

## CHEM 116

### Molecular Structure, Acid Strength

November 16, 2006  
Prof. Sevian



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### Agenda

- A closer look at titration
  - Titration endpoint/equivalence point
  - Buffer region of a titration
  - When its ok to use Henderson-Hasselbach equation
  - Titrating polyprotic acids
- How molecular structure influences acid strength
- Lewis theory
- Group problem
  
- Exam #3 is on Tuesday. Do NOT forget to bring a calculator!
  
- The **final exam** is scheduled for Monday, December 18, 11:30AM-2:30PM. Location TBA.

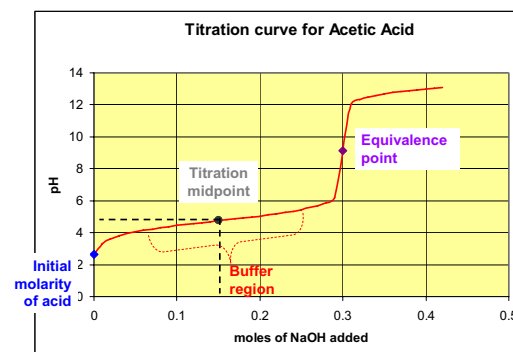
### There are only 3 ways to prepare a buffer

Goal: to create approximately equal quantities of weak acid and its conjugate base in the same solution

1. Add 1 part HA and 1 part A<sup>-</sup> to water at the same time.
2. Add 1 part HA and 0.5 parts OH<sup>-</sup> to water. The OH<sup>-</sup> will react and convert 0.5 part of the HA to its conjugate, leaving 0.5 parts HA and 0.5 parts A<sup>-</sup>.
3. Add 1 part A<sup>-</sup> and 0.5 parts H<sup>+</sup> to water. The H<sup>+</sup> will react and convert 0.5 part of the A<sup>-</sup> to its conjugate, leaving 0.5 parts A<sup>-</sup> and 0.5 parts HA.

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### Main points about titration



### What's so special about the titration midpoint?

- It's in the buffer region
- It is where you have added exactly 0.5 parts of strong base for 1 part of weak acid
- So, stoichiometry predicts these initial conditions:

	$\text{CH}_3\text{COO}^- (aq) + \text{H}_2\text{O} (l) \rightleftharpoons \text{OH}^- (aq) + \text{CH}_3\text{COOH} (aq)$		
	0 M	0.150 M	0.300 M
	+ 0.150	- 0.150	- 0.150
Initial conditions	0.150	$10^{-7}$	0.150
Change	- x	+ x	+ x
Equilibrium	$0.150 - x \approx 0.150$	y	$0.150 + x \approx 0.150$

- Carrying this further, to the equilibrium point:

### At the titration midpoint

$$K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} = [\text{OH}^-] \quad \text{but ONLY at the titration midpoint}$$

What does this mean?

$$K_b = [\text{OH}^-] \quad \text{means}$$

$$pK_b = p\text{OH}$$

so

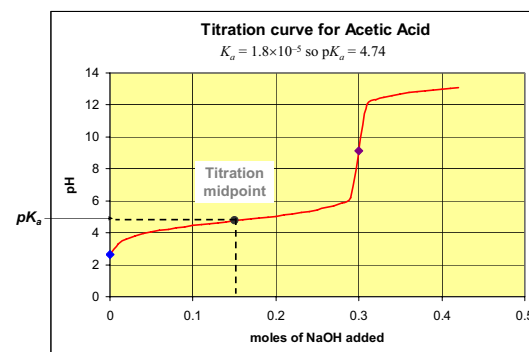
$$pK_w - pK_a = pK_w - p\text{H}$$

or

$$pK_a = p\text{H} \quad \text{but only at the titration midpoint!}$$

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### Titration midpoint on the titration curve



