CH 302 – Unit 3 Review 1

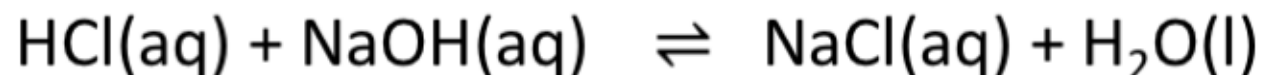BUFFERS

"THINKING LIKE A CHEMIST"

Neutralization Reactions: Salts

- The product of a neutralization reaction is a salt. In acid/base chemistry, your salt can be neutral, acidic, or basic depending on the reaction.
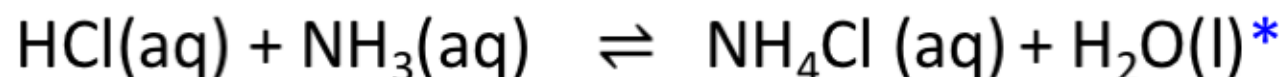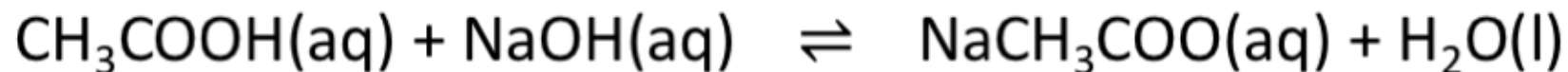
1. GENERIC REACTION (very helpful):

   $Acid(aq) + Base(aq) \rightleftharpoons Salt(aq) + Water(l)$

2. Strong Acid, Strong Base: results in a neutral salt

   $HCl(aq) + NaOH(aq) \rightleftharpoons NaCl(aq) + H_2O(l)$

3. Strong Acid to weak base: results in an acidic salt

   $HCl(aq) + NH_3(aq) \rightleftharpoons NH_4Cl(aq) + H_2O(l)$*

4. Strong base to weak acid: results in a basic salt

   $CH_3COOH(aq) + NaOH(aq) \rightleftharpoons NaCH_3COO(aq) + H_2O(l)$

Warm Up Question

$moles_A = moles_B$

Suppose it takes 15mL of 0.5M NaOH to completely neutralize 50mL of HCl solution. What was your original HCl concentration? What is the pH of your sample if you then add 5 mL MORE NaOH?

$$acid + base \rightarrow salt + H_2O$$

$$HCl + NaOH \rightarrow NaCl + H_2O$$

$$C_A V_A = C_B V_B$$

$$\frac{(0.5M)(0.015L)}{0.050L} = C_{HCl} =$$

15mL 0.5M ⟶ 50mL ?M
NaOH   HCl

@ neutralization,

moles NaOH = moles HCl

moles NaOH = $0.5 \frac{mol}{L} \times 0.015 L = 0.0075$ moles

$\frac{mol\ HCl}{L\ HCl} = M\ HCl = \frac{0.0075\ mol\ HCl}{0.050\ mL}$

$= 0.15M\ HCl$

$0.5M\ NaOH \times 0.005L = 0.0025$ mol NaOH

$[OH^-] = \frac{0.0025\ mol}{(0.050L + 0.015L + 0.005\ L)}$ ← excess

← dilution

$= 0.036M$

$pOH = -log(0.036)$

$= 1.44$, $pH = 14 - 1.44$

$= 12.56$

Acid and Base Question Types (Simplified)

In addition to real world applications of acid/base problems, you should be able to put yourself into the mindset of a chemist doing these experiments in the following scenarios:

- Strong acid, strong base questions
  - Simple relationships converting $[H_3O^+]$ and $[OH^-]$ to pH, pOH

- Weak acid, weak base questions
  - Approximations or quadratic formula (if necessary) with your general formula:
  - $HA \rightleftharpoons H^+ + A^-$ OR $B \rightleftharpoons BH^+ + OH^-$
  - Solve for $[H^+]$ using K_a Solve for $[OH^-]$ using K_b

- **Buffer questions**
  - Mixtures of a weak acid and its salt (conjugate base) ; weak base and its salt (conjugate acid)
  - Solve for pH, pOH using Henderson-Hasselbalch equation

- **Neutralization reactions and titration experiments**
  - By adding a titrant to an analyte solution, you can neutralize your original species. Depending where you are in the neutralization experiment, you will make different calculations based on the three scenarios above.

