5.111 Principles of Chemical Science
Fall 2008

5.111 Lecture Summary #24

Topics: Oxidation States, and Balancing Oxidation/Reduction Reactions (Read Section K, Chapter 12)

FROM MONDAY: Titrations Curves for Weak acid/Strong base and for Weak base/Strong acid

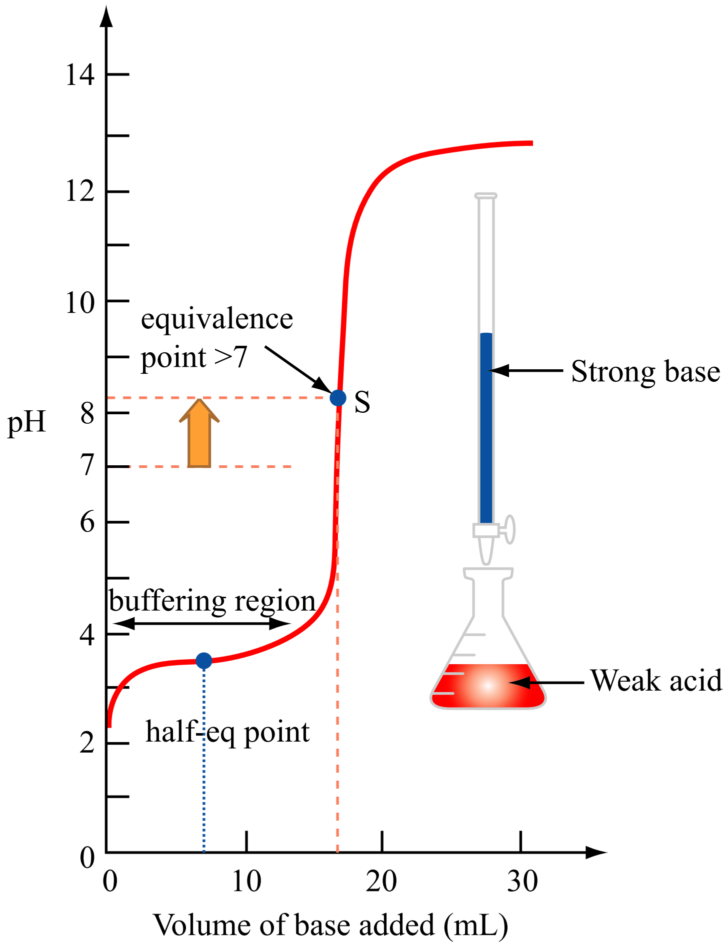

Figure by MIT OpenCourseWare.

$V > V_{eq}$ **strong base in water**

$V = V_{eq}$ **(salt) conj. base of weak acid**

A^- A^- A^- A^-

$V=V_{half\text{-}eq}$ **special category of buffer**

HA HA $=$ A^- A^-

$0 < V < V_{eq}$ **buffer**

HA HA HA A^-

Start $V = 0$ **weak acid in water**

HA HA HA HA

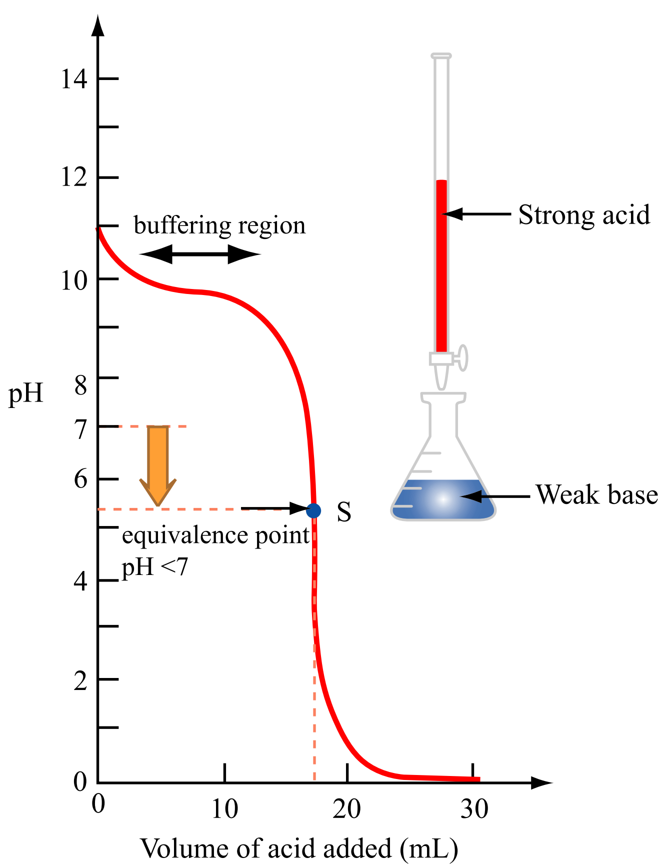

Figure by MIT OpenCourseWare.