### Titration of a polyprotic acid (e.g., $\text{H}_2\text{C}_2\text{O}_4$ )

Starting with 100 mL of 0.100 M oxalic acid and adding 0.100 M NaOH to it

and

Adding 0.100 M NaOH to it

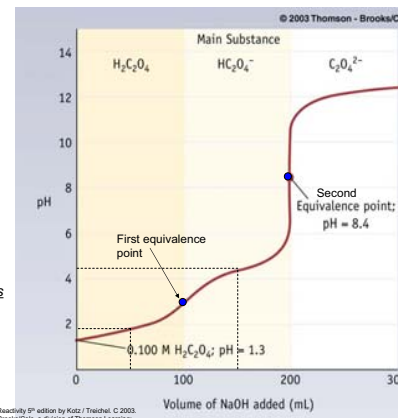
*Titration midpoints*

$$K_{a1} = 5.9 \times 10^{-2}$$

$$pK_{a1} = 1.23$$

$$K_{a2} = 6.4 \times 10^{-5}$$

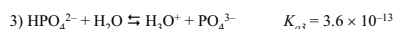
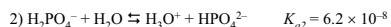
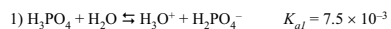
$$pK_{a2} = 4.19$$



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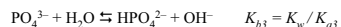
### More about polyprotic acids

Example: phosphoric acid is triprotic



Conclusions:

- The first proton is the dominant reaction and produces the vast majority of the acidity of a phosphoric acid solution
- If phosphate were added to water, the first ionization step



would produce the vast majority of the OH<sup>-</sup> in the resulting basic solution

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### Example: pH of a solution of polyprotic acid

Exercise 16.13, pp. 692-693

What is the pH of a 0.10 M solution of oxalic acid, H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>?

What are the concentrations of H<sub>3</sub>O<sup>+</sup>, HC<sub>2</sub>O<sub>4</sub><sup>-</sup>, and oxalate ion C<sub>2</sub>O<sub>4</sub><sup>2-</sup>?  $K_{a1} = 5.9 \times 10^{-2}$ ,  $K_{a2} = 6.4 \times 10^{-5}$

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### Henderson-Hasselbalch equation is valid in buffer region only!

(K <sub>b</sub> equation)	A <sup>-</sup> (aq) + H <sub>2</sub> O (l) ⇌	OH <sup>-</sup> (aq) +	HA (aq)
Initial	[A <sup>-</sup> ] <sub>0</sub>	10 <sup>-7</sup>	[HA] <sub>0</sub>
Change	-x	+x	+x
Equilibrium	[A <sup>-</sup> ] <sub>0</sub> - x ≈ [A <sup>-</sup> ] <sub>0</sub>	10 <sup>-7</sup> + x = y	[HA] <sub>0</sub> + x ≈ [HA] <sub>0</sub>

Henderson-Hasselbalch equation is just the approximation that x is small compared to [A<sup>-</sup>]<sub>0</sub> and [HA]<sub>0</sub>

$$K_b = \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]} = \frac{([\text{HA}]_0 - x)[\text{OH}^-]}{([\text{A}^-]_0 + x)} \approx \frac{[\text{HA}]_0[\text{OH}^-]}{[\text{A}^-]_0}$$

Rearranging,

$$[\text{OH}^-] = K_b \left( \frac{[\text{A}^-]_0}{[\text{HA}]_0} \right) \Rightarrow \text{pOH} = \text{p}K_b + \log \left( \frac{[\text{A}^-]_0}{[\text{HA}]_0} \right)$$

### The small x approximation with a buffer

(K <sub>b</sub> equation)	A <sup>-</sup> (aq) + H <sub>2</sub> O (l) ⇌	OH <sup>-</sup> (aq)	HA (aq)
Initial	[A <sup>-</sup> ] <sub>0</sub>	10 <sup>-7</sup>	[HA] <sub>0</sub>
Change	-x	+x	+x
Equilibrium	[A <sup>-</sup> ] <sub>0</sub> - x ≈ [A <sup>-</sup> ] <sub>0</sub>	10 <sup>-7</sup> + x = y	[HA] <sub>0</sub> + x ≈ [HA] <sub>0</sub>

