PART 5 – Acids and Bases

Reference: Chapter 15, 16.1—16.4 in textbook

Brønsted-Lowey Definition

- Acid
  - Compound that can increase the hydrogen ion (H^+) concentration when dissolved in water.
    - e.g. HCl (aq) + H_2O (l) → H_3O^+ (aq) + Cl^- (aq),
    - e.g. HCN (aq) + H2O (l) → H_3O^+ (aq) + CN^- (aq)
- Base
  - Compound that can increase the hydroxide ion (OH^-) concentration when dissolved in water.
    - e.g. NaOH (aq) → Na^+ (aq) + OH^-(aq)
    - e.g. NH_3 (aq) + H_2O (l) → NH_4^+ (aq) + OH^- (aq)

Strong and Weak Acid (Base)

- Strong acid (base)
  - Strong acid: completely dissociated into H^+ & anions in water (e.g. HCl, HNO_3, H_2SO_4, HBr, HI, $HClO_4$, …)
  - Strong base: completely dissociated into OH^- & cations in water (all IA, IIA cations' hydroxide, e.g. NaOH, $Ba(OH)_2$, …)
- Weak acid (base)
  - Weak acid: partially dissociated, majority as molecules
    - e.g. HF, HClO, HCN, H_2S, HCOOH (formic acid), CH_3COOH (acetic acid), HCO_3^-, H_2O, …
  - Weak base: partially dissociated, majority as molecules
    - e.g. NH_3, $(CH_3)NH_2$, $(CH_3)_3N$, $C_6H_5NH_2$ (aniline), HCO_3^-, H_2O, …

Conjugate Acid-Base Pair

- Acid: $HA + H_2O \rightarrow H_3O^+ + A^-$
  Base: $B + H_2O \rightarrow HB^+ + OH^-$
  - HA and A^- , or HB^+ and B, are called conjugate acid-base pair.
  - Q: Write the conjugate acid/base of species in the previous slide?
    - Weak acid: HF, HClO, HCN, H_2S, HCOOH, CH_3COOH, HCO_3^-, $Fe(H_2O)_6^{2+}$
    - Weak base: NH_3, $(CH_3)NH_2$, $(CH_3)_2NH$, $(CH_3)_3N$, $C_6H_5NH_2$ (aniline), HCO_3^-, $Fe(H_2O)_5(OH)^+$
    - How about strong acids? Strong base? H_2O?

Poly-protic acid

- Define: contain more than one mole ionizable hydronium ions.
  - e.g. H_2SO_4, H_2CO_3, H_3PO_4, $H_2C_2O_4$
    - Is it a strong acid or weak acid?
    - For strong acid, each step is fully dissociation.
    - For weak acid, each step is partial dissociation.
  - Identify the conjugate acid-base pairs of each dissociation equation.

Amphoteric Substance

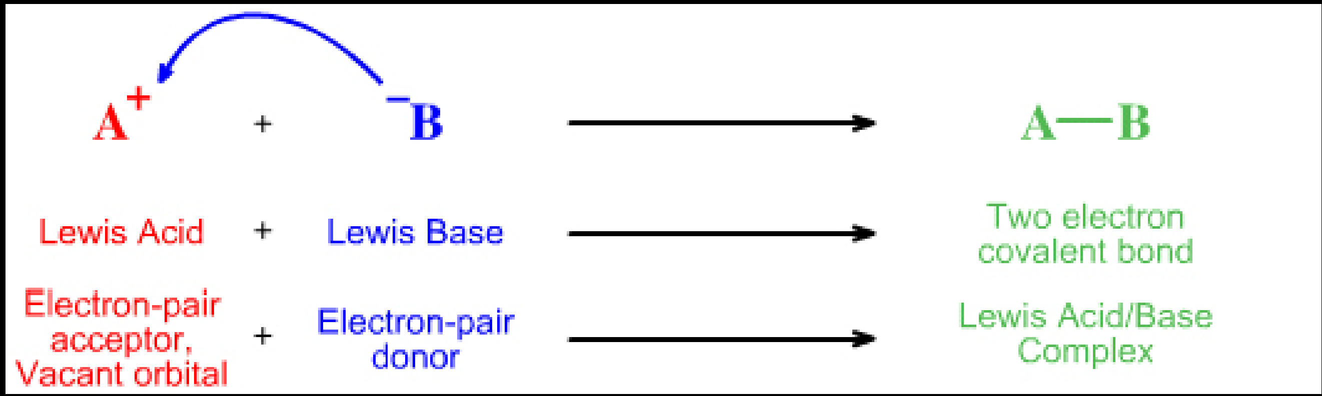
- Define (*loosely*): can react as either an acid or base under different circumstances
- Normally it is a poly-protic weak acid or base
- Example:
  - $NaHCO_3 + HCl \rightarrow NaCl + H_2CO_3$

