CHEM 116
Acid-Base Equilibrium

Lecture 19
Prof. Sevian

Today's agenda

- Mathematical relationships
  - Converting between pH and $[H^+]$
  - Using equilibrium constant for water (K_w) to calculate $[OH^-]$
  - Using the mathematical relationships
    - between K_a, K_b and K_w
    - between K_w, $[H^+]$ and $[OH^-]$
- Equilibrium in acid-base systems
  - Strong vs. weak acids (and strong vs. weak bases)

<u>Announcements</u>

- There will be a graded extra credit assignment during discussion sections on Thursday Nov 20 and Tuesday Nov 25. You must attend discussion to do it.
- Next exam is Exam 3 on Tuesday, Dec 2 (first lecture after Thanksgiving break) – note date change from syllabus
- Final exam has been scheduled for Tuesday, Dec 16, 3:00pm

Key points about acids and bases so far

- Arrhenius definition is acids have H^+ while bases have OH^-
- Bronsted-Lowry definition encompasses Arrhenius definition, plus more
- Bronsted-Lowry definition focuses on transfer of proton (H^+) from acid to base
- Conjugate acid base pairs differ by an H^+
- General acid-base reaction has acid1 becoming base1, while simultaneously base2 becomes acid2: in other words, acid1 gives an H^+ to base1
- Acid ionization constant (K_a) is a measure of acid strength, when K_a is larger, the acid is stronger (it goes more toward products, which include H^+)
- The stronger the acid, the weaker its conjugate base, and vice versa
- $K_a K_b = K_w$ for any acid-base conjugate pair

Two clicker questions to practice what we went over in the previous lecture

1. Identify the acid on the left and its conjugate base on the right. Similarly, identify the base on the left and its conjugate acid on the right.

$$\underset{(a)}{HPO_4^{2-}\ (aq)} + \underset{(b)}{HCO_3^-\ (l)} \rightleftarrows \underset{(c)}{CO_3^{2-}\ (aq)} + \underset{(d)}{H_2PO_4^-\ (aq)}$$

2. Does the equilibrium lie primarily to the right or to the left?

Question 1

A = (a) is an acid, (c) is its conjugate base
(b) is a base, (d) is its conjugate acid

B = (b) is an acid, (c) is its conjugate base
(a) is an acid, (d) is its conjugate base

C = (a) is a base, (c) is its conjugate acid
(b) is a base, (d) is its conjugate acid

D = (b) is an acid, (d) is its conjugate base
(a) is a base, (c) is its conjugate acid

Question 2 data

HPO_4^{2-}	$K_a = 3.6 \times 10^{-13}$
HCO_3^-	$K_a = 5.61 \times 10^{-11}$
$H_2PO_4^-$	$K_a = 6.23 \times 10^{-8}$

Options for answers

A = equilibrium lies to the right

B = equilibrium lies to the left

What we measure in the laboratory is pH

- What is pH?
- How is it related to the H_3O^+ (aka, H^+) concentration?
- Why is it useful? What other things can you infer if you know the pH?

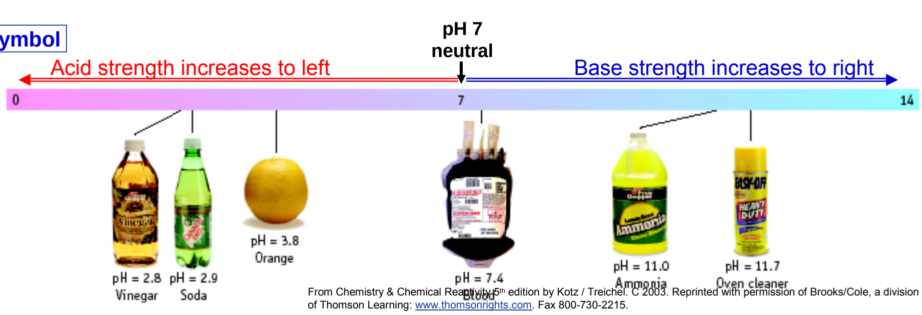
What is the pH scale?

Macro Provides information about whether a material (aqueous solution) is acid or base, and how strong it is

Particle Actually measures hydronium ion (H^+ or H_3O^+) concentration

- Hydrogen ions (H^+) do not actually exist in solution
- Instead, H^+ ions attach to water molecules and form H_3O^+ ions
- H_3O^+ ions are called <u>hydronium</u> ions
- Now that you know this, they are often abbreviated H^+

Symbol



What is pH?

