Advanced Acid Equilibrium

AP Chemistry 30L – Ms. Hayduk

Recall…

- pH is a simplified measure of H^+ ions in a solution
  - $[H^+] = [OH^-]$, solution is neutral
  - $[H^+] > [OH^-]$, solution is acidic
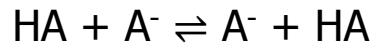 - $[H^+] = [OH^-]$, solution is basic

Buffers

- Purpose: resist changes in pH in a solution after addition of strong acid or base
- Composition: weak acid and conjugate base, or weak base and conjugate acid
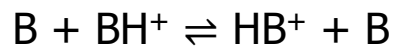
pH Without a Buffer

- H_2O + strong acid = $\uparrow[H^+]$, $\downarrow$pH
- H_2O + strong base = $\uparrow[OH^-]$, $\uparrow$pH

- pH change is significant in both cases

Buffer Solutions

- Weak acid:

$$HA + A^- \rightleftharpoons A^- + HA$$
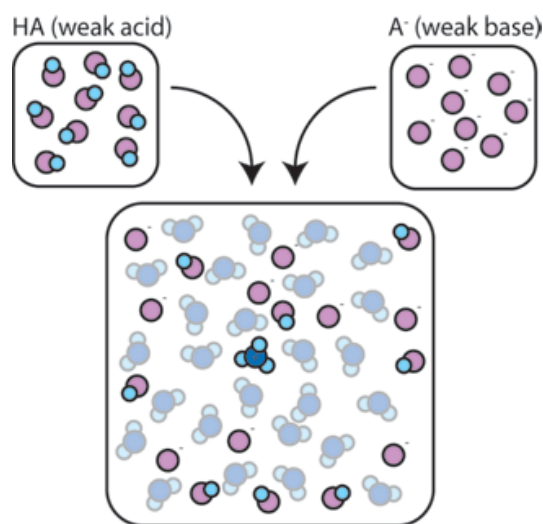
- Weak base:

$$B + BH^+ \rightleftharpoons HB^+ + B$$

- Regardless of equilibrium shift, all [] stay constant ($\therefore$ pH is constant)

Buffer Solutions

Buffer Equation

Useful version…

$$[H_3O^+] = K_a \frac{[acid]}{[base]}$$

- K_a for weak acid in buffer
- [acid] for weak acid OR conjugate of weak base
- [base] for weak base OR conjugate of weak acid

Alternate…

$$[H_3O^+] = K_a \left(\frac{n_{acid}}{n_{base}}\right)$$

Solving Buffer Problems

1. Identify weak acid and weak base (HA/A⁻ or BH⁺/B)
2. Determine K_a (recall: $K_a = K_w/K_b$)
3. If you have two separate solutions being mixed, calculate diluted concentrations ($C_1V_1 = C_2V_2$) OR n_{acid} and n_{base} (moles)

Example 1: Buffer Problems

Determine the pH of a solution containing 0.63 M lactic acid, $HC_3H_5O_3$ ($K_a = 1.4 \times 10^{-4}$) and 0.33 M sodium lactate, $NaC_3H_5O_3$.

Example 2: Buffer Problems

Determine the pH of a solution containing 0.482 M ammonia, NH_3 ($K_b = 1.8 \times 10^{-5}$) and 0.800 M ammonium chloride, NH_4Cl.

Example 3: Buffer Problems
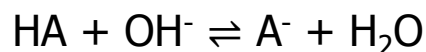
Determine the pH of a solution prepared by mixing:

20.0 mL of 0.300 M acetic acid, $HC_2H_3O_2$

20.0 mL of 0.350 M sodium acetate, $NaC_2H_3O_2$

For acetic acid, $K_a = 1.8 \times 10^{-5}$

Buffer + Strong Base

- Simplifying with weak acid as buffer, but would work the same with a weak base

$$HA + OH^- \rightleftharpoons A^- + H_2O$$

- Weak acid neutralizes OH^- (equilibrium shifts right)
- pH stays constant until HA is depleted
- $[HA]\downarrow$, $[A^-]\uparrow$