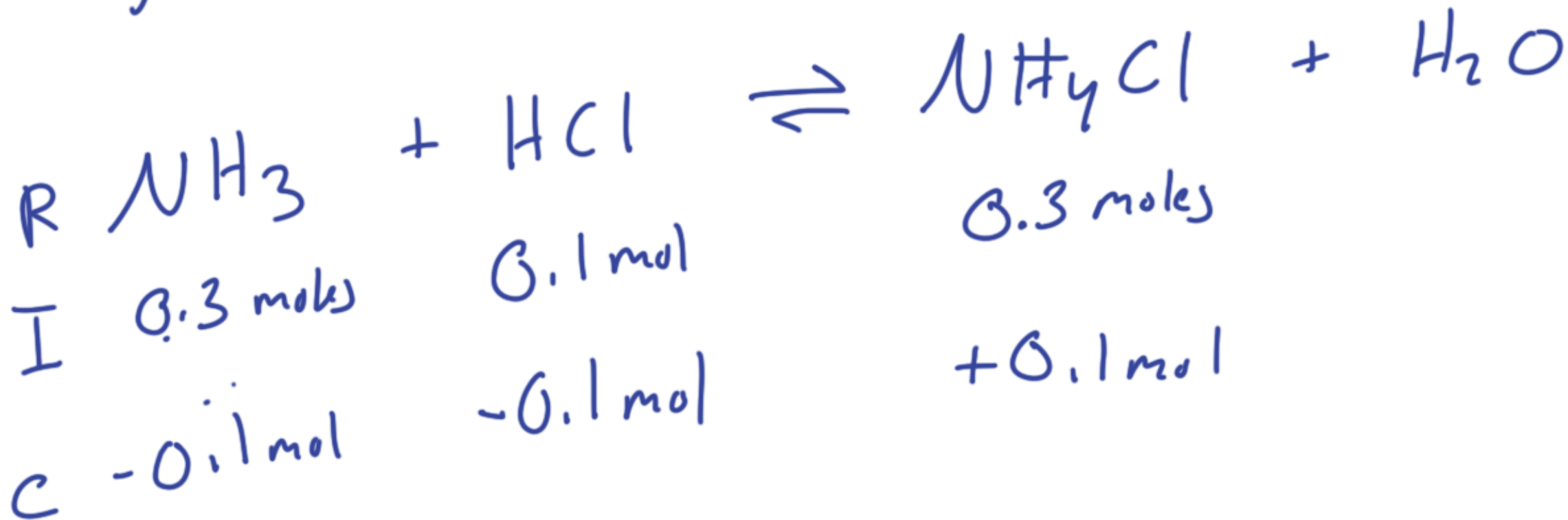*(handwritten) Type 1*

(handwritten) Type 2

What is a Buffer?

→ Resist changes in pH

1) Weak acid + salt

2) Weak base + salt

Type II, use **moles**

$$NH_3 + HCl \rightleftharpoons NH_4Cl + H_2O$$

	NH_3	HCl	NH_4Cl	H_2O
R			0.3 moles	
I	0.3 moles	0.1 mol		
C	-0.1 mol	-0.1 mol	+0.1 mol	

E 0.2   0   0.4

R $HCl + H_2O \longrightarrow H^+ \quad + \quad Cl^-$

I   0.1

C   -0.1   +0.1   +0.1
_____

E   0   0.1   0.1

Buffers: Conceptual, Calculation

→ base

- The purpose of a buffer is to resist changes in pH.

- Here's the idea:
  - If you add 0.1 mole of NaOH to pure water, you are adding 0.1 mole of OH^-. This results in a pretty big change in pH
  - If you add 0.1 mole of NaOH to a solution of acetic acid and sodium acetate, you are just creating 0.1 mole more of sodium acetate. This *barely* increases the pH.

$$pH = pK_a + \log(\tfrac{A^-}{HA})$$

→ acid

$$pOH = pK_b + \log(\tfrac{BH^+}{B})$$

- By definition, a buffer is made of:
  - A weak acid and its salt (conjugate base)
  - A weak base and its salt (conjugate acid)

- By definition, a buffer is effective when:
  - The pH is within about +/- 1 of the pK_a or pK_b
  - This favorable ratio of the weak acid : salt (or weak base : salt) is known as the "Buffer Zone"

$$pH = pK_a + \log(\tfrac{A^-}{HA})$$

$\dfrac{1}{1}$

$\varnothing$

Choosing a Buffer

- A buffer only functions in the "Buffer Zone," which is +/- 1 pH point of the pK_a (for a weak acid buffer) or pK_b (generally the standard for a weak base buffer).

- Buffers are used in the real world (reaction chemistry, physiology, pharmacology, etc.) to maintain a stable pH environment. You choose a buffer with a pK_a closest to the pH environment you want to hold constant.

