CHEM 116
Acid-Base Equilibria

November 7, 2006
Prof. Sevian

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Agenda

- **Acids and Bases** (ch. 16)
  - Recognizing/predicting conjugate acid-base pairs
  - Strong vs. weak acids and bases
  - Comparing strengths of weak acids or of weak bases
  - Predicting products of acid-base reactions using tabulated K_a values
- **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

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

A note about the group problem from last week

- Nearly all difficulties were with algebra
- As part of Assignment 9, I included algebra worksheets. These are optional – you can decide whether they are appropriate for your own needs. Their purpose is to help you increase speed and accuracy with solving algebra problems.

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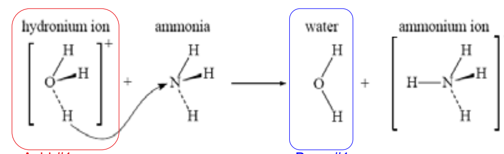
Conjugate acid-base pairs



Acid #1
Proton donor

Base #1
After Acid #1 (H_3O^+) donated the proton

Pair #1: an acid on one side and its conjugate base on the other side

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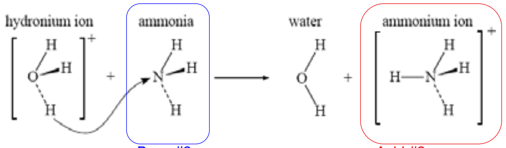
Conjugate acid-base pairs



Base #2
Proton
acceptor

Acid #2
After Base #2
(NH_3) accepted
the proton

Pair #2: a base on one side and its conjugate acid on the other side

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Amphiprotic substances

- Some chemicals can be an acid or a base
- Water is the most important amphiprotic substance (water can be the proton donor and its own proton acceptor)
- Autoionization of water is a fast equilibrium reaction that <u>always</u> is occurring wherever there is water present

$H_2O + H_2O \leftrightarrows H_3O^+ + OH^-$

Net: $2\,H_2O \leftrightarrows H_3O^+ + OH^-$

Shorthand: $H_2O \leftrightarrows H^+ + OH^-$

- Equilibrium constant

  $K_c = [H_3O^+]\,[OH^-]$ (or $K_c = [H^+]\,[OH^-]$ in shorthand)

  $= 1.0 \times 10^{-14}$ at 25ºC

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You practice it

A Precursor to Practice Exercises on p. 673

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.

1. $HNO_3\,(aq) + NH_3\,(g) \leftrightarrows NH_4^+\,(aq) + NO_3^-\,(aq)$
2. $CN^-\,(aq) + HClO\,(aq) \leftrightarrows HCN\,(aq) + ClO^-\,(aq)$
3. $HCO_3^-\,(aq) + H_2O\,(l) \leftrightarrows CO_3^{2-}\,(aq) + H_3O^+\,(aq)$

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Acid (or base) ionization constant K_a (or K_b)

Acid ionization (with water acting as the base):

- General form: $HA + H_2O \leftrightarrows A^- + H_3O^+$
- Examples
  - $HF + H_2O \leftrightarrows F^- + H_3O^+$
  - $H_2S + H_2O \leftrightarrows HS^- + H_3O^+$
  - $HSO_4^- + H_2O \leftrightarrows SO_4^{2-} + H_3O^+$

$$K_a = \frac{[A^-]\,[H_3O^+]}{[HA]}$$

Base ionization (with water acting as the acid):

- General form: $B + H_2O \leftrightarrows HB^+ + OH^-$
- Examples
  - $NH_3 + H_2O \leftrightarrows NH_4^+ + OH^-$
  - $F^- + H_2O \leftrightarrows HF + OH^-$
  - $HPO_4^{2-} + H_2O \leftrightarrows H_2PO_4^- + OH^-$

$$K_b = \frac{[HB^+]\,[OH^-]}{[B]}$$

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Comparing Bronsted acids (see handout)

Write your notes here about how to use K_a values to compare the relative strengths of acids and bases.

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 to products, which include H^+)
- The stronger the acid, the weaker its conjugate base, and vice versa

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Using the K_a values to predict the position of a proton-transfer equilibrium

Similar to Practice Exercise, p. 676

Use the table of ionization constants for acids and bases to answer the following questions.

1. Which is the stronger acid, H_2SO_4 or H_2SO_3?
2. To which direction does this equilibrium lie?
   $$H_2SO_4 + HSO_3^- \leftrightarrows H_2SO_3 + HSO_4^-$$
3. Is benzoic acid (C_6H_5COOH) stronger or weaker than acetic acid?
4. Which has the stronger conjugate base, acetic acid or boric acid?
5. Which is the stronger base, ammonia or the acetate ion?
6. Which has the stronger conjugate acid, ammonia or the acetate ion?