- If the equilibrium constant (in this case K<sub>b</sub>) is very small, then very little A<sup>-</sup> will hydrolyze, so x will be small
- If x is small, then subtracting or adding it to the A<sup>-</sup> and HA concentrations will not affect them very much, so the A<sup>-</sup> and HA concentrations at equilibrium will not be very different from what they were initially
- At equilibrium, the OH<sup>-</sup> concentration will be some value, call it y
- Since x no longer appears in the equilibrium concentrations, you have only one variable to solve for (y)

### Henderson-Hasselbalch equation/approximation

Only works when:

- Approximately equal quantities of HA and A<sup>-</sup> present (*i.e.*, buffer region)
- The small  $x$  approximation must be valid

$$pOH = pK_b + \log\left(\frac{[A^-]_0}{[HA]_0}\right)$$

$$pH = pK_a + \log\left(\frac{[A^-]_0}{[HA]_0}\right)$$

- Advice: don't use the H-H equation unless you are absolutely sure you are in the region where it is valid

### Let's say you want to make a buffer solution

What do you need to consider?

- What pH do you need the buffer to hold?
- How robust do you want the buffer to be?
- What chemicals could be used to make a buffer?
- What chemicals do you have available?

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### An authentic buffer problem

You desire to make a buffer with pH 3.50. The buffer needs to be able to withstand dilution (adding water) and addition of small amounts (0.01 moles) of strong acid or base. The chemicals you have available are:

- Acetic acid and sodium acetate
- Citric acid and sodium citrate
- Oxalic acid, sodium hydrogen oxalate, and sodium oxalate
- Monosodium hydrogen phosphate, disodium hydrogen phosphate, and sodium phosphate

Which two chemicals should you choose, and in what quantities?

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### An authentic titration problem



- You have a weak acid (monoprotic) solution of known concentration and a strong base (monohydroxide) solution of unknown concentration. You wish to find out the concentration of the strong base solution.
- The concentration of weak acid is 0.100 M. The  $K_a$  value is  $4.5 \times 10^{-4}$
- Which indicator is appropriate?
- How should the titration proceed? (Which solution goes in the Erlenmeyer flask, and which goes in the burette?)

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### Key points about titration and buffers

- Always ask yourself first if the acid and base are weak and/or strong
- There are four regions in a titration:
  - Before any titrant has been added: concentrations of chemicals determined by  $K_a$  or  $K_b$  equation for whatever the **analyte** is
  - Buffer region where near equal molar amounts of conjugate acid and base present, range is  $\pm 1$  pH from  $pK_a$  (or  $pK_b$ ): use equilibrium calculation/ICE chart or H-H equation
    - Titration midpoint is halfway to equivalence point and is where perfect buffer exists
    - At titration midpoint,  $pH = pK_a$  (or  $pOH = pK_b$ )
  - Equivalence point where moles acid = moles base: if not strong acid + strong base, then use equilibrium for hydrolysis reaction
  - Beyond equivalence point where excess titrant: figure out how much titrant in excess
- Use an indicator that changes color near the equivalence pt

### Molecular structure informs properties of acids

- Binary acids (HX where X is a nonmetal)
- Oxoacids (formula  $HOXO_n$  where X is a nonmetal)
- Carboxylic acids ( $RCOOH$  where R is a carbon group)

The question is – how easily can the  $H^+$  be let go?