Buffer + Strong Base

$$OH^- + HA \rightleftharpoons A^- + H_2O$$

Buffer + Strong Acid

$$HCl + A^- \rightleftharpoons HA + Cl^-$$
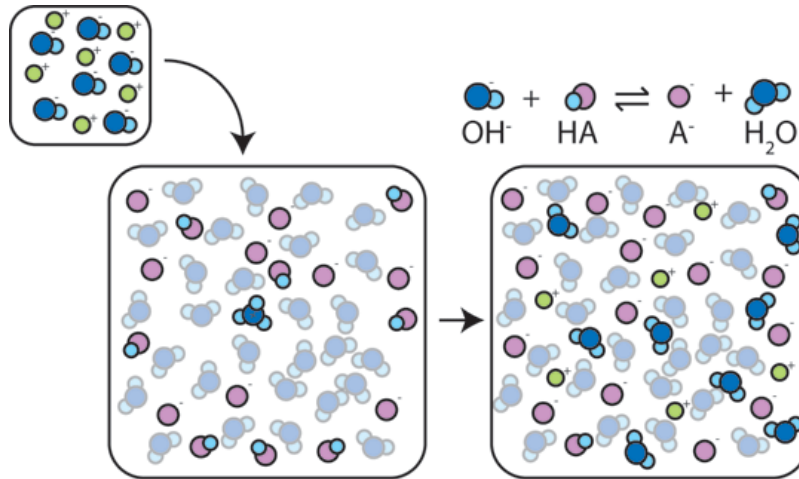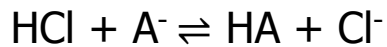
- Weak base neutralizes H^+ (equilibrium shifts right)
- pH stays constant until A^- is depleted
- $[A^-]\downarrow$, $[HA]\uparrow$

Buffer + Strong Acid

$$HCl_{(g)} + A^- \rightleftharpoons HA + Cl^-$$
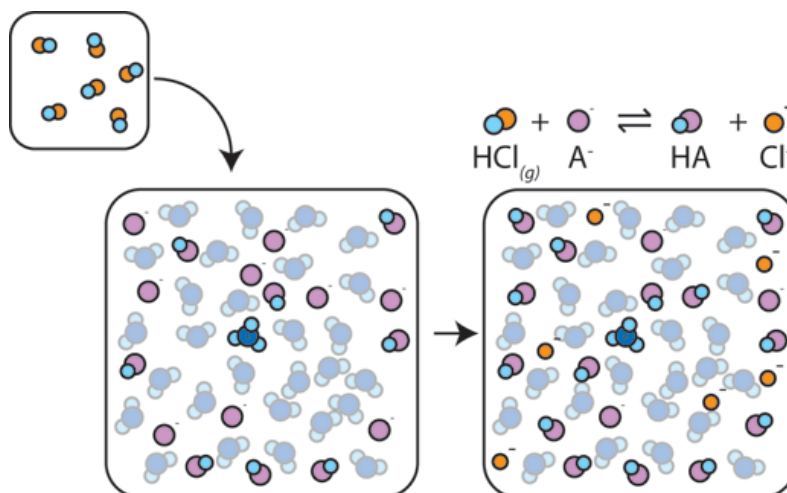
Buffer Equilibrium

- Think of it as:

  $$HA(BH^+) + H_2O \rightleftharpoons A^-(B) + H_3O^+$$

- Using Le Chatelier's Principle:
  - What do you change when you add a strong acid? Which way will the equilibrium shift?
  - What do you change when you add a strong base? Which way will the equilibrium shift?