    $NaHCO_3 + NaOH \rightarrow Na_2CO_3 + H_2O$
  - Na_2HPO_4, NaH_2PO_4
  - H_2O
  - $Fe(H_2O)^{2+}$, $Al(H_2O)^{3+}$, $Ni(H_2O)^5(OH)^+$
- However, even a "strong acid" may behave as a base, when it encounters with a stronger acid.

Lewis Acid & Base Theory

- Lewis Acid (electron pair acceptor)
  - Has an empty orbital and can accept an e^- pair
  - e.g. BF_3, H^+,
- Lewis Base (electron pair donor)
  - Has an e- pair and can donate (to a Lewis Acid)
  - e.g. NH_3, Cl-,
- Comprises the Brønsted-Lowey definition
  - A Brønsted-Lowey acid/base is a Lewis acid/base;
  - A Lewis acid/base may not be a Brønsted-Lowey acid/base

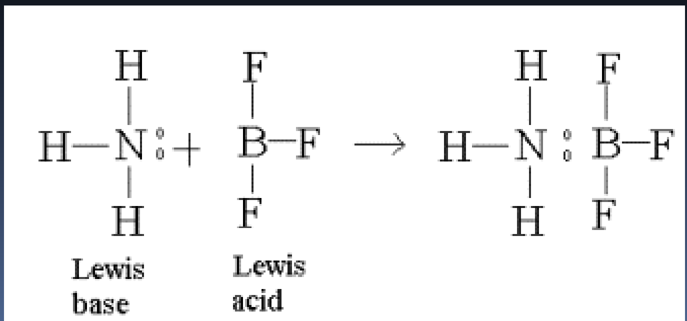
Lewis Acid & Base Theory

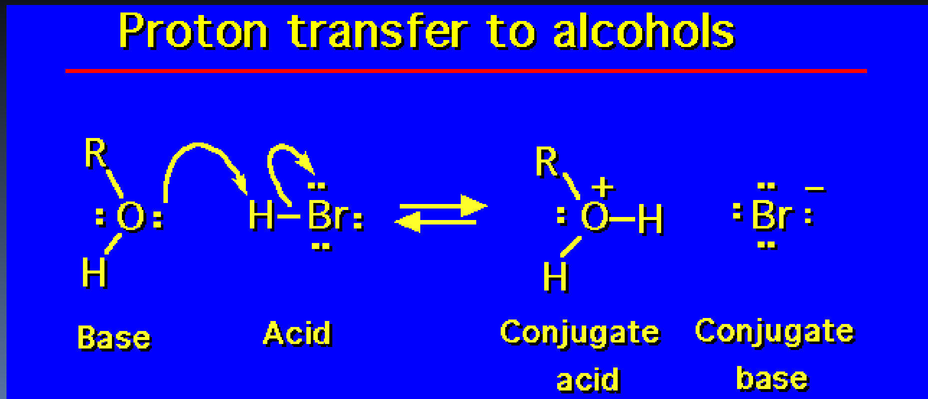


- Examples

$H^+ + {}^-O\text{-}H \rightarrow H\text{-}O\text{-}H$

CaO	+ SO_3	$\longrightarrow$	$CaSO_4$
Lewis base	Lewis acid		Calcium sulphate





Ion Product for Water, K_w

- $H_2O + H_2O \leftrightarrow H_3O^+ + OH^-$
- $K_w = [H_3O^+] * [OH^-] = 1.0 \times 10^{-14}$ (@ 25°C)
  - An equilibrium constant, used in all aqueous solution, (i.e. acid, base, salt, or their mixture).
- Calculate $[H_3O^+]$ and $[OH^-]$:
  - $[H_3O^+] > 1.0 \times 10^{-7} > [OH^-]$ (acidic solution)
  - $[H_3O^+] = 1.0 \times 10^{-7} = [OH^-]$ (neutral solution)
  - $[H_3O^+] < 1.0 \times 10^{-7} < [OH^-]$ (basic solution)

pH value

- Define: $pH = -\log [H^+]$
- Deduction:
  - $pKw = -\log [10^{-14}] = 14$
