CHEM 116
Measuring Acid-Base Equilibria

November 9, 2006
Prof. Sevian

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Agenda

- Mathematical relationships
  - Converting between pH and $[H^+]$
  - Using equilibrium constant for water (K_w) to calculate $[OH^-]$
  - Relationship between K_a, K_b and K_w
- Equilibrium in acid-base systems
  - Strong acid + strong base
  - Weak acid + strong base
  - Strong acid + weak base
  - Weak acid + weak base
- Adding acids and bases to water
  - Strong vs. weak
  - Calculating pH, and concentrations of all other species present
  - Adding “salts” to water, also known as hydrolysis reactions

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

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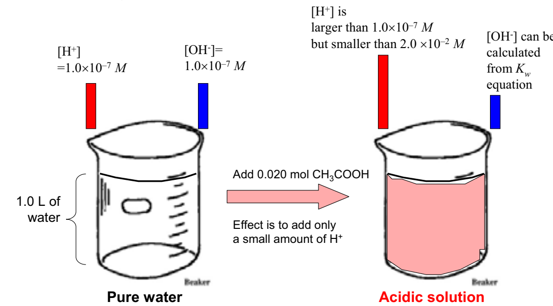
What happens when you add a weak acid (or base) to water?

It dissociates, but only partially, because K_a (or K_b) is small. In other words, not all the HA reacts.



How much does a weak acid or base dissociate?

You must use equilibrium calculations to solve this. You need to know K_a to solve the problem.

Example: If you added 0.020 moles of CH_3COOH to water, what would be the pH? $K_a = 1.8 \times 10^{-5}$

	$CH_3COOH\ (aq)$	$+ H_2O\ (l)$	$\rightleftarrows$	$H_3O^+\ (aq)$	$+$	$CH_3COO^-\ (aq)$
Initial	0.020 M			1.0×10^{-7} M		0 M
Change	$-x$			$+x$		$+x$
Equilibrium	$0.020 - x$			$1.0\times10^{-7} + x$		x

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$$

$$1.8\times10^{-5} = \frac{x\left(1.0\times10^{-7} + x\right)}{0.020 - x}$$

Solving this exactly yields $x = 6.0\times10^{-4}$ which means pH = 3.22

There are two important approximations that can simplify the calculations…

Approximations

The amount of H^+ present in neutral water (1.0×10^{-7} *M*) is negligible compared to the amount of H^+ contributed by adding the weak acid (or base) to water.
That is, the value of x is much larger than 1.0×10^{-7}

	$CH_3COOH\ (aq)$ + $H_2O\ (l)$	⇆ $H_3O^+\ (aq)$	+ $CH_3COO^-\ (aq)$
Initial	0.020 M	1.0×10^{-7} M	0 M
Change	$-x$	$+x$	$+x$
Equilibrium	≈ 0.020	$\approx x$	x

The amount that the weak acid dissociates is negligible compared to the amount of acid that remains.
That is, the starting amount of acid is much greater than the value of x.

Recall that an exact solution for x yielded $x = 6.0\times10^{-4}$, or 0.00060. So, are these assumptions justified?

In general, when are the assumptions justified?

Comparing strong and weak acids

Strong acid	Weak acid
0.020 M HCl solution	0.020 M CH_3COOH solution
• Acid dissociates completely	• Acid does not dissociate completely • Need to know K_a to solve • Must use equilibrium calculation to solve
• $[H^+]$ is equal to [HCl]	• $[H^+] \approx \sqrt{C_A \cdot K_a}$
• $[H^+]$ = 0.020 M	= 0.00060 M
• pH = 1.70	• pH = 3.22

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How to recognize strong vs. weak acids

Memorize the strongest acids
- All halides except fluoride: HCl, HBr, HI
- Nitric acid: HNO_3
- Sulfuric acid (only the first H^+): H_2SO_4
- Perchloric acid: $HClO_4$

Weak acids are listed in the K_a table

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Adding a "salt" to water

- Is the salt a conjugate of a strong acid/base or of a weak acid/base?
- If it is a salt of a strong acid or base, then nothing will happen (like adding table salt to water – no change in pH).
- If it is a conjugate of a weak acid or base, then the "salt" is itself also a weak base or acid. So it hydrolyzes and makes some H^+ or OH^-, which changes the pH.