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Reminder: How equilibrium constants change when you manipulate the reactions

Compare these reactions

1. $A \rightarrow B$ $\qquad K_1 = \frac{[B]}{[A]}$
2. $B \rightarrow A$ is $(-1)\times(A \rightarrow B)$ $\qquad K_2 = \frac{[A]}{[B]}$ is $(K_1)^{-1}$
3. $2A \rightarrow 2B$ is $(2)\times(A \rightarrow B)$ $\qquad K_3 = \frac{[B]^2}{[A]^2}$ is $(K_1)^2$

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Adding reactions

Add these reactions

1. A → B $\quad K_1 = \frac{[B]}{[A]}$

2. C → D $\quad K_2 = \frac{[D]}{[C]}$

3. A + C → B + D $\quad K_3 = \frac{[B]\,[D]}{[A]\,[C]}$ is $(K_1)(K_2)$

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When the A's and B's are acids and bases

Adding acid-base reactions

1. Acid1 + H_2O → Base1 + H_3O^+ $\quad K_1 = \frac{[\text{Base1}]\,[H_3O^+]}{[\text{Acid1}]} = K_{a1}$

2. Base2 + H_3O^+ → Acid2 + H_2O $\quad K_2 = \frac{[\text{Acid2}]}{[\text{Base2}]\,[H_3O^+]} = (K_{a2})^{-1}$

SUM: Acid1 + Base2 → Base1 + Acid2

$$K_3 = \frac{[\text{Base1}][\text{Acid2}]}{[\text{Acid1}][\text{Base2}]} = K_1 \cdot K_2 = (K_{a1})(K_{a2})^{-1} = \frac{K_{a1}}{K_{a2}}$$

$$K_1 \cdot K_2 = \left(\frac{[\text{Base1}][H_3O^+]}{[\text{Acid1}]}\right) \cdot \left(\frac{[\text{Acid2}]}{[\text{Base2}]\,[H_3O^+]}\right) = \frac{[\text{Base1}][\text{Acid2}]}{[\text{Acid1}][\text{Base2}]}$$

Predict the products of the reaction, if any

$$HCO_3^-\,(aq) + HSO_3^-\,(aq) \leftrightarrows CO_3^{2-}\,(aq) + H_2SO_3\,(aq)$$

acid1 base2 base1 acid2

$K_{a1} = 4.8 \times 10^{-11}$ $\quad K_{a2} = 1.2 \times 10^{-2}$

$$\frac{K_{a1}}{K_{a2}} = \frac{4.8\times10^{-11}}{1.2\times10^{-2}} = 4.0\times10^{-9}$$

$$HCO_3^-\,(aq) + HSO_3^-\,(aq) \leftrightarrows H_2CO_3\,(aq) + SO_3^{2-}\,(aq)$$

base2 acid1 acid2 base1

$K_{a1} = 6.2 \times 10^{-8}$ $\quad K_{a2} = 4.2 \times 10^{-7}$

$$\frac{K_{a1}}{K_{a2}} = \frac{6.2\times10^{-8}}{4.2\times10^{-7}} = 0.15$$

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A general acid-base reaction

- It can be broken down as a sum of a forward K_{a1} and a reverse K_{a2}
- K_{sum} is equal to K_{a1} / K_{a2}
- To determine whether the reaction occurs to any reasonable extent, you can compare the magnitudes of K_{a1} and K_{a2}
- Whichever is larger will "win"

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What is K_b? How is it related to K_a?

- General acid reaction

  $\text{Acid1} + H_2O \leftrightarrows \text{Base1} + H_3O^+$ $\quad K_a = \frac{[\text{Base1}]\,[H_3O^+]}{[\text{Acid1}]}$

- General base reaction involving the same pair

  $\text{Base1} + H_2O \leftrightarrows \text{Acid1} + OH^-$ $\quad K_b = \frac{[\text{Acid1}]\,[OH^-]}{[\text{Base1}]}$

- These ought to be related to each other

  $\text{Acid1} + H_2O \leftrightarrows \text{Base1} + H_3O^+$

  $\underline{\text{Base1} + H_2O \leftrightarrows \text{Acid1} + OH^-}$

Sum: $2\,H_2O \leftrightarrows H_3O^+ + OH^-$

but this is just $K_w = [H_3O^+]\,[OH^-]$

Therefore, $K_w = K_a K_b$

and K_w is always equal to 1.0×10^{-14}

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?

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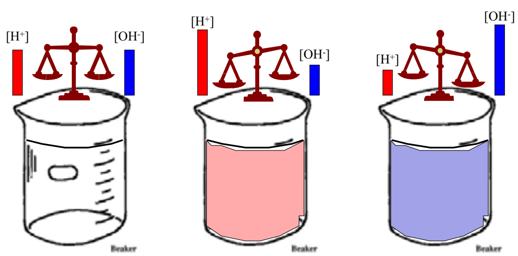
A little more about K_w

$2\,H_2O \leftrightarrows H_3O^+ + OH^-$ or more simply, $H_2O \leftrightarrows H^+ + OH^-$ is a fast equilibrium. This means it comes back into equilibrium balance very quickly after it is disturbed, in such a way that always

$$K_w = [H_3O^+]\,[OH^-] = 1.0 \times 10^{-14}$$



Pure water | Acidic solution | Basic solution

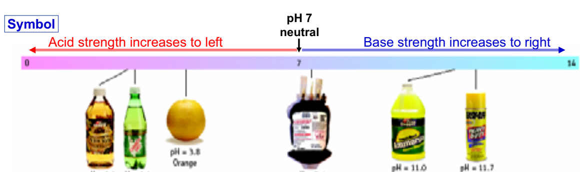
What is the pH scale?