  - In water or neutral solution, $pH = -\log [10^{-7}] = 7$
  - In acidic solution, $pH < 7$
  - In basic solution, $pH > 7$
- $pOH = -\log [OH^-]$
  - $pH + pOH = (-\log [H^+]) + (-\log [OH^-]) = pK_w = 14$

Calculation of $[H_3O^+]$ & $[OH^-]$

- In a strong acid solution:
  - Focus on the dominated species, i.e. $[H_3O^+]$
  - Strong acid dissociates completely;
  - Determine whether $[H_3O^+]$ from H_2O can be ignored?
    - Yes → Use strong acid only to calculate $[H_3O^+]$;
    - No → Should also consider water dissociation.
  - Use $[H_3O^+]$ to calculate $[OH^-]$, pH, pOH.

Practice

- Calculate $[H_3O^+]$, $[OH^-]$, pH, pOH of the following aqueous solution at 25 ^oC:
  - 1 M HCl
  - 0.0005 M H_2SO_4
  - 10^{-6} M HCl
  - 10^{-9} M HCl
  - 0.001 M NaOH
  - 10^{-7} M KOH

Calculation of $[H_3O^+]$ & $[OH^-]$

- In a <u>strong base</u> solution:
  - Focus on the dominated species, i.e. $[OH^-]$
  - Strong base dissociates completely;
  - Determine whether [OH-] from H_2O can be ignored?
    - Yes → Use strong base only to calculate $[OH^-]$;
    - No → Should also consider water dissociation.
  - Use $[OH^-]$ to calculate $[H_3O^+]$, pH, pOH.

K_a Value for Acids

- A value to define the strength of an acid
- Definition:
  - For an acid (HA): $HA + H_2O \leftrightarrow H_3O^+ + A^-$

    $K_a = [H_3O^+] * [A^-] / [HA]$
  - K_a is an equilibrium constant for a specific acid.
  - Can be used to compare the strength of an acid.
- $pK_a = - \log [K_a]$