Adding Strong Acid/Base to Buffer

- If acid is added:
  - Add moles added to n_{acid}
  - Subtract moles added from n_{base}

- If base is added:
  - Add moles added to n_{base}
  - Subtract moles added from n_{acid}

Example: Adding Strong Acid

Determine the pH of a 0.500 L solution containing 0.50 M formic acid ($K_a = 1.8 \times 10^{-4}$) and 0.70 M sodium formate <u>before</u> and <u>after</u> adding 10.0 mL of 1.00 M HCl.

pK$_a$

- Simplifies values, similar to pH:

$$pK_a = -\log K_a \qquad pK_b = -\log K_b$$

- Henderson-Hasselbalch equation (on AP formula sheet):

$$pH = pK_a + \log\frac{[base]}{[acid]}$$

Preparing Buffers

- Choose 0.10 M to 1.00 M solutions
- Choose weak acid/base with $K_a \approx [H_3O^+]$ (pH $\approx$ pK$_a$), then calculate ratio
- IMPORTANT
  - What matters is relative MOLES of acid & base ratio – ratio will stay constant even if water is added

Example: Buffer Prep

Determine the acid-to-base ratio you would need to prepare an acetic acid/sodium acetate buffer with a pH of 5.00. Acetic acid has a K_a of 1.8×10^{-5}.

Thinking Activity

You need a solution buffered at pH of 4.30 and can choose from these acids and their conjugates:
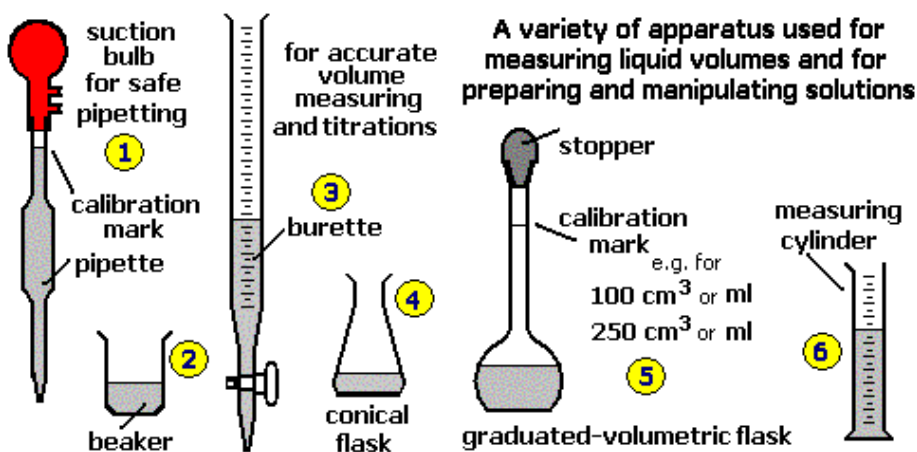
a. Chloroacetic acid $\quad K_a = 1.35 \times 10^{-3}$

b. Propanoic acid $\quad K_a = 1.3 \times 10^{-5}$

c. Benzoic acid $\quad K_a = 6.4 \times 10^{-5}$

d. Hypochlorous acid $\quad K_a = 3.5 \times 10^{-8}$

Which system works best? Why?

Acid-Base Titrations

- Mixing an acid (or base) with known concentration to determine the unknown concentration of a base (or acid)
- Uses an indicator which changes colour to indicate **end point**
- **Equivalence point** is when enough titrant is added to completely neutralize analyte
- Ideally, end point = equivalence point

Important Titration Equipment

suction bulb for safe pipetting **1**

calibration mark

pipette

beaker **2**

for accurate volume measuring and titrations **3**

burette

conical flask **4**

A variety of apparatus used for measuring liquid volumes and for preparing and manipulating solutions

