CHEM 116

Titration, Buffers and the Common Ion Effect

November 14, 2006
Prof. Sevian

Reminder: please wait until 2:25 to enter the lecture hall today, to allow the class before us to finish taking an exam.

Agenda

- Mixing (titrating) a weak + strong combination of acid + base
  - When mixed in equal molar quantities
  - When there is an excess of the strong one
  - When there is not enough of the strong one to use up all of the weak one in reaction
  - How this relates to titration
- Common ion effect
- 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
- Thurs: How molecular structure influences acid strength, Lewis theory, and Group problem

The **final exam** is scheduled for Monday, December 18, 11:30AM-2:30PM. Location TBA.

Mixing an acid with a base (in water)

1. Strong acid (H^+) + strong base (MOH)
2. Weak acid (HA) + strong base (MOH)
3. Strong acid (H^+) + weak base (B)
4. Weak acid (HA) + weak base (B)

Mixing a weak acid + strong base: 3 possibilities

1. Equal molar quantities mixed: reaction proceeds to completion and conjugate base of the weak acid then hydrolyzes
   - Example: What is the pH if you add 0.300 moles of CH_3COOH and 0.300 moles of NaOH to 1.00 L of water?
2. Excess strong base: all the weak acid is used up, remaining base dominates pH
   - Example: What is the pH if you add 0.300 moles of CH_3COOH and 0.400 moles of NaOH to 1.00 L of water?
3. Not enough strong base to react with all of the weak acid: base converts some of the weak acid to its conjugate base and some weak acid is left unreacted; solution contains both weak acid and its conjugate base – this is a buffer
   - Example: What is the pH if you add 0.300 moles of CH_3COOH and 0.200 moles of NaOH to 1.00 L of water?

What is a buffer?

Macroscopic observation: A solution that resists changes in pH when small amounts of acid or base are added.

Particle-level explanation: Both a weak acid (HA) and its own conjugate base (A^-) are present in solution at similar concentrations (within an order of magnitude of each other)

How does it do this?

- Since both the weak acid and its conjugate are present:
  - If H^+ is added, it reacts with the weak base to produce more conjugate acid
  - If OH^- is added, it reacts with the weak acid to produce more conjugate base

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

Speciation

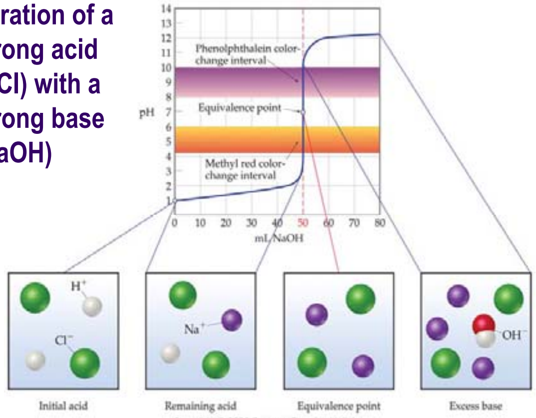
- The concept that at equilibrium there are stable quantities of several different chemicals present simultaneously
- The key to solving a problem is to figure out which species are present, and then choose to use either the K_a equation or the K_b equation

Common ion effect

- A fancy way of stating that a solution has significant (not near zero) amounts of more than one species that is part of K_{eq}
- Examples:
  - Add some HA and some A^- to water
  - Add some HNO_3 and some $NaNO_3$ to water
- If you start first with a weak acid solution, and then add some soluble salt containing the conjugate base of that weak acid, le Chatelier's principle predicts that reaction shifts toward acid to come back to equilibrium

1) Start with $CH_3COOH + H_2O \leftrightarrows CH_3COO^- + H_3O^+$ at equilibrium
2) Then add some $NaCH_3COO$ (which breaks into Na^+ and CH_3COO^- when it dissolves)
3) Reaction shifts toward reactants to try to un-do the disturbance

Titration of a strong acid (HCl) with a strong base (NaOH)



Consider a starting solution of 0.300 moles of acetic acid in 1.00 L of water

There are three equilibrium reactions that are simultaneously at fast equilibrium. Only two are mathematically independent.