K_a Values of Some Common Acids

K_a Values			K_a Values		
Name of Acid	**Acid**	**K_a**	**Name of Acid**	**Acid**	**K_a**
Sulfuric acid	H_2SO_4	large	Hexaaquaaluminum ion	$Al(H_2O)_6^{3+}$	7.9×10^{-6}
Hydrochloric acid	HCl	large	Carbonic acid	H_2CO_3	4.2×10^{-7}
Nitric acid	HNO_3	large	Hydrogen sulfide	H_2S	1×10^{-7}
Hydronium ion	H_3O^+	1.0	Dihydrogen phosphate ion	$H_2PO_4^-$	6.2×10^{-8}
Hydrogen sulfate ion	HSO_4^-	1.2×10^{-2}	Hypochlorous acid	$HClO$	3.5×10^{-8}
Phosphoric acid	H_3PO_4	7.5×10^{-3}	Ammonium ion	NH_4^+	5.6×10^{-10}
Hexaaquairon(III) ion	$Fe(H_2O)_6^{3+}$	6.3×10^{-3}	Hydrocyanic acid	HCN	4.0×10^{-10}
Hydrofluoric acid	HF	7.4×10^{-4}	Hexaaquairon(II) ion	$Fe(H_2O)_6^{2+}$	3.2×10^{-10}
Formic acid	HCO_2H	1.8×10^{-4}	Hydrogen carbonate ion	HCO_3^-	4.8×10^{-11}
Benzoic acid	$C_6H_5CO_2H$	6.3×10^{-5}	Hydrogen phosphate ion	HPO_4^{2-}	3.6×10^{-13}
Acetic acid	CH_3CO_2H	1.8×10^{-5}	Water	H_2O	1.0×10^{-14}
			Hydrogen sulfide ion	HS^-	1×10^{-19}

- $pK_a > 14$ (or $K_a > 10^{-14}$), the solution is acidic.
- The strongest acidic specie that can exist in water is hydronium ion, $[H_3O^+]$.

Practice

- Calculate $[H_3O^+]$, $[OH^-]$, pH, pOH of the following aqueous solution at 25 °C:

a) 0.1 M HF

b) 1×10^{-2} M acetic acid (CH_3COOH)

c) 5×10^{-3} M carbonic acid (H_2CO_3)

d) 2×10^{-4} M phosphoric acid (H_3PO_4)

e) 0.01 M NH_3 ($K_b = 1.9 \times 10^{-5}$)

f) 10^{-3} M NaHS ($K_a = 1.0 \times 10^{-19}$)

K_b Value for Bases

- A value to define the strength of a base
- Definition:
  - For a base (B): $B + H_2O \leftrightarrow HB^+ + OH^-$

    $K_b = [HB^+] * [OH^-] / [B]$
  - K_b is an equilibrium constant for a specific base.
  - Can be used to compare the strength of a base.
- $pK_b = - \log [K_b]$
- $K_a * K_b = K_w$; $pK_a + pK_b = pK_w$

Hydrolysis

- Indeed, hydrolysis is an acid-base reaction
- Reaction of a basic anion with water to become its conjugate acid:
  - $A^- (aq) + H_2O (l) \leftrightarrow HA (aq) + OH^- (aq)$
  - e.g. $HCO_3^- (aq) + H_2O (l) \leftrightarrow H_2CO_3 (aq) + OH^- (aq)$
- Reaction of an acidic cation with water to become its conjugate base:
  - $M^{n+} (aq) + H_2O (l) \leftrightarrow M(OH)^{(n-1)+} (aq) + H^+ (aq)$
  - e.g. $Al(H_2O)_6^{3+} (aq) + H_2O (l) \leftrightarrow Al(H_2O)_5(OH)^{2+} (aq) + H_3O^+ (aq)$

Is a Salt Solution Acidic or Basic?

- For a given salt, analyze its "original acid and base reactants", and if:
  - Strong acid vs. Strong base → neutral
  - Strong acid vs. Weak base → acidic
  - Weak acid vs. Strong base → basic
  - Weak acid vs. Weak base → compare with K_a and K_b
- <u>Q: Predict the solutions are acidic/basic?</u>
  - (a) $NaCl$; (b) NH_4I; (c) $Cr(NO_3)_3 \cdot 9H_2O$; (d) KCN; (e) NH_4F (HF $K_a = 3.5 \times 10^{-4}$, $NH_3 \cdot H_2O$ $K_b = 1.7 \times 10^{-5}$); (f) NH_4HSO_3 (H_2SO_3 $K_{a1} = 1.5 \times 10^{-2}$, $K_{a2} = 1.0 \times 10^{-7}$)