stopper

calibration mark
e.g. for
100 cm^3 or ml
250 cm^3 or ml **5**

graduated-volumetric flask

measuring cylinder

6
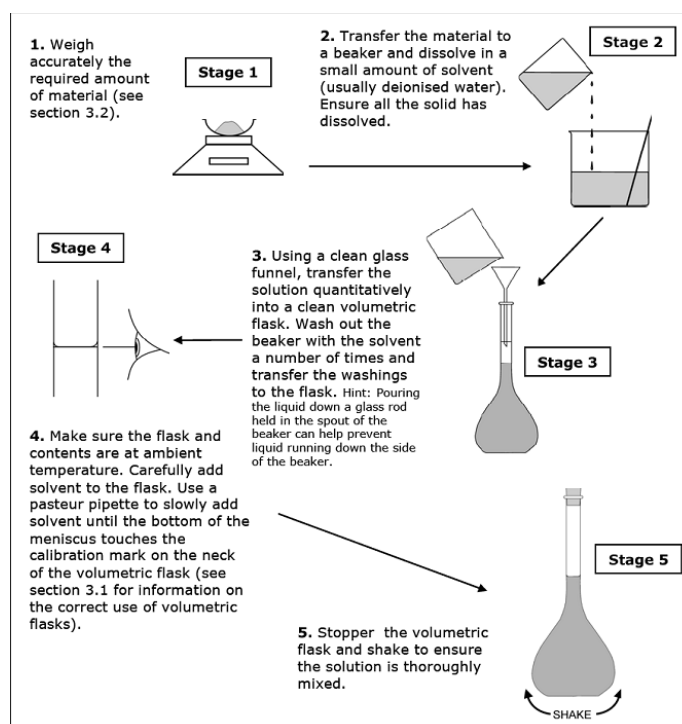
Preparing Solutions

- "Preparing a solution" refers to the procedure of dissolving a solid substance in water to make an aqueous solution.
- Some calculations are usually required to determine the correct mass of the solid or resulting concentration of the solution.

Preparing Solutions

1. Weigh accurately the required amount of material (see section 3.2).

Stage 1

2. Transfer the material to a beaker and dissolve in a small amount of solvent (usually deionised water). Ensure all the solid has dissolved.

Stage 2

Stage 4

3. Using a clean glass funnel, transfer the solution quantitatively into a clean volumetric flask. Wash out the beaker with the solvent a number of times and transfer the washings to the flask. Hint: Pouring the liquid down a glass rod held in the spout of the beaker can help prevent liquid running down the side of the beaker.

Stage 3

4. Make sure the flask and contents are at ambient temperature. Carefully add solvent to the flask. Use a pasteur pipette to slowly add solvent until the bottom of the meniscus touches the calibration mark on the neck of the volumetric flask (see section 3.1 for information on the correct use of volumetric flasks).

5. Stopper the volumetric flask and shake to ensure the solution is thoroughly mixed.

Stage 5

SHAKE

Preparing Solutions

<u>DO</u>:

• Use VERY clean equipment
• Take your time weighing solid and filling the flask

<u>DO NOT</u>:

• Put solid back into the original container
• Put material directly into the flask

Preparing Solutions

THIS IS VERY IMPORTANT!

In MOST cases, getting an exact concentration is not important. Instead, start with an approximate mass of solute (e.g. 3 g). Record the exact mass used and find the exact concentration from that.

DO NOT CONTAMINATE THE CHEMICAL IN THE ORIGINAL CONTAINER!

Example: Preparing Solutions

1. You want to make 50.0 mL of a 0.10 M sodium chloride solution. How much solid sodium chloride do you need?

Example: Preparing Solutions

2. When you are preparing your solution, you aim for the mass of solid you need, but end up using a little extra. The mass you use to prepare the solution is 0.35 g. What is the actual concentration of the solution?

Example: Preparing Solutions

3. Which is better:

- Throwing away solid/putting it back in the container to get the exact mass (and then exact concentration) that you wanted, OR,

- Getting an approximate mass based on your calculations, and then determining the exact concentration you used?

Strong Acid + Strong Base

- Net ionic: $H^+ + OH^- \rightarrow H_2O$
- pH at equivalence point is 7.0 (neutral)
- Treat as a stoichiometry problem with a limiting reactant ("excess" determines pH)
- Do your work in moles