Example Question: The human bloodstream is held constant by a buffer system at pH = 7.35 Which of the following buffer systems is likely found in the bloodstream?

a. Carbonic Acid, pKa = 6.37 $5.37 - 7.37$

b. Acetic Acid, pKa = 4.75 $3.75 - 5.75$

c. Hydrofluoric Acid, pKa = 3.14 $2.14 - 4.14$

d. Ammonium, pKa = 9.21 $8.21 - 10.21$

Question

$$pH = pk_a + \log \frac{C_{A^-}}{C_{HA}}$$

$pk_a = 3.20$

$C_{A^-} \rightarrow$ use moles!

What is the pH of a solution consisting of 50mL 0.8M HF and 60mL 0.7M NaF (don't try this at home)? K_a for HF is 6.3×10^{-4}.
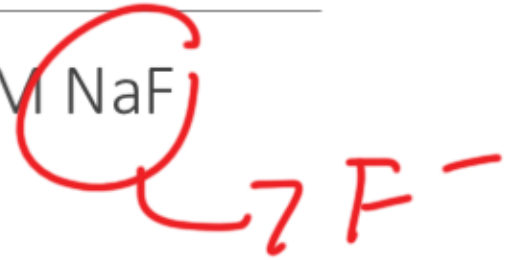
$\rightarrow F^-$

50mL 0.8M HF + 60mL 0.7M NaF $\implies$ 110mL

$HF \rightarrow 0.050L \times 0.8M = 0.04$ moles

$NaF \rightarrow 0.060 \times 0.7M = 0.042$ moles

$$pH = 3.20 + \log\left(\frac{0.042}{0.04}\right)$$

$$3.22 = pH$$

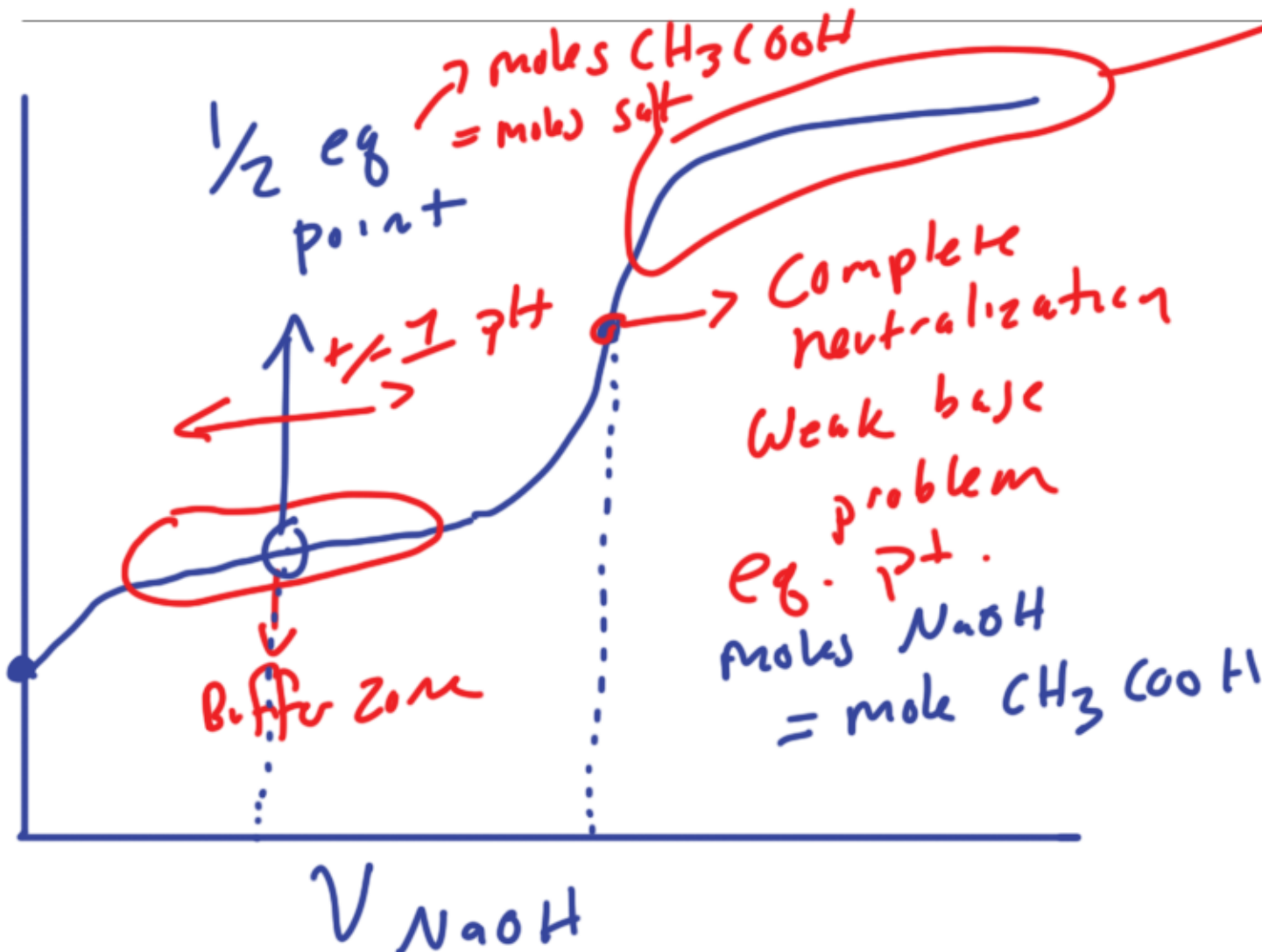# Titration Experiments: NaOH added to CH_3COOH