Summary of Calculation of $[H_3O^+]$

- Single component (original *C_{acid} or C_{base}*)
  - Strong acid: $[H_3O^+] = C_{acid}$, $[OH^-] = K_w / [H_3O^+]$
  - Strong base: $[OH^-] = C_{base}$, $[H_3O^+] = K_w / [OH^-]$
  - Weak acid:
    - Poly-protic acid (K_{a1}, K_{a2}, …), only consider K_{a1};
    - if $C_{acid}/K_a > 100$, $[H_3O^+] = \sqrt{(K_a \times C_{acid})}$;
    - if $C_{acid}/K_a \leq 100$, then we need to solve the equation.
  - Weak base:
    - if $C_{base}/K_b > 100$, $[OH^-] = \sqrt{(K_b \times C_{base})}$;
    - if $C_{base}/K_b \leq 100$, then we need to solve the equation.

Summary of Calculation of $[H_3O^+]$

- Salt solution – hydrolysis
  - Similar to a weak acid: $[H_3O^+] = \sqrt{(K_a \times C_{acid})}$, or a weak base: $[OH^-] = \sqrt{(K_b \times C_{base})}$
- Multiple components
  - Strong acid + Weak acid, or Strong base + Weak base
    - Unless $C_{strong} << C_{weak}$, otherwise only consider the strong one
  - Strong acid + Weak base, or Strong base + Weak acid
    - (1) First, use the original concentrations to calculate the acid-base reaction;
    - (2) If the weak species are in excess → Buffer solution calculation

Practice

- <u>Q1 (*Book pg.618, 15.129-a*):</u>
  - In 1.00 x 10^{-7} M NaOH, what is $[OH^-]$? What percentage of the OH^- comes from water?
- <u>Q2 (*Book pg.618, 15.131*):</u>
  - (a) What is the pH of a solution that is 0.025 M in HCl and 0.032 M in CH_3COOH? ($K_{a\ (CH3COOH)}$ = 1.7 x 10^{-5})
  - (b) What is the pH of a solution prepared by mixing 50.0 ml of 0.025 M HCl and 50.0 ml of 0.032 M CH_3COOH?

Buffer Solution

- Solution containing both a weak acid (HA) and its conjugate base (A^-)
  - A buffer solution can resist significant change in pH.
  - Buffer capacity
    - It requires $C_{HA} / C_{A-} = 0.1 – 10$ for a buffer's high capacity.
  - For a buffer:

$[H_3O^+] = K_a \times (C_{HA} / C_{A-})$;

or $[OH^-] = K_b \times (C_{A-} / C_{HA})$

Calculation of pH in Buffers

- (a) 0.05 M CH_3COOH (Note $K_{a\ (CH3COOH)} = 1.7 \times 10^{-5}$)
- (b) 0.10 M CH_3COOH with equal volume of 0.05 M HCl
- (c) 0.10 M CH_3COOH with equal volume of 0.01 M NaOH
- (d) 0.10 M CH_3COOH with equal volume of 0.05 M NaOH
- (e) 0.10 M CH_3COOH with equal volume of 0.09 M NaOH
- (f) 0.10 M CH_3COOH with equal volume of 0.10 M NaOH
- (g) 0.10 M CH_3COOH with equal volume of 0.11 M NaOH

