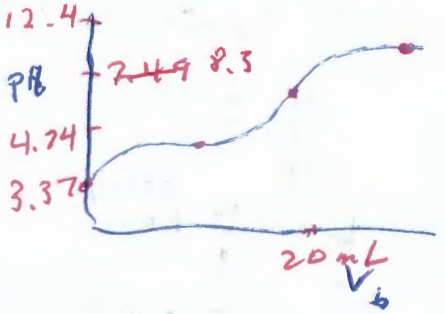
Problems : ~~find pH ...~~

① sketch titration curve

25 mM NaOH

10 mM HAc
50 mL



i) @ $V_b = 0$

Find pH of 10 mM HAc

- $HAc + H_2O \rightleftharpoons H_3O^+ + Ac^-$

I	10 mM	0	0
C	$-x$	$+x$	$+x$
E	$10\,mM - x$	x	x

- $K_a = \frac{[H_3O^+][Ac^-]}{[HAc]}$

$1.8 \cdot 10^{-5} = \frac{x^2}{0.01 - x} \approx \frac{x^2}{0.01}$

$x = \sqrt{0.01(1.8 \cdot 10^{-5})} = 4.24 \cdot 10^{-4}$

- $pH = -\log_{10}[H^+] = -\log_{10}(4.24 \cdot 10^{-4})$

$= \underline{3.37}$

ii) @ $V_{b,eq}$

$[A]V_A = [B]V_B$

$10\,mM\,(50\,mL) = 25\,mM\,V_B$

$V_b = \underline{20\,mL}$

iii) pH @ $V_{b,eq}$

- $n_{HAc} = [HAc]V_{HAc} = 10\,\frac{mmol}{L} \cdot 50\,mL \cdot \frac{L}{10^3\,mL}$

$= 0.5\,mmol\,HAc$

- $n_{NaOH} = [NaOH]V_{NaOH} = 25\,\frac{mM}{L} \cdot 20\,mL \cdot \frac{L}{10^3\,mL}$

$= 0.5\,mmol\,NaOH$

$NaOH + HAc \rightarrow H_2O + NaAc$

n_I	0.5 mmol	0.5 mmol	0	0
n_C	−0.5 mol	−0.5 mmol		+
n_E	