1) titrant

3) Indicator

This is the titrant. For this experiment, the titrant is NaOH (strong base). It is added drop-wise to the analyte. We know the concentration of the titrant.

This is the analyte. For this experiment, the analyte is acetic acid (weak acid). We don't always know the concentration of the analyte. There is an indicator in the analyte that changes color at a specific pH.

pH

Vol
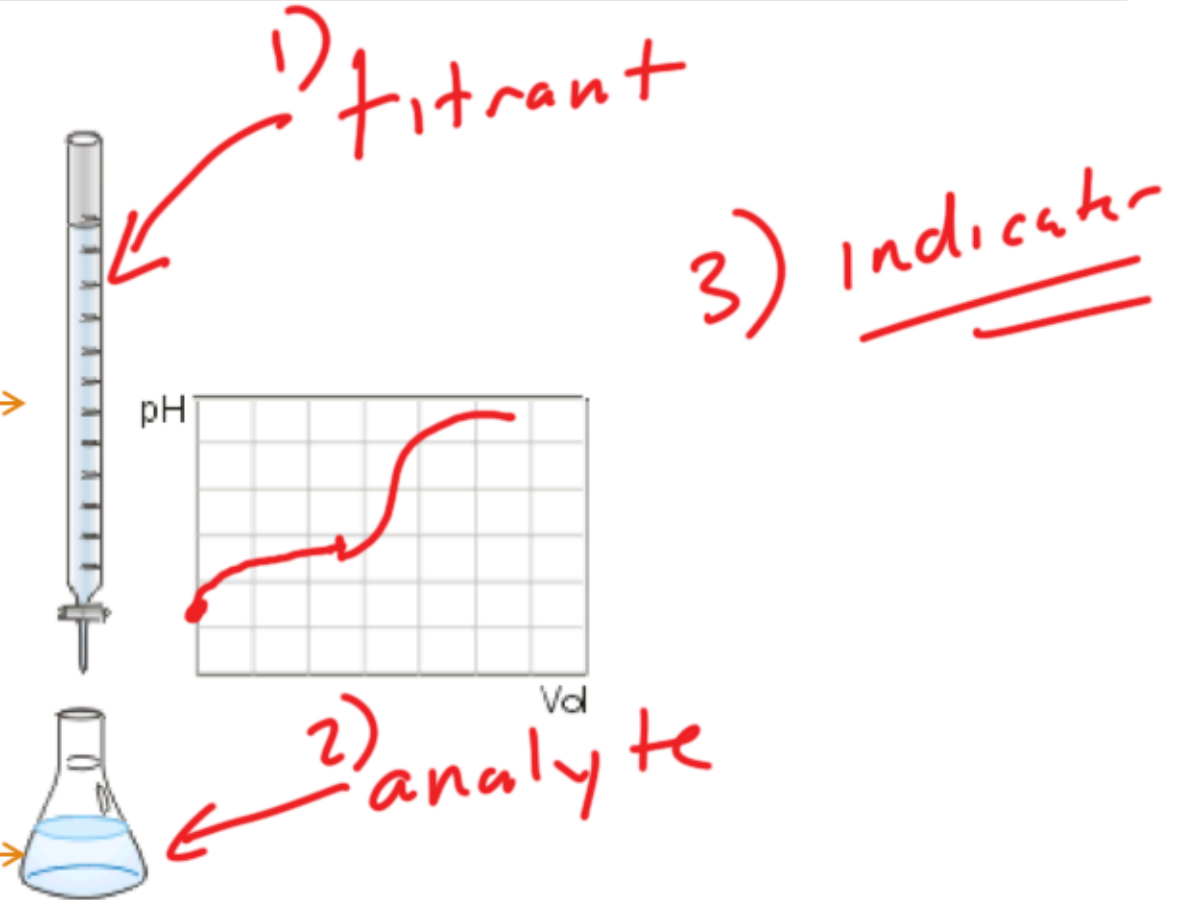
2) analyte

The objective of a titration experiment is to fully neutralize the analyte solution. This will form a neutral, basic, or acidic salt, depending on the experiment.