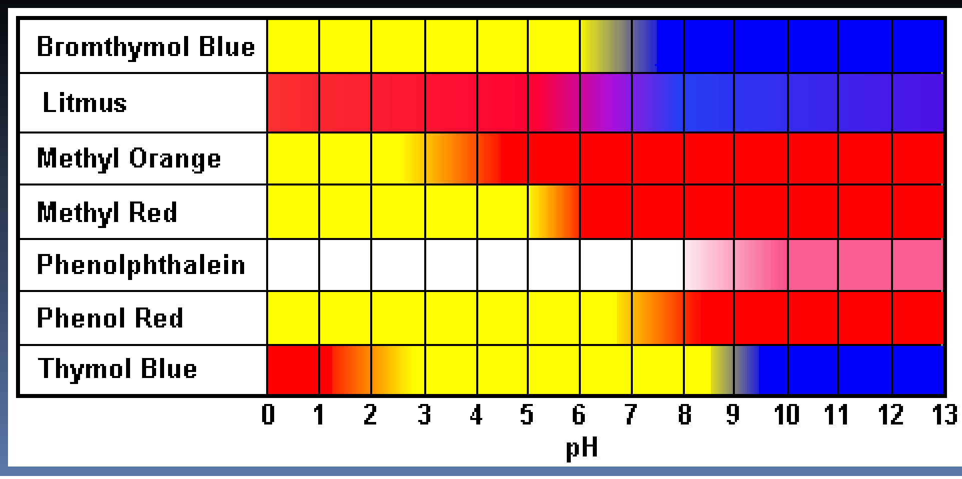
- Solution: pH = (a) 3.0; (b) 1.6; (c) 3.8; (d) 4.8; (e) 5.7; (f) 8.7; (g) 11.7

Practice

- Q1 (*Book pg.618, 15.130*):
  - If the pH of a 0.020 M solution of aniline ($C_6H_5NH_2$) is reduced to 5.50 by the addition of HCl, what percentage of the aniline is present in the form of anilinium ions? ($K_{b\ (aniline)} = 4.3 \times 10^{-10}$)
- Q2: Which pair of compounds should be used to prepare a buffer with pH = 3.20:
  - (a) HCOOH + HCOONa ($K_{a\ HCOOH} = 1.8 \times 10^{-4}$);
  - (b) CH_3COOH + CH_3COONa ($K_{a\ CH3COOH} = 1.7 \times 10^{-5}$);
  - (c) H_3BO_3 + NaH_2BO_3 ($K_{a\ H3BO3} = 7.3 \times 10^{-10}$)

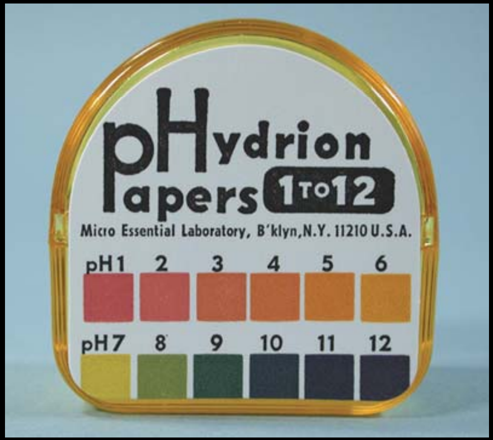
Titration

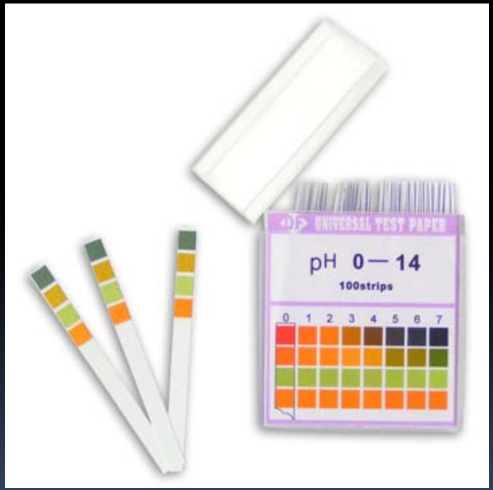
- Acid-Base titration
  - Use a standard solution (with known concentration) to determine the amount of a substance in an unknown solution.
  - Equivalent point – equal amount of reactants.
  - Indicators (*a weak acid/base w/ color change*)
    - $HIn \leftrightarrow H^{+} + In^{-}$