**Titration Curve for Titration of 20 mL of 0.300 mol/L HCl(aq)
with 0.300 mol/L NaOH(aq)**
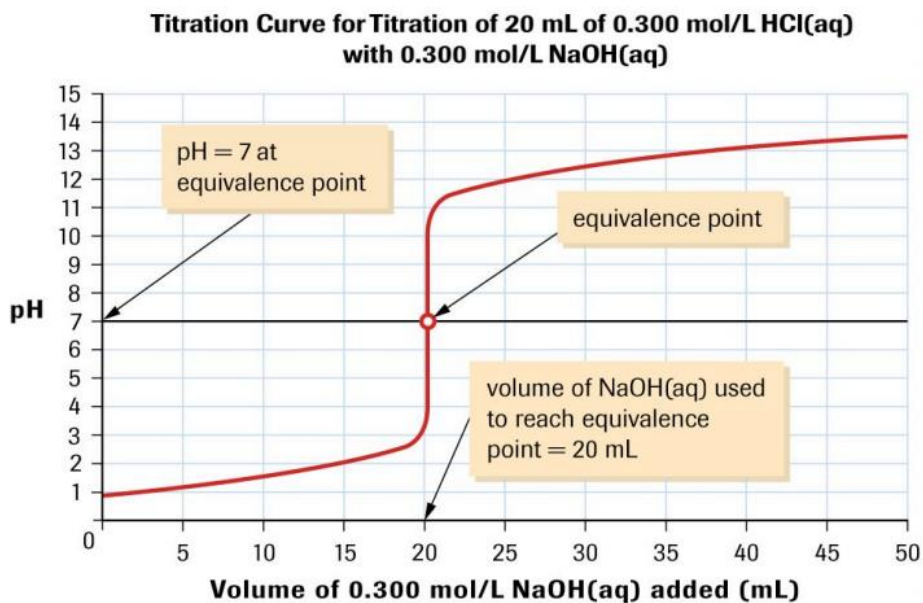
Weak Acid + Strong Base

- Equivalence point pH > 7

Zone 1

- pH of weak acid before titration begins
- Determine pH using K_a of weak acid and K_a expression:

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

Zone 2

- pH during titration before equivalence point
- Weak acid reacts with strong base to make salt (conjugate base of acid) and water
- Determine pH like a buffer problem:

$$[H_3O^+] = K_a \frac{[acid]}{[base]}$$

- TIP: at ½ equivalence point, [acid]=[base], so [H_3O^+] = K_a

More About Zone 2

1. Write a stoichiometry problem first:
   a. Determine moles of acid and moles of base
   b. All strong base will react (limiting), so subtract that from moles of acid and add it to the weak base conjugate
2. Equilibrium problem next:
   a. Determine initial molarity of acid and salt based on moles and total volume
   b. Use K_a expression solve for x ([H^+])

Zone 3

- pH at equivalence point
- All of weak acid has reacted with strong base to make salt (conjugate base of acid) and water
- Moles of strong base added = moles of weak acid reacted = moles of salt made
- [salt] = moles formed/total volume of solution
- Determine pH like a weak base problem:

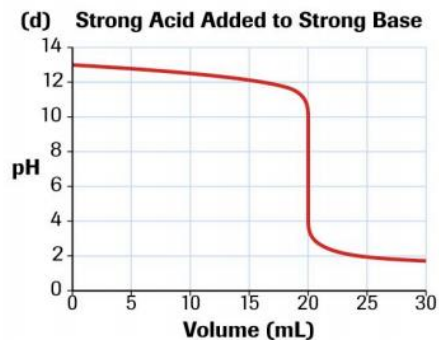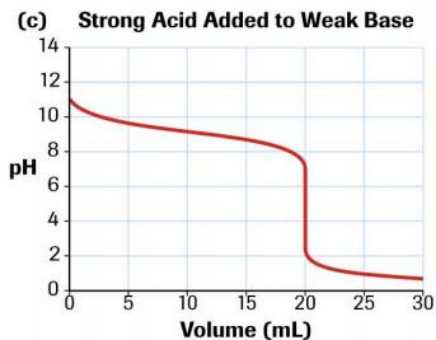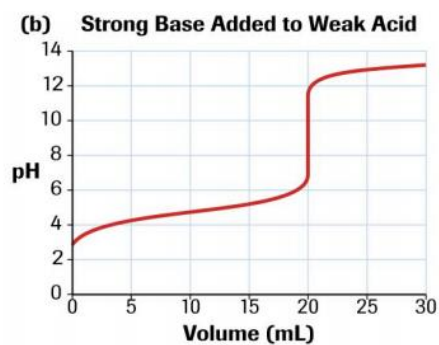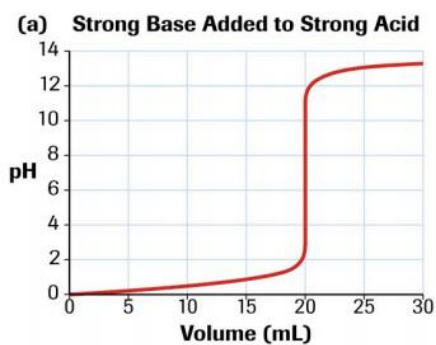$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