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 hydronium ions
- Now that you know this, they are often abbreviated H^+

Symbol



From Chemistry & Chemical Reactivity 5th edition by Kotz / Treichel. C 2003. Reprinted with permission of Brooks/Cole, a division of Thomson Learning: www.thomsonrights.com. Fax 800-730-2215.

What is pH?

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

pH = $-\log_{10} [H^+]$

pOH = $-\log_{10} [OH^-]$

pK_a = $-\log_{10} [K_a]$

pK_b = $-\log_{10} [K_b]$

pK_w = $-\log_{10} [K_w]$

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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.
  $10^5 \times 10^{-2} = 10^{5+(-2)} = 10^3$
  $10^{-3} / 10^1 = 10^{(-3)-1} = 10^{-4}$

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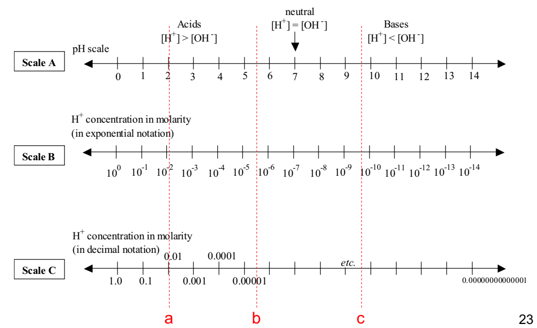
What does pH mean mathematically?

pH scale is a logarithmic scale



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from Sevian et al, *Active Chemistry* (2004)

The pH scale, mathematically

- The logarithm (base 10) of a number is just the exponent of the power of 10 when you express the number as a power of 10
  log 100 = log 10^2 = 2
  log 0.00001 = log 10^{-5} = -5
- Numbers that are not integer powers of 10 can still be represented as powers of 10
  45.6 = $4.56 \times 10^1 = 10^{1.659}$
  log 45.6 = 1.659
  0.000000821 = $8.21 \times 10^{-7} = 10^{-6.086}$
  log (0. 000000821)= -6.086
  (Note: sig figs of logarithms are only counted <u>after</u> the decimal point, because the integer comes from the exponent of 10)
- Make sure you know how to do this on your calculator

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The pH scale, mathematically

- pH values range from 1 to 14 and pH = -log $[H^+]$
- If you know the $[H^+]$, you can get pH
  $[H^+]$ = 0.00010 *M*, therefore pH = -log(0.0001) = 4.00
  $[H^+]$ = 0.00000050 *M*, therefore pH = -log(0.00000050) = 6.301
  You try it:
  $[H^+]$ = 0.0025 *M*, therefore pH = ?
- If you know the pH, you can get $[H^+]$
  $[H^+]$ = antilog(-pH) or 10^{-pH}
  pH = 4.00, therefore $[H^+]$ = antilog(-4.00) = 10^{-4} = 0.00010 *M*
  pH = 8.200, therefore $[H^+]$ = antilog(-8.200) = $10^{-8.2}$ = 6.31×10^{-9} *M*
  You try it:
  pH = 2.3, therefore $[H^+]$ = ?

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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

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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.

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^-

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

Some neat math tricks to make it easier

- We know that K_w always equals 1.0×10^{-14}
- We also know that $K_w = [H^+][OH^-]$

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

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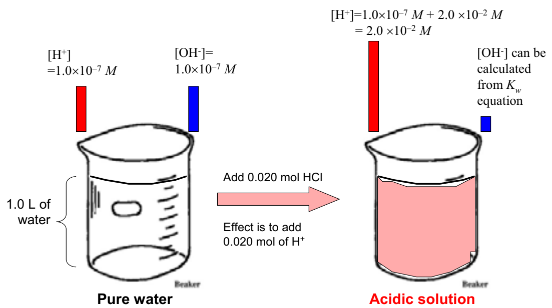
Adding a strong acid to water

If you added 0.020 mol of HCl to 1.0 L of water, what would be the pH?



Example of strong base calculations

Similar to Practice Exercise, p.

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?

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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 $[OH^-]$

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

- Identify conjugate acid-base pairs and predict reactions
- Equilibrium
- Titration
- Lewis acids and bases
- 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)

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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
- $K_w = [H^+]\,[OH^-] = 1.0 \times 10^{-14}$
- Because of this, pH + pOH = 14
- Also, $K_w = K_a\, K_b$