pH Meter and pH Paper

pH meter

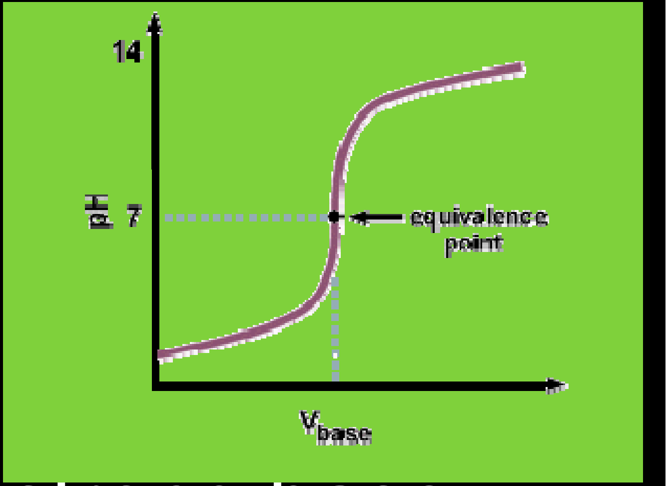




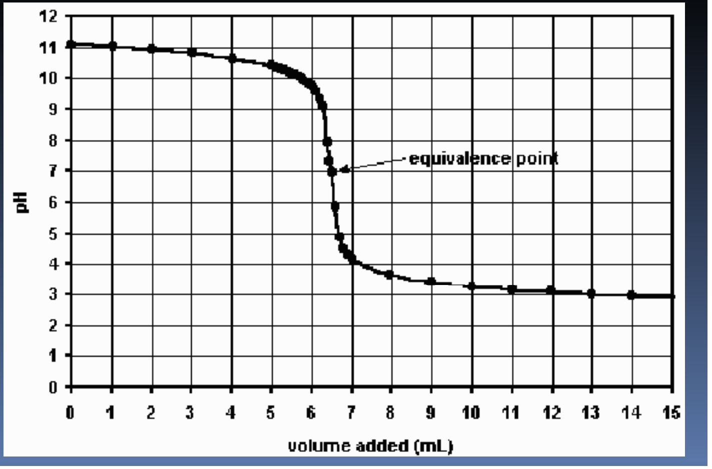
pH paper

Curve – Strong base + Strong acid

- Use a strong base to titrate a strong acid
  - Slow rise at start/end
  - Fast jump close to Equivalent pt
  - Equivalent point: pH = 7