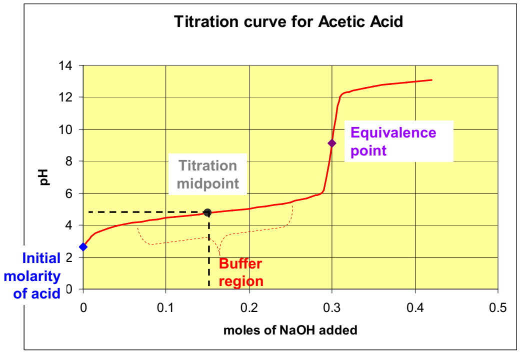
$2\ H_2O \leftrightharpoons H_3O^+ + OH^-$ $\quad K_w$

$CH_3COOH + H_2O \leftrightharpoons CH_3COO^- + H_3O^+$ $\quad K_a$

$CH_3COO^- + H_2O \leftrightharpoons CH_3COOH + OH^-$ $\quad K_b$

- What is the initial pH?
- What is the pH after the solution comes to equilibrium after adding 0.200 moles of NaOH?
- What is the equilibrium pH after adding 0.300 moles of NaOH? Equivalence point! (Why is it called this? What is equivalent?)
- What is the equilibrium pH after adding 0.400 moles of NaOH?

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:

	$CH_3COO^-\ (aq)$	$+\ H_2O\ (l)$	$\leftrightharpoons$	$OH^-\ (aq)$	$+$	$CH_3COOH\ (aq)$
	0 M			0.150 M		0.300 M
	+ 0.150			- 0.150		- 0.150
Initial conditions	0.150			0		0.150

- Carrying this further, to the equilibrium point:

Change	- x			+ x		+ x
Equilibrium	0.150–x ≈ 0.150			0		0.150+x ≈ 0.150

At the titration midpoint

$$K_b = \frac{[\mathrm{CH_3COOH}][\mathrm{OH^-}]}{[\mathrm{CH_3COO^-}]} = [\mathrm{OH^-}] \quad \textit{but ONLY at the titration midpoint}$$

What does this mean?

$K_b = [\mathrm{OH^-}]$ *means*

$pK_b = p\mathrm{OH}$

so

$pK_w - pK_a = pK_w - \mathrm{pH}$

or

$pK_a = \mathrm{pH}$ *but only at the titration midpoint!*

Titration of a polyprotic acid (*e.g.*, $H_2C_2O_4$)

Starting with 100 mL of 0.100 M oxalic acid

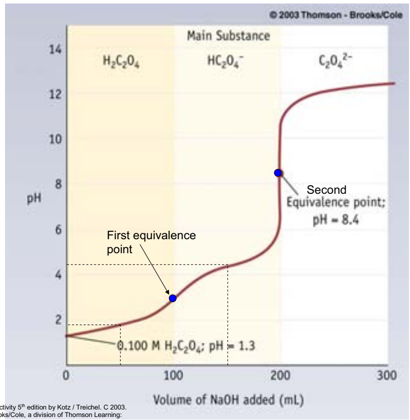
and

Adding 0.100 M NaOH to it

Titration midpoints

K_{a1} = 5.9x10^{-2}
pK_{a1} = 1.23

K_{a2} = 6.4x10^{-5}
pK_{a2} = 4.19



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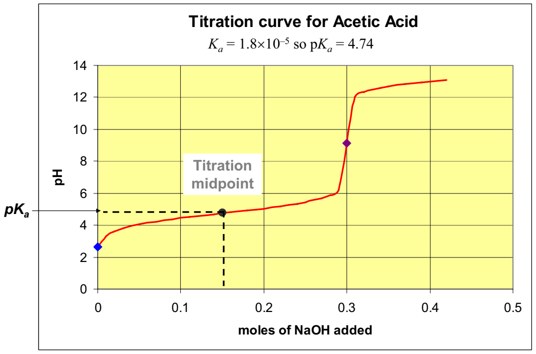
Titration midpoint on the titration curve