$V = 0$ **weak base in water**

B B B B

$0 < V < V_{eq}$ **buffer**

HB^+ B B B

$V=V_{half\ eq}$ **special category of buffer**

HB^+ HB^+ $=$ B B

$V = V_{eq}$ **(salt) conj. acid of weak base**

HB^+ HB^+ HB^+ HB^+

$V > V_{eq}$ **strong acid in water**

Example: Titration of weak acid with strong base
25.0 mL of 0.10 M HCOOH with 0.15 M NaOH ($K_a = 1.77 \times 10^{-4}$ for HCOOH)

1. Volume = 0 mL of NaOH added
Before any NaOH is added, the problem is that of an ionization of a weak acid in water.

$$HCOOH\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + HCO_2^-\ (aq)$$

	HCOOH (aq)	H_3O^+ (aq) +	HCO_2^- (aq)
initial molarity	0.10 M	0	0
change in molarity	-x	+x	+x
equilibrium molarity	0.10-x	x	x

$K_a = 1.77 \times 10^{-4} = (x)^2/(0.10-x) \sim= (x)^2/0.10$

x = 0.00421 (check 0.00421 is 4.2% of 0.10) okay

pH = -log [0.00421] = 2.38 (to how many sig figs?)

2. $0 < V < V_{eq}$
In this range, the acid has been partly ionized by the strong base (buffering region).

Calculate the pH of the solution resulting from the addition of 5.0 mL of 0.15 M NaOH.
Because OH^- is a stronger base than HCO_2^-, it reacts almost completely with HCOOH.
$HCOOH\ (aq) + OH^-\ (aq) \rightarrow H_2O\ (l) + HCO_2^-\ (aq)$ K>>1

Initial Moles

For HCOOH, $(25.0 \times 10^{-3}\ L)(0.10M) = 2.5 \times 10^{-3}$ moles

For OH^-, $(5.0 \times 10^{-3}\ L)(0.15M) = 0.75 \times 10^{-3}$ moles

Moles after Reaction

2.5×10^{-3} moles - 0.75×10^{-3} moles = 1.75×10^{-3} moles of HCOOH left

0.75×10^{-3} moles OH^- produces ______________of HCO_2^-

Molarity

1.75×10^{-3} moles of HCOOH/ (0.0250 + 0.0050 L) = 0.0583 M HCOOH

0.75×10^{-3} moles of HCO_2^- / (0.0250 + 0.0050 L) = 0.0250 M HCO_2^-

Option 1

	HCOOH	H_3O^+ +	HCO_2^-
initial molarity	0.0583	0	0.0250
change in molarity	-x	+x	+x
equilibrium molarity	0.0583 -x	+x	0.0250 + x

$K_a = 1.77 \times 10^{-4} = \frac{(0.0250 + x)(x)}{(0.0583 - x)}$ assume x is small $\sim= \frac{0.0250x}{0.0583}$

$x = 4.13 \times 10^{-4}$

Check assumption: 4.13×10^{-4} is 1.65% of 0.025 and is 0.7% of 0.0583 okay

pH = -log [4.13×10^{-4}] = 3.38

Option 2

pH ~= pK_a - log ([HA]/[A^-])

pH ~= 3.75 - log ([0.0583]/[0.0250]) = 3.75 - 0.368 = 3.38

check assumption: for a pH of 3.38, [H_3O^+] = 4.2×10^{-4} and that is <5% of 0.0583 and is <5% of 0.0250. Okay

If the 5% assumption is not valid, than option 1 must be used and

$K_a = 1.77 \times 10^{-4} = (0.0250 + x)(x)/(0.0583 - x)$ can not be simplified.

Must solve by quadratic equation.

Note: when the volume of NaOH added is between 0 and the equivalence volume V_{eq}, the problems are similar to buffer problems. This region of the titration curve is called the "buffering region."

Half-equivalence point

When the volume of NaOH added is equal to half the equivalence volume, [HA] = [A^-].

pH ~= pK_a - log ([HA]/[A^-])
pH ~=pKa -log (1)
pH ~=pKa

3. $V = V_{eq}$

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 salt formed during the neutralization process. HCOOH and NaOH form $NaHCO_2$ and H_2O. Na^+ has ___________ on pH and HCO_2^- is ___________. Thus at the equivalence point, the pH is >7.

Calculate the pH at the equivalence point

Calculate total volume at equivalence point

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

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

Total volume = 0.0250 L + 0.0167 L = 0.0417 L

Molarity of HCO_2^-

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

This is an ionization of **weak base** in water problem.

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

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 x 10^{-6} M. Then calculate pOH = 5.74. From pOH, calculate pH.
pH = 8.26 (which is >7)

4. $V > V_{eq}$

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 x 10^{-6} M), the pOH and pH are determined by the amount of excess NaOH added. This problem is similar to a strong acid/strong base problem.

At 5.00 mL past the equivalence point:

0.00500 L x 0.15 M = 7.5 x 10^{-4} moles excess OH^-

7.5 x 10^{-4} moles OH^- /(0.00500 L + 0.0250 L+ 0.0167 L) = 0.016 M OH^-

pOH = -log [0.16] = 1.79

pH = 12.21

Today's material

OXIDATION/REDUCTION REACTIONS
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. For 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

Definitions
Oxidation -
Reduction -
Oxidizing agent -
Reducing agent -

Disproportionation Reaction

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

$NaClO \Rightarrow NaClO_3 + NaCl$ in basic solution

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

$ClO^- \Rightarrow ClO_3^-$

$ClO^- \Rightarrow Cl^-$

Balancing Redox Reactions (Ch12.2)

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 (Book has a different approach. You can use either.)

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

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