The letter "p" stands for "the negative logarithm base-10 of"

Some symbols that you will see include pH, pOH, pK_a, pK_b and pK_w

pH = -log$_{10}$ $[H^+]$

pOH = -log$_{10}$ $[OH^-]$

pK_a = -log$_{10}$ $[K_a]$

pK_b = -log$_{10}$ $[K_b]$

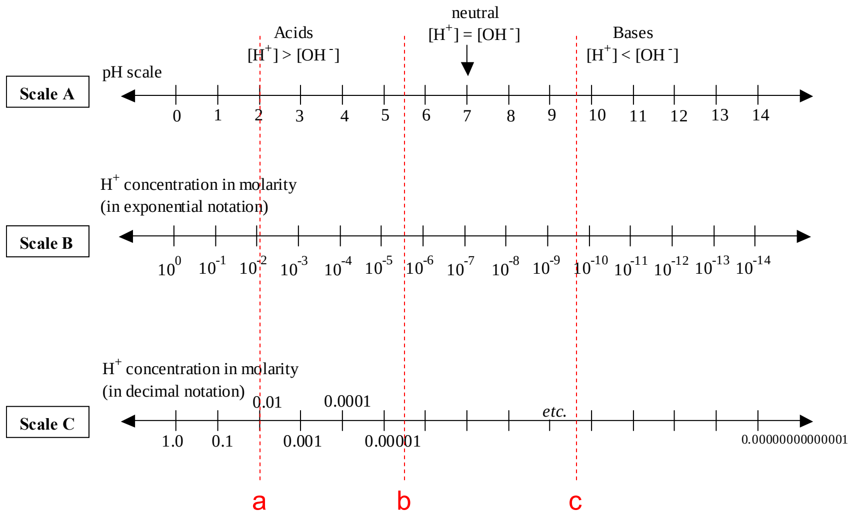
pK_w = -log$_{10}$ $[K_w]$

Review of Powers of 10 Math

- All numbers can be written as powers of 10. Most important to remember where the decimal point is.
  (Key: is it a big or small number? If big then exponent is positive. If small, then exponent is negative.)
  - $10{,}000 = 10^4$
  - $100 = 10^2$
  - $10 = 10^1$
  - $1 = 10^0$
  - $0.1 = 10^{-1}$
  - $0.001 = 10^{-3}$
  - $0.000001 = 10^{-6}$
- When multiplying two powers of 10, add the exponents. When dividing, subtract the exponents.
  $10^5 \times 10^{-2} = 10^{5+(-2)} = 10^3$
  $10^{-3} / 10^1 = 10^{(-3)-1} = 10^{-4}$

What does pH mean mathematically?

pH scale is a logarithmic scale



from Sevian et al, *Active Chemistry* (2006)

There are only three type of acid-base problems

1. Predict the pH: given the amount of acid, base and/or salt added to some water, predict the pH of the solution.
   - How you approach calculating the pH depends on what you added to the water, so that's the first thing you have to figure out
   - Variables are: strong or weak, acid or base
   - "Salts" in the Bronsted-Lowry scheme are actually acids or bases – their conjugates are more familiar to you
2. Equilibrium: given the measured pH of a solution, figure out how much acid, base or salt must have been added to some water to make the pH be that value.
   - These are always equilibrium problems
3. Titration: given a solution of unknown (acid or base) concentration, neutralize it with a known amount of (base or acid) to figure out the unknown concentration.
   - Involves stoichiometry since a neutralization reaction is occurring
   - If a weak acid or base is involved, it will also involve equilibrium calculations

What you need to be good at

<u>Concepts</u>

- Acid vs. base
- Figuring out conjugates
- Strong vs. weak
- Writing acid + water, and base + water, reactions and recognizing them as K_a and K_b reactions, respectively
- Applying strong/weak arguments to determine whether reactions go to completion

<u>Calculation skills</u>

- Molarity
- Comparing magnitudes of numbers to figure out when certain approximations will work
- Setting up an ICE table

Titration

Titration involving acid + base

You need an indicator to be able to tell when you reach the equivalence point

- Strong acid + strong base will have equivalence point of pH 7 (neutral)
- Strong acid + weak base will have equivalence point more acidic than pH 7 (i.e., pH < 7)
- Weak acid + strong base will have equivalence point more basic than pH 7 (i.e., pH > 7)

Basic idea: at equivalence point, moles of acid = moles of base

Predict pH

Adding strong acid or strong base to water

Not complicated. It just dissociates completely.
Strong acids include HCl, H_2SO_4, HNO_3, $HClO_4$ and HBr
Strong bases include most metal cations with OH^- ions

Examples:

- 1 mole of HCl turns into 1 mole of H^+ and 1 mole of Cl^-
- 1 mole of H_2SO_4 turns into 1 mole of H^+ and 1 mole of HSO_4^-
- (note that HSO_4^- is a weak acid, so you cannot assume it dissociates completely)
- 1 mole of NaOH turns into 1 mole of Na^+ and 1 mole of OH^-
- 1 mole of $Ba(OH)_2$ turns into 1 mole of Ba^{2+} and 2 moles of OH^-

To figure out [H^+] or [OH^-], calculate moles of it per liter of solution

A neat math trick to make it easier

- We know that K_w always equals 1.0×10^{-14} at 25ºC
  (note: K_w has a different value at different temperatures because K_w is an equilibrium constant so it depends on temperature)