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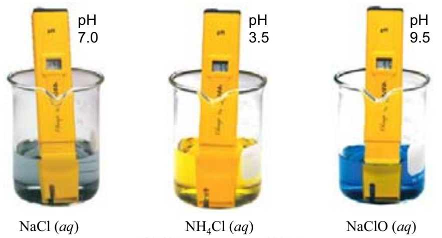
Acid-base properties of salt solutions: hydrolysis



When you add a salt to water, if it is soluble to any extent, it breaks apart into its constituent + and – ions. These ions can be weak acids or weak bases themselves. If they are, they "hydrolyze" to form either H^+ or OH^-, which changes the pH away from neutral pH 7 of the water.

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Hydrolysis of a salt: comparing weak vs. strong

Salt of a strong acid

- What is the pH of a 0.020 M solution of NaBr?
- Is Na^+ a conjugate of anything? No.
- Is Br^- a conjugate of anything? Yes. Of HBr.
- Is HBr strong or weak?
- HBr is a strong acid, so Br^- is a very weak base.

$$Br^- + H_2O \leftrightarrows HBr + OH^-$$

- K_a for HBr is very large, so K_b for Br^- is very small.
- Equilibrium lies so strongly to the left that OH^- does not get produced in significant enough quantity to rival 1.0×10^{-7} M that exists in water.

Salt of a weak acid

- What is the pH of a 0.020 M solution of NaBrO?
- Is Na^+ a conjugate of anything? No.
- Is BrO^- a conjugate of anything? Yes. Of HBrO.
- Is HBrO strong or weak?
- HBrO is a weak acid, so BrO^- is a weak base, but not very weak.

$$BrO^- + H_2O \leftrightarrows HBrO + OH^-$$

- K_a for HBrO is 2.5×10^{-9}, so K_b for BrO^- is 4.0×10^{-6}.
- Rxn occurs to enough extent that OH^- gets produced in significant enough quantity to make solution basic.

Mixing an acid with a base (in water)

1. Strong acid + strong base
   - Fast rxn: Strong acid dissociates completely into H^+ and something
   - Fast rxn: Strong base dissociates completely into something and OH^-
   - Fast rxn: H^+ and OH^- produce water
   - Whichever one (H^+ or OH^-) there is more left over of determines the pH of the solution (calculated as moles of it per liter of solution, just like in strong acid/base problem)

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Mixing an acid with a base (in water)

2. Weak acid (HA) + strong base (MOH)
   - Fast rxn: Strong base dissociates completely into M^+ and OH^-
   - Fast rxn: $HA + OH^- \leftrightarrows A^- + H_2O$
     Proceeds nearly to completion because OH^- is strong
   - What's left over?

   1. If HA and OH^- were initially added in equal molar quantities ⇒ solution is just as if some amount of A^- were initially added to water
   2. If original moles HA < original moles OH^- ⇒ excess OH^-, therefore $[OH^-]$ can be calculated as moles of remaining OH^- per liter of solution
   3. If original moles HA > original moles OH^- ⇒ only some of the HA reacts to produce A^-, and solution contains significant quantities of both HA and A^- (buffer, ch. 17)

Mixing an acid with a base (in water)

3. Strong acid (H^+) + weak base (B)
   - Analogous but opposite: $B + H_3O^+ \leftrightarrows HB^+ + H_2O$ favors products
   - What's left over?

1. If strong acid and weak base were initially added in equal molar quantities ⇒ solution is just as if some amount of HB^+ were initially added to water
2. If original moles H^+ > original moles B ⇒ excess H^+, therefore $[H^+]$ can be calculated as moles of remaining H^+ per liter of solution
3. If original moles H^+ < original moles B ⇒ only some of the B reacts to produce HB^+, and solution contains significant quantities of both B and HB^+ (buffer, ch. 17)

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?

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Mixing an acid with a base (in water)

4. Weak acid (HA) + weak base (B)
   - Both HA acid reaction and B base reaction occur
   - Overall K for reaction depends on both the K_a for the acid and the K_b for the base
   - pH of solution depends on what's left over

Key points about the mathematics of acid-base equilibria

- When strategizing how to solve an acid-base problem, you have to first figure out whether the acid and/or base is strong or weak
- A strong acid (or base) dissociates completely
- A weak acid (or base) does not, so you have to figure out the H^+ (or OH^-) concentration by doing an equilibrium calculation
- If you are given a solution that has both acid and base added to it, first figure out if strong or weak, then determine whether equal moles of each were added
  - Equal moles of each:
    - Strong acid + strong base → neutral
    - Strong acid + weak base → acidic
    - Weak acid + strong base → basic
  - More moles of the strong one:
    - If it was a strong acid, then pH acidic by however much excess acid
    - If it was a strong base, then pH basic by however much strong base
  - More moles of the weak one: buffer (next chapter)