Titrations of Buffered Solutions

overshoot

moles CH_3COOH
= moles salt

½ eq point

+/- 1 pH

Complete neutralization

Weak base problem

eg. pt.

moles NaOH
= mole CH_3COOH

pH

100%
weak acid

Buffer Zone

V NaOH

A) **Before you have started:**
   Calculate pH using the approximation formula or using $K_a = [H^+][A^-] / [HA]$.

B) **Within the buffer zone:**
   $pH = pKa + \log ([A^-]/[HA])$
   Also: when $pKa = pH$ (middle of the buffer zone)

C) **At the equivalence point:**
   You only have the salt of your weak acid in solution. Use $K_w = K_aK_b$, then solve for $[OH^-]$, pOH, then convert to pH

D) **After the equivalence point:**
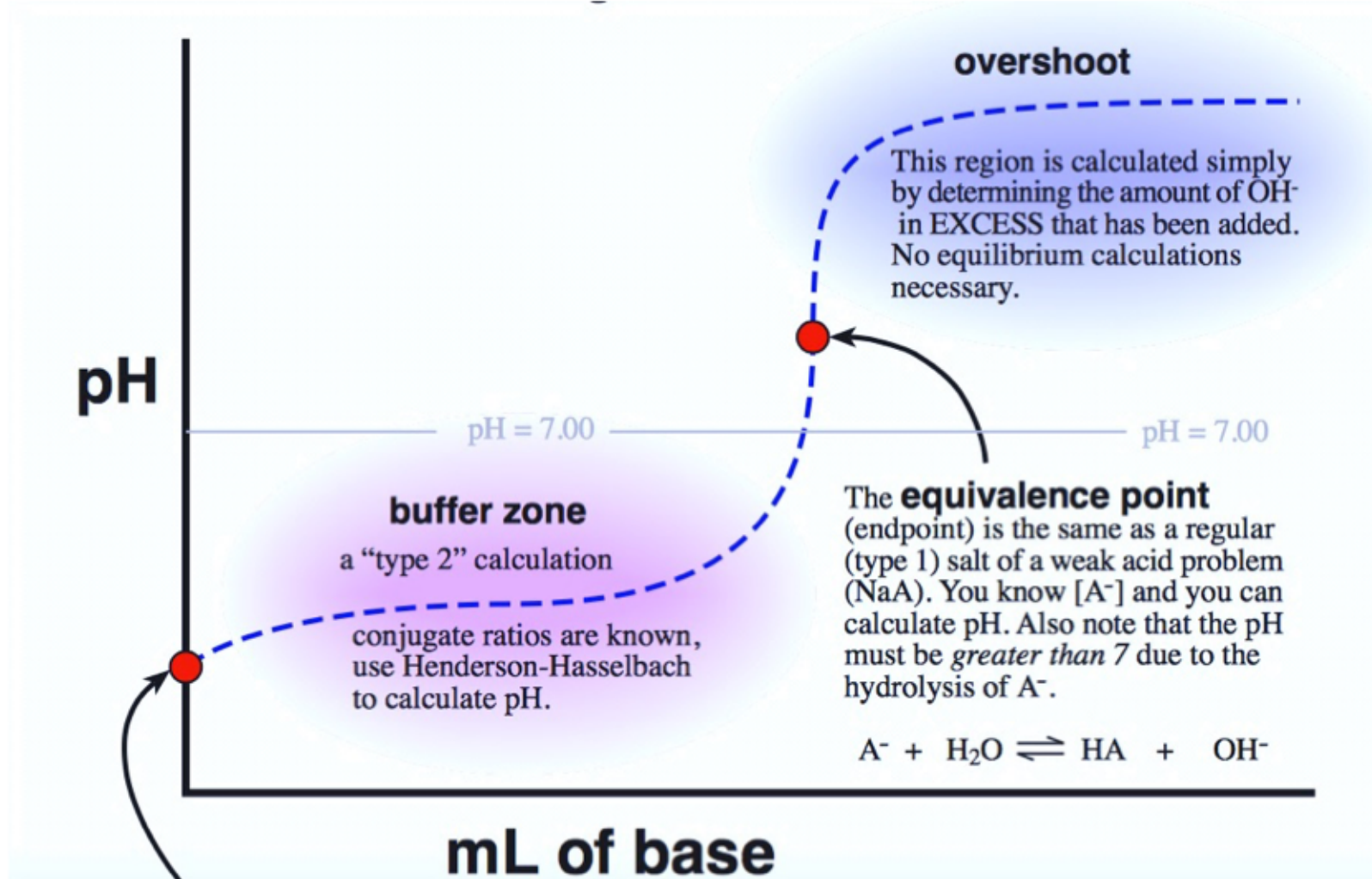   Find the pH using the excess base in solution
   $pOH = -\log ([excess\ base])$
   $pH = 14 - pOH$