- We also know that $K_w = [H^+]\,[OH^-]$

$$\begin{array}{ccccc}
K_w & = & [H^+] & \cdot & [OH^-] \\
1.0\times10^{-14} & = & [H^+] & \cdot & [OH^-] \\
-\log\left(1.0\times10^{-14}\right) & = & -\log\left([H^+]\right. & \cdot & \left.[OH^-]\right) \\
14 & = & -\log\left([H^+]\right) & + & -\log\left([OH^-]\right) \\
14 & = & pH & + & pOH
\end{array}$$

Example of strong base calculations

Similar to Practice Exercises, pp. 683-684

a) What is the pH of a 0.0012 M NaOH solution?

b) If the pH of a solution of the strong base $Sr(OH)_2$ is 10.46, what is the concentration of $Sr(OH)_2$ in mol/L?

Important distinction between strong and weak

- Strong acids (and bases) dissociate completely, so if you know the moles of acid (or base) you can determine the $[H^+]$ concentration (or $[OH^-]$)
- Weak acids do not dissociate completely, so you can't figure out their $[H^+]$ concentration from knowing how much acid you added. Must use equilibrium calculation with K_a
- Same idea for weak bases, but use K_b to get $[OH^-]$

Key points about acid-base equilibria

- The difference between a strong acid and a weak acid is that a strong acid dissociates completely into H^+ and A^-, while a weak acid dissociates only partially (and similar idea for bases)
- The general acid reaction has equilibrium constant K_a and is of the form $HA + H_2O \leftrightarrows A^- + H_3O^+$
- The general base reaction has equilibrium constant K_b and is of the form $B + H_2O \leftrightarrows HB^+ + OH^-$
- If you have an acid-base reaction, you can determine whether equilibrium lies to the left or right by comparing strengths of the acids via their K_a values
- pH is a logarithmic scale used for:
  - Reporting the $[H^+]$
  - Making calculations involving $[H^+]$ simpler

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? $K_a = 1.8 \times 10^{-5}$

	$CH_3COOH\ (aq)$	$+\ H_2O\ (l)$	$\leftrightarrows$	$H_3O^+\ (aq)$	$+$	$CH_3COO^-\ (aq)$
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

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

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

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}

	$CH_3COOH\ (aq)$ + $H_2O\ (l)$	$\leftrightarrows$ $H_3O^+\ (aq)$	+ $CH_3COO^-\ (aq)$
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
0.020 M HCl solution

- Acid dissociates completely
- $[H^+]$ is equal to [HCl]
- $[H^+]$ = 0.020 M
- pH = 1.70

Weak acid
0.020 M CH_3COOH solution

- Acid does not dissociate completely
- Need to know K_a to solve
- Must use equilibrium calculation to solve
- $[H^+] \approx \sqrt{C_A \cdot K_a}$ = 0.00060 M
- pH = 3.22

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

Acids and Bases in general: What you (will) need to be able to do

- Identify conjugate acid-base pairs and predict reactions
- Equilibrium
- Titration
- Buffers
  - Equations to use as shortcuts for solving problems

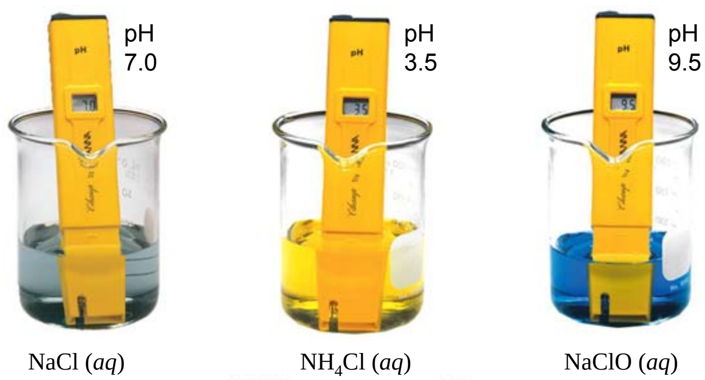
Strategies to master:

- Using the math tricks to solve problems
- Deciding on the right approach to solving a problem: recognizing acid-base equilibrium problems
- Recognizing hydrolysis reactions – “hydrolysis” is a fancy name for adding a weak acid or weak base to water (unfortunately referred to as a “salt” because it’s the conjugate that happens to be more familiar)

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.

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.

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.

$$\mathbf{Br^- + H_2O \leftrightarrows HBr + OH^-}$$

- 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.

$$\mathbf{BrO^- + H_2O \leftrightarrows HBrO + OH^-}$$

- 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.

Hydrolysis example

Exercise similar to 16.17, p. 701

Which of the following salts, when added to water, would produce the most acidic solution?

a) KBr
b) NH_4NO_3
c) $AlCl_3$
d) Na_2HPO_4