Zone 4

- pH after equivalence point
- Determine pH based on excess strong base
- Calculate [base] using dilution formula ($C_1V_1 = C_2V_2$), then determine pH

$$pOH = -\log[OH^-]$$

Strong Acid + Weak Base

- Follow same process as weak acid + strong base:
  1. Weak base problem
  2. Buffer problem
 3. Hydrolysis of a salt/weak acid problem
  4. Strong acid problem

(a) Strong Base Added to Strong Acid
(b) Strong Base Added to Weak Acid
(c) Strong Acid Added to Weak Base
(d) Strong Acid Added to Strong Base

Example: Weak Acid + Strong Base

Hydrogen cyanide gas (HCN) is a weak acid when dissolved in water ($K_a = 6.2 \times 10^{-10}$). If a 50.0 mL sample of 0.100 M HCN is titrated with 0.100 M NaOH, determine the pH of the solution:

a. Before the titration begins

b. After 8.00 mL of 0.100 M NaOH is added

c. At the halfway point of the titration

d. At the equivalence point of the titration

Indicator Choice

- Ideally, end point = equivalence point
- Determine pH at equivalence point, then choose indicator that has pK_a close to pH at equivalence point
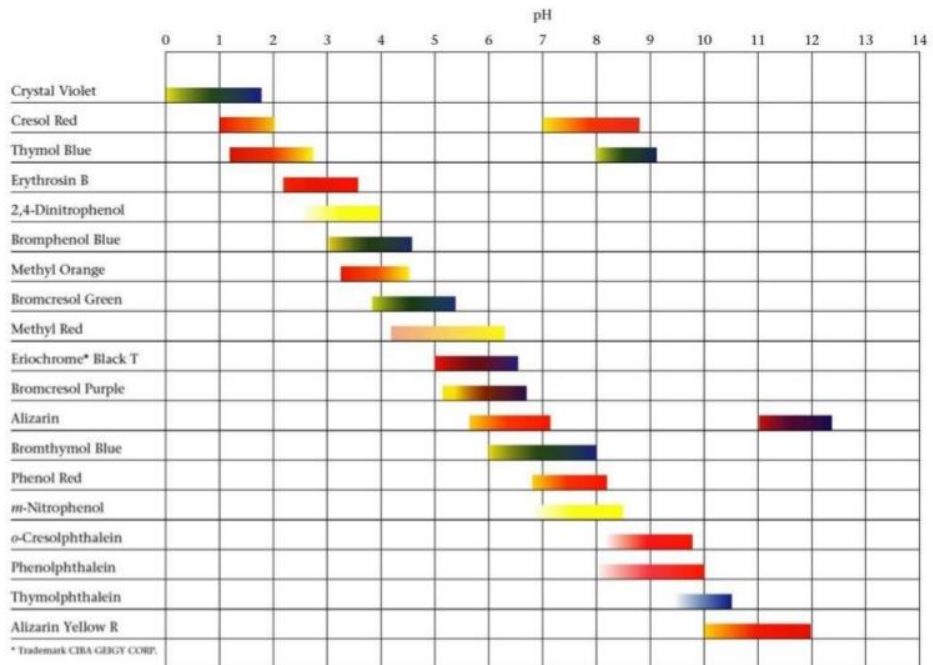
The pH ranges shown are approximate. Specific transition ranges depend on the indicator solvent chosen.