Points to know:
- Equivalence point
- End Point
- Half-equivalence point
- Buffer Zone

Titrations of Buffered Solutions

overshoot

This region is calculated simply by determining the amount of OH⁻ in EXCESS that has been added. No equilibrium calculations necessary.

pH

pH = 7.00 ————— pH = 7.00

buffer zone

a "type 2" calculation

conjugate ratios are known, use Henderson-Hasselbach to calculate pH.

The **equivalence point** (endpoint) is the same as a regular (type 1) salt of a weak acid problem (NaA). You know [A⁻] and you can calculate pH. Also note that the pH must be *greater than 7* due to the hydrolysis of A⁻.

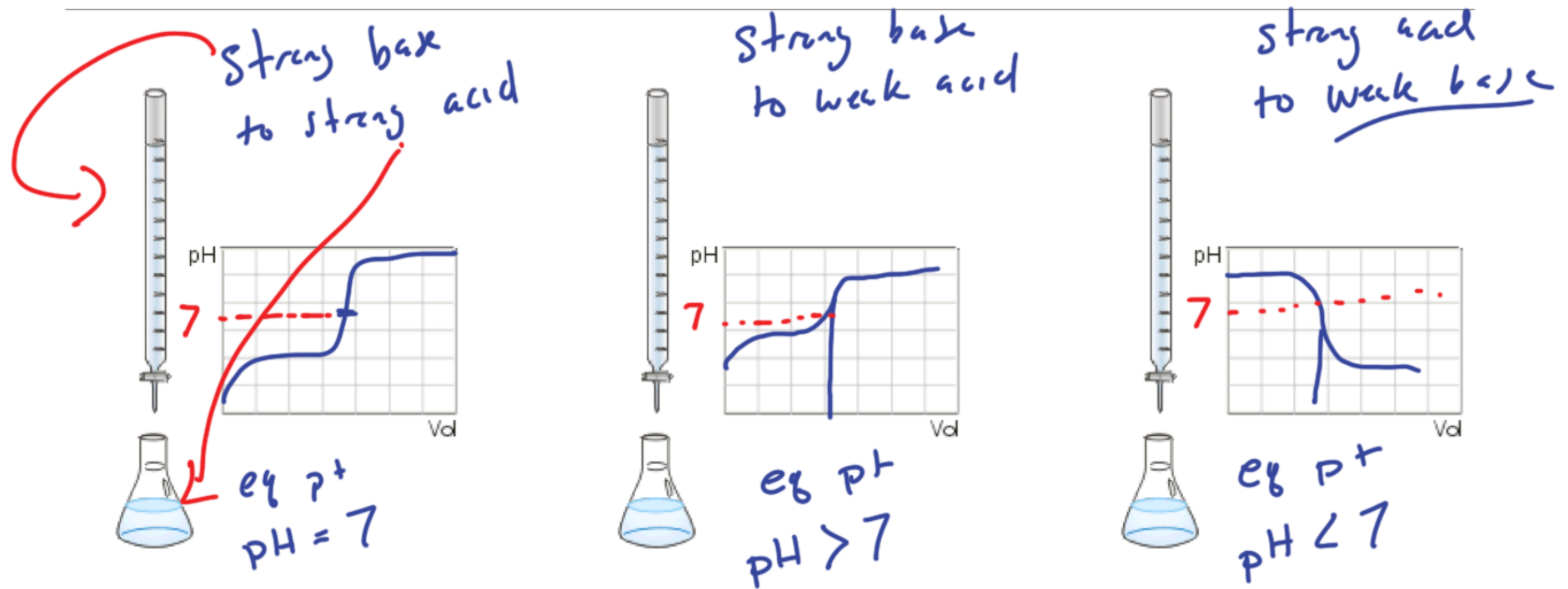$$A^- + H_2O \rightleftharpoons HA + OH^-$$

mL of base

A) Before you have started:
   Calculate pH using the approximation formula or using $K_a = [H^+][A^-] / [HA]$.
B) Within the buffer zone:
   $pH = pKa + \log ([A^-]/[HA])$
C) At the equivalence point:
   You only have the salt of your weak acid in solution. Use $K_w = K_aK_b$, then solve for [OH⁻], pOH, then convert to pH
D) After the equivalence point:
   Find the pH using the excess base in solution
   $pOH = -\log ([excess\ base])$
   $pH = 14- pOH$

Points to know:
- Equivalence point
- End Point
- Half-equivalence point
- Buffer Zone

Titration Experiments

Strong base to strong acid

eq p⁺ pH = 7

Strong base to weak acid

eq p⁺ pH > 7

Strong acid to weak base

eq p⁺ pH < 7

Titration Questions

You titrate 50mL of 0.5M acetic acid with 1M NaOH.

