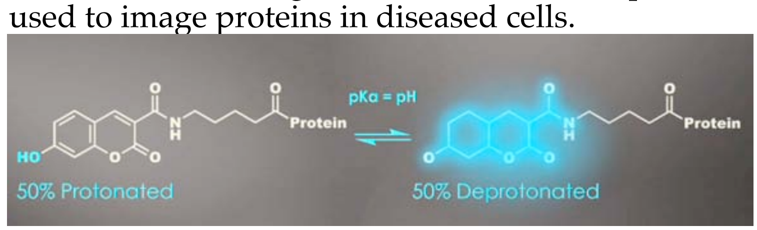


Figure by MIT OpenCourseWare.

IN THEIR OWN WORDS: THE IMPORTANCE OF pKa

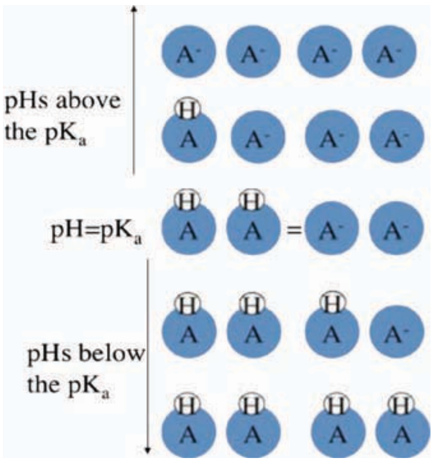
Samuel Thompson discusses his research on designing tools to track the movement of proteins in cells. Understanding the relationship between pKa and pH was critical to design a sensor that he hopes will be used to image proteins in diseased cells.



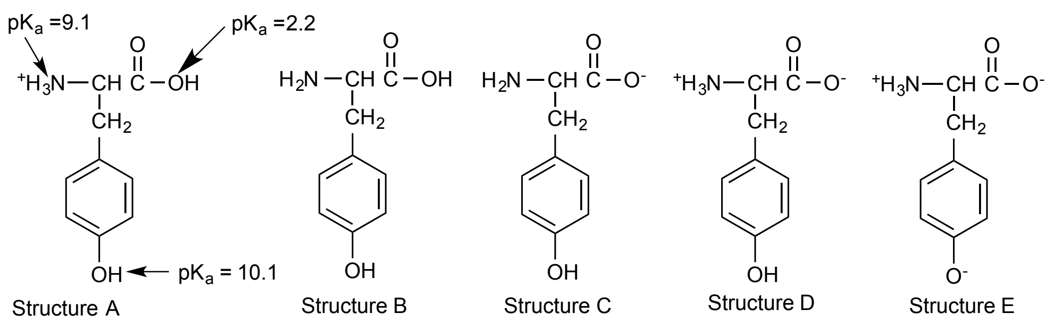
Samuel's s video can be found at: http://chemvideos.mit.edu/all-videos/.

MORE ABOUT pK_a

Example 1. Consider a probe (HA) that only glows in the deprotonated state. The pK_a of the probe is 10.0. Estimate how much of the probe will glow at pH of 7.4?



Example 2. Which structure would you predict the amino acid tyrosine to have at pH 7.4?



END OF EXAM 3 MATERIAL

II. INTRODUCTION TO OXIDATION-REDUCTION (REDOX) REACTIONS

Redox reactions are a major class of chemical reactions in which there is an exchange of electrons from one species to another.

For example, $2Mg\ (s) + O_2\ (g) \rightarrow 2MgO$

Definitions

Oxidation:

Reduction:

Oxidizing agent:

Reducing agent:

Guidelines for Assigning Oxidation Numbers

1) In free elements, each atom has an oxidation number of zero. Example H_2

2) For ions composed of only one atom the oxidation number is equal to the charge on the ion. Thus Li^{+1} has an oxidation number of +1. Group 1 and group 2 metals have oxidation numbers of +1 and +2, respectively. Aluminum has an oxidation number of +3 in all its compounds.

3) The oxidation number of oxygen in most compounds is -2. However, in peroxides such as H_2O_2 and O_2^{-2}, oxygen has an oxidation state of -1.

4) The oxidation number of hydrogen is +1, except when it is bonded to metals in binary compounds, such as LiH, NaH, CaH_2. In these cases, its oxidation number is -1.