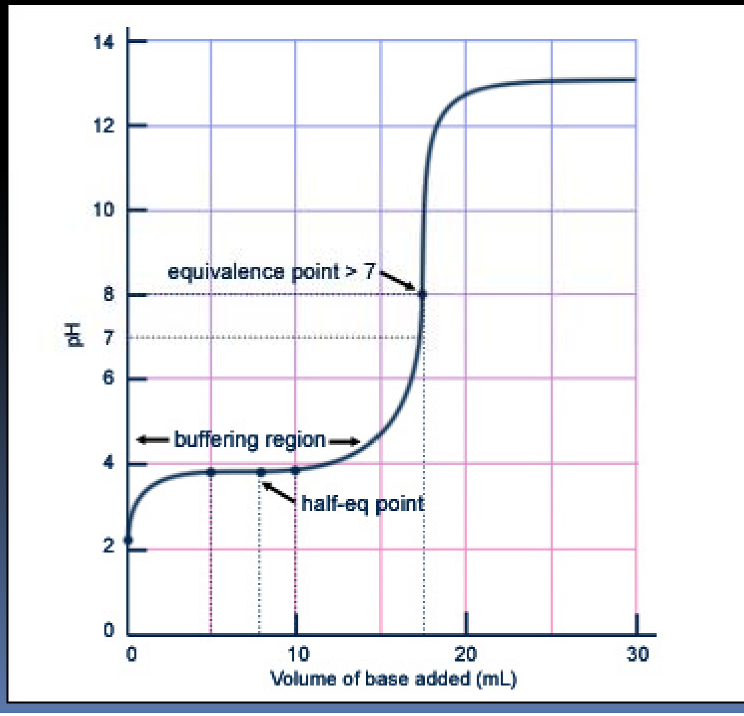


- Use a strong acid to titrate a strong base
  - Similar as above



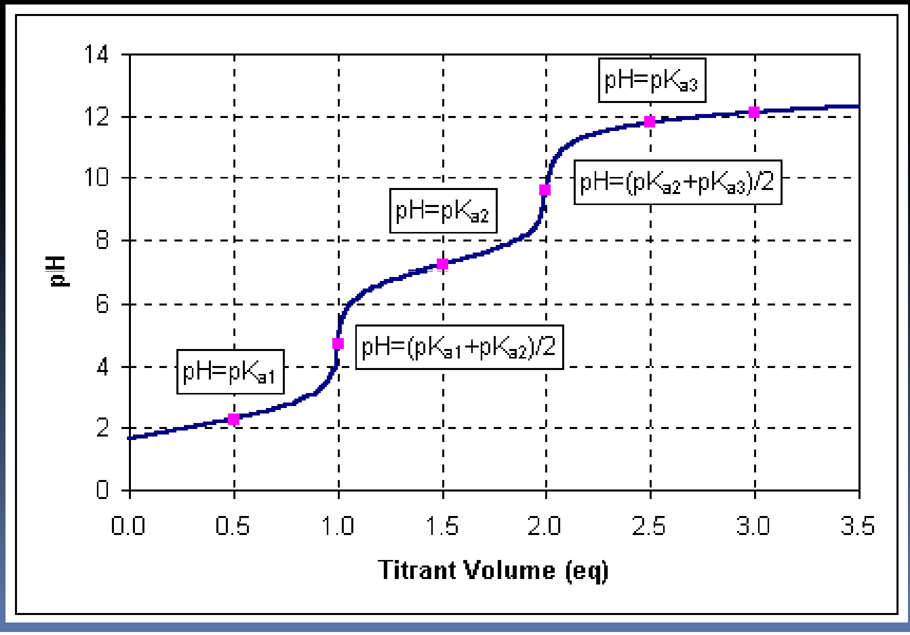
Curve – Strong base + Weak acid

- Use a strong base to titrate a monoprotic weak acid
  - A small, fast jump at beginning
  - Slow and flat rise in the buffer region
  - Half equivalent point
    - $[H_3O^+] = K_a$, $pH = pK_a$
  - Fast jump close to Equiv. pt.
  - Equivalent point: pH > 7
    - $[H_3O^+] = \sqrt{(K_wC/K_b)}$
  - Slow rise at the end



Curve – Strong base + Weak acid

- Use a strong base to titrate a poly-protic weak acid
  - Half equivalent point (of each proton reaction)
    - pH = pK_{a1}, pK_{a2}, …
  - Equivalent point: pH = $(pK_{a1} + pK_{a2})/2$, …



Questions of Acid-Base Titration

- (Q1:) 20.0 ml sample of hydrochloric acid (HCl) was titrated with 0.500 M NaOH. A total of 26.0 ml of NaOH was required to reach the end point. (a) What was the molarity of the original hydrochloric acid? (b) What is the solution's pH at the end point?

- (Q2:) In the question above, if the original acid is a formic acid (HCOOH), what will be the answers of the above two questions? ($K_{a\ (HCOOH)} = 1.8 \times 10^{-4}$)

Homework #5 (due on 12/17, Mon)

Acid-base Reaction:

① Acid-base reaction (Book pg. 614—618):
15.37, 15.39, 15.60, 15.125, 15.126, 15.137

② Sample questions in this chapter's PPT slides:

- Slide 16
- Slide 19
- Slide 22 (2 questions)
- Slide 24
- Slide 25 (2 questions)
- Slide 31 (2 questions)