K_a for acetic acid is 1.75×10^{-5}. $pK_a = 4.76$

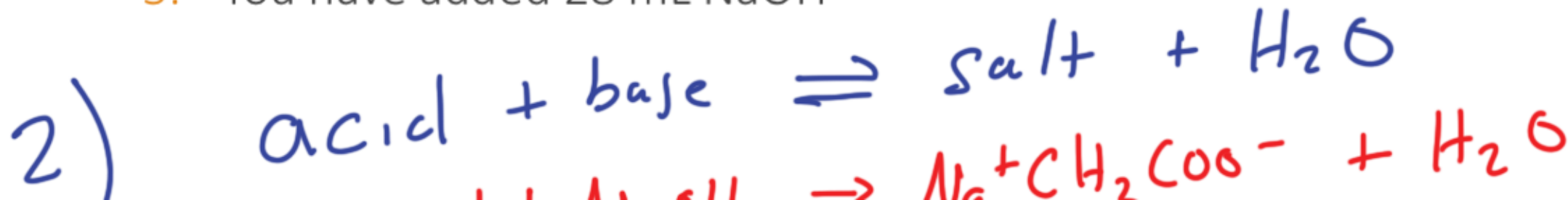What is the pH when:

1. You start the experiment. → Weak acid

2. You have added 10 mL NaOH → buffer calc

3. You have added 12.5 mL NaOH (to original solution)

4. You reach the end point → weak base calc

5. You have added 28 mL NaOH

2) acid + base ⇌ salt + H_2O

→ $Na^+CH_2COO^- + H_2O$

R $CH_3COOH + NaOH$

		0.01		∅
I	0.025			+0.01
C	-0.01	-0.01		
E	0.015	∅		0.01

$$pH = pK_a + \log \frac{A^-}{HA}$$

$$4.68 = 4.76 + \log \frac{0.01}{0.015}$$

3) End point/eq point:

$$pH = -\log [H^+]$$

$$[H^+] = \sqrt{K_a \cdot C_{HA}}$$

$$0.003M = \sqrt{(1.75 \times 10^{-5})(0.5)}$$

$$pH = -\log(0.003M) = 2.5$$

2) moles $HA = 0.5 \frac{mol}{L} \times 0.050L = 0.025 mol$

$+$ moles $NaOH = \cancel{0.025} \overset{1M}{} \frac{mol}{L} \times 0.00\overset{10}{\cancel{0}}L = 0.010 mol$

─────────────────

60L solution, 0.015 mol HA
0.010 mol A^-

$$[HA] = \frac{0.015 mol}{.060L} = 0.25M \ HA$$

$$[A^-] = \frac{0.010 mol}{0.060L} = 0.17M \ A^-$$

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

$$4.76 + \log\left(\frac{0.17}{0.25}\right) = 4.60$$

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moles CH_3COOH = moles $NaOH$
$\downarrow$ = 0.025 moles $\downarrow$

50mL

$$\frac{1.0 \frac{mol}{L}}{0.025 \, moles} = 25mL$$

Final solution @ eq point will have

0.025 moles $Na \, CH_3COOH$, 75mL

$$K_b = \frac{K_w}{K_a} \quad , \quad pOH = -\log[OH^-]$$

$$5.7 \times 10^{-10} \qquad [OH^-] = \sqrt{K_b \cdot C_B}$$

$$\frac{0.025 mol}{0.075L} \approx 0.33$$

$$pOH = 4.86$$
$$pH = 9.13$$

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4) excess $NaOH$ = 26mL - 25mL