5) F has an oxidation number of -1 in all its compounds. Other halogens (Cl, Br, and I) have negative oxidation numbers when they occur as halide ions in compounds (Ex. NaCl). However, when combined with oxygen (oxoacids), they have positive oxidation numbers (Ex. ClO^-).

6) In a neutral molecule, the sum of the oxidation numbers of all the atoms must be zero. In a polyatomic ion, the sum of oxidation numbers of all the elements in the ion must be equal to the net charge of the ion.

Example NH_4^+

H is ________ N is ________ Sum is ____________

7) Oxidation numbers do not have to be integers. For example, the oxidation number of oxygen in superoxide O_2^{-1} is __________

Examples:

Li_2O PCl_5

HNO_3 N_2O

Disproportionation Reactions

A reactant element in one oxidation state is **both** oxidized and reduced.

$$NaClO \Rightarrow NaClO_3 + NaCl$$

Write the half reactions and determine the changes in oxidation state. Na^+ is a spectator ion so:

$$ClO^- \Rightarrow ClO_3^-$$

$$ClO^- \Rightarrow Cl^-$$

III. BALANCING REDOX REACTIONS

A. BALANCE IN **ACIDIC** SOLUTION

$Fe^{2+} + Cr_2O_7^{2-} \Rightarrow Cr^{3+} + Fe^{3+}$

(1) Write two unbalanced half reactions for oxidized and reduced species.

$Cr_2O_7^{2-} \Rightarrow Cr^{3+}$

$Fe^{2+} \Rightarrow Fe^{3+}$

(2) Insert coefficients to make the number of atoms of all elements except oxygen and hydrogen equal on the two sides of each equation.

$Cr_2O_7^{2-} \Rightarrow Cr^{3+}$

$Fe^{2+} \Rightarrow Fe^{3+}$

(3) Add H_2O to balance oxygen

$Cr_2O_7^{2-} \Rightarrow 2Cr^{3+}$

$Fe^{2+} \Rightarrow Fe^{3+}$

(4) Balance hydrogen with H^+

$Cr_2O_7^{2-} \Rightarrow 2Cr^{3+} + 7H_2O$

$Fe^{2+} \Rightarrow Fe^{3+}$

(5) Balance the charge by inserting electrons

$14H^+ + Cr_2O_7^{2-} \Rightarrow 2Cr^{3+} + 7H_2O$

$Fe^{2+} \Rightarrow Fe^{3+}$

(6) Multiply the half reactions so that the number of electrons given off in the oxidation equals the number of electrons accepted in the reduction.

$6e^- + 14H^+ + Cr_2O_7^{2-} \Rightarrow 2Cr^{3+} + 7H_2O$

$Fe^{2+} \Rightarrow Fe^{3+} + e^-$

(7) Add half reaction, make appropriate cancellations.

$\cancel{6e^-} + 14H^+ + Cr_2O_7^{2-} + 6Fe^{2+} \Rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+} + \cancel{6e^-}$

B. BALANCE IN **BASIC** SOLUTION.

$Fe^{2+} + Cr_2O_7^{2-} \Rightarrow Cr^{3+} + Fe^{3+}$

Follow steps (1-7) to get your answer for acidic solution:

$14H^+ + Cr_2O_7^{2-} + 6Fe^{2+} \Rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+}$

(8) Then "adjust pH" by adding OH^- to both sides to neutralize H^+.

$14OH^- + 14H^+ + Cr_2O_7^{2-} + 6Fe^{2+} \Rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+} + 14OH^-$

OR

$14H_2O + Cr_2O_7^{2-} + 6Fe^{2+} \Rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+} + 14OH^-$

CANCEL

$\overset{7}{\cancel{14H_2O}} + Cr_2O_7^{2-} + 6Fe^{2+} \Rightarrow 2Cr^{3+} + \cancel{7H_2O} + 6Fe^{3+} + 14OH^-$

Thus: $7H_2O + Cr_2O_7^{2-} + 6Fe^{2+} \Rightarrow 2Cr^{3+} + 6Fe^{3+} + 14OH^-$

<u>Summary</u>

Acidic: $14H^+ + Cr_2O_7^{2-} + 6Fe^{2+} \Rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$

Basic: $7H_2O + Cr_2O_7^{2-} + 6Fe^{2+} \Rightarrow 2Cr^{3+} + 6Fe^{3+} + 14OH^-$

5.111 Principles of Chemical Science
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