Answer always depends on how much electron density gets drawn away from the H in the acid molecule

Look for the one feature that differs and therefore must be responsible for the trend

Arguments can depend on:

- Comparing sizes of atoms when  $H^+$  is to be removed from a single atom (leaving behind X)
- Comparing electronegativities of nonmetals when structures are the same
- Looking at “formal charges” of all atoms when structures differ to gauge where electron density is being drawn to

### Compare binary acids

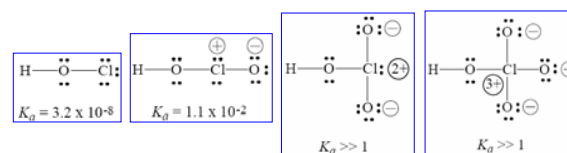
Ordered according to  $K_a$  value (smallest  $K_a$  value on left)

- $HF < HCl < HBr < HI$
- $H_2O < H_2S < H_2Se$
- $H_3N$  (usually written  $NH_3$ )  $< H_2O < HF$

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### Compare oxoacids ( $HOXO_n$ )

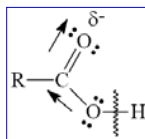
- Compare formulas  $HOX$   
 $HOI < HOBr < HOCl$
- Compare  $HOXO_n$   
 $HOCl < HOClO < HOClO_2 < HOClO_3$



### Compare carboxylic acids

Effect of "acidifying" the H can be accomplished by placing electron-hungry atoms within the R group

Acid	$K_a$
$\text{CH}_3\text{CO}_2\text{H}$	$1.77 \times 10^{-5}$
$\text{BrCH}_2\text{CO}_2\text{H}$	$2.05 \times 10^{-3}$
$\text{ClCH}_2\text{CO}_2\text{H}$	$1.40 \times 10^{-3}$
$\text{Cl}_2\text{CHCO}_2\text{H}$	$3.32 \times 10^{-2}$
$\text{Cl}_3\text{CCO}_2\text{H}$	$2 \times 10^{-1}$
$\text{F}_3\text{CCO}_2\text{H}$	$5 \times 10^{-1}$

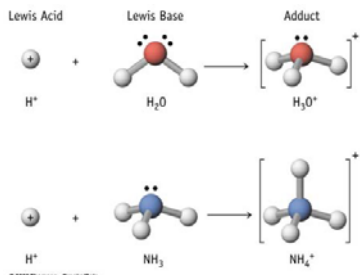


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### Lewis acids and bases

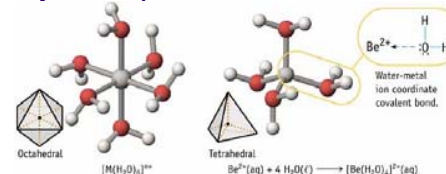
- Lewis acid = accepts a pair of electrons
- Lewis base = donates a pair of electrons

Definition is more general than Bronsted-Lowry



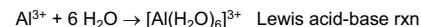
From Chemistry & Chemical Reactivity, 9e, edited by AGEL, Trovati, C. 2003. Macmillan/McGraw-Hill, a division of The McGraw-Hill Companies. ISBN 0-07-296215-5.

### Metal cations form complexes with water in a "hydration sphere"

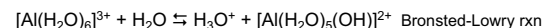


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Most metal cations have 6 waters in the hydration sphere



Since O's electron lone pairs are busy being attracted to the metal cation, it is relatively easy for an  $\text{H}_2\text{O}$  to let go of an  $\text{H}^+$



### Group Problem

Formic acid ( $\text{HCO}_2\text{H}$ ) has  $K_a = 1.9 \times 10^{-4}$ . Begin with 0.200 moles of formic acid in 1.00 L of solution. Gradually add NaOH to the solution while titrating the acid solution. (Assume that the addition of titrant affects the total volume of solution negligibly.)

- What is the pH of the initial 0.200 M solution of formic acid?
- What is the pH after 0.100 moles of NaOH have been added to the solution?
- What is the pH after 0.200 moles of NaOH have been added to the solution?
- What is the pH after 0.300 moles of NaOH have been added to the solution?
- Sketch the titration curve. Label the equivalence point.