More about polyprotic acids

Example: phosphoric acid is triprotic

1) $H_3PO_4 + H_2O \leftrightarrows H_3O^+ + H_2PO_4^-$ $\quad K_{a1} = 7.5 \times 10^{-3}$

2) $H_2PO_4^- + H_2O \leftrightarrows H_3O^+ + HPO_4^{2-}$ $\quad K_{a2} = 6.2 \times 10^{-8}$

3) $HPO_4^{2-} + H_2O \leftrightarrows H_3O^+ + PO_4^{3-}$ $\quad K_{a3} = 3.6 \times 10^{-13}$

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

  $$PO_4^{3-} + H_2O \leftrightarrows HPO_4^{2-} + OH^- \qquad K_{b3} = K_w / K_{a3}$$

  would produce the vast majority of the OH^- in the resulting basic solution

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, $H_2C_2O_4$? What are the concentrations of H_3O^+, $HC_2O_4^-$, and oxalate ion $C_2O_4^{2-}$? $K_{a1} = 5.9\times10^{-2}$, $K_{a2} = 6.4\times10^{-5}$

Henderson-Hasslebalch equation/approximation

Only works when:

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

$$p\text{OH} = pK_b + \log\left(\frac{[\text{A}^-]_o}{[\text{HA}]_o}\right)$$

$$p\text{H} = pK_a + \log\left(\frac{[\text{A}^-]_o}{[\text{HA}]_o}\right)$$

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

Henderson-Hasslebalch equation is valid in buffer region only!

(K_b equation)	$A^-(aq)$	+	$H_2O(l)$	⇆	$OH^-(aq)$	+	$HA(aq)$
Intial	$[A^-]_o$				0		$[HA]_o$
Change	$-x$				$+x$		$+x$
Equilibrium	$[A^-]_o - x \approx [A^-]_o$				x		$[HA]_o + x \approx [HA]_o$

Henderson-Hasslebalch equation is just the approximation that x is small compared to $[A^-]_o$ and $[HA]_o$

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

Rearranging,

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

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?

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:

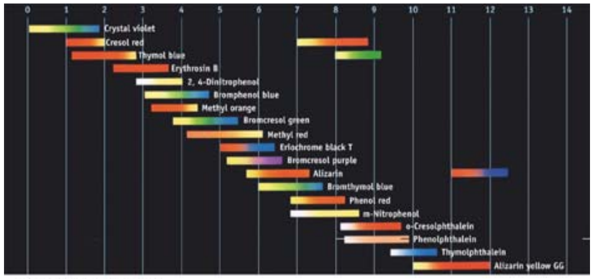
- Acetic acid and sodium acetate
- Citric acid and sodium citrate
- Oxalic acid, sodium hydrogen oxalate, and sodium oxalate
- Monosodium hydrogen phosphate, disodium hydrogen phosphate, and sodium phosphate

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

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 4.5×10^{-4}
- Which indicator is appropriate?
- How should the titration proceed? (Which solution goes in the Erlenmeyer flask, and which goes in the burette?)

Indicators



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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:
  1. Before any titrant has been added: concentrations of chemicals determined by Ka or Kb equation for whatever the titrant is
  2. Buffer region where near equal molar amounts of conjugate acid and base present, range is ±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 that point, pH = pK_a (or pOH = pK_b)
  3. Equivalence point where moles acid = moles base: if not strong acid + strong base, then use equilibrium for hydrolysis reaction
  4. Beyond equivalence point where excess titrant: figure out how much titrant in excess
- Use an indicator that changes color near the equivalence pt