1mL excess

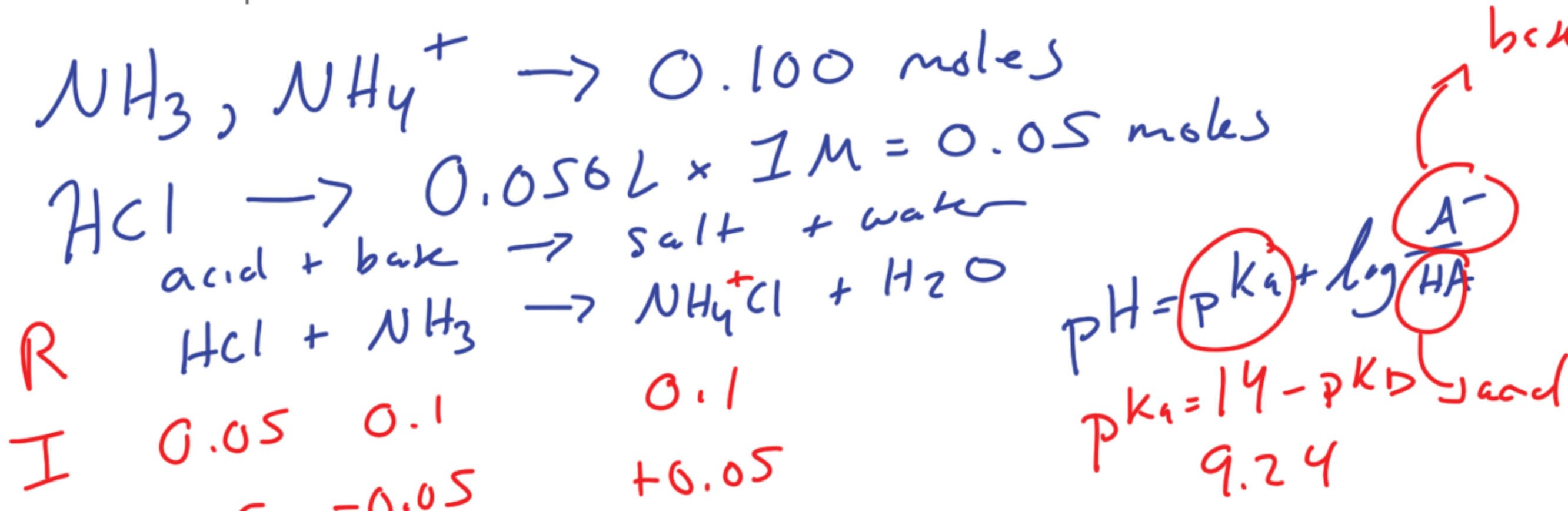$$[OH^-] = \left(\frac{0.001L \cdot 1\frac{mol}{L}}{76mL \cdot \frac{1}{1000}}\right)$$

$$pH = 12.11$$

Exam Question

A buffer was prepared by mixing 0.200 mole of ammonia ($K_b = 1.8 \times 10^{-5}$, $pK_b = 4.76$) and 0.200 mole of ammonium chloride to form an aqueous solution with a total volume of 500 mL. To 250 mL of this solution was added 50.0 mL of 1.00 M HCl. What is the pH of this solution?

$$NH_3, NH_4^+ \longrightarrow 0.100 \text{ moles}$$

$$HCl \longrightarrow 0.050L \times 1M = 0.05 \text{ moles}$$

$$\text{acid} + \text{base} \longrightarrow \text{salt} + \text{water}$$

$$HCl + NH_3 \longrightarrow NH_4^+Cl + H_2O$$

$$
\begin{array}{c|ccc}
R \\
I & 0.05 & 0.1 & & 0.1 \\
 & -0.05 & & & +0.05
\end{array}
$$

$$base$$

$$pH = pK_a + \log \frac{A^-}{HA}$$

$$pK_a = 14 - pK_b \quad \text{acid}$$

$$9.24$$

$$C \quad -0.05$$

$$\overline{E} \quad \emptyset \quad \boxed{0.05} \quad \boxed{0.15}$$

$$A^- \qquad HA$$

$$pH = 9.24 + \log \frac{0.05}{0.15}$$

$$= 8.76$$

Fraction of Species

- For weak acids, especially for organic compounds and polyprotic acids, you can determine the "protonation-state" of your molecule at any given pH.

- A few simple rules go a long way with answering these types of questions:

  1. Think about your molecule. Your pK_a represents the pH where you have equal protonated and deprotonated states.

  2. Think about your environment. The pH compared to the pK_a will tell you whether your molecule is protonated or deprotonated.

  3. If pH < pK_a ; you have too many hydrogen ions in solution for it to be favorable for a hydrogen ion on your molecule to "pop off"

     ◦ Think about it: when the environment is more acidic, it is more "proton-donating,"

  4. If pH > pK_a ; the environment around your molecule is thirsty for hydrogen ions, so it is favorable for a hydrogen ion on your molecule to pop off

     ◦ Think about it: when the environment is more basic, it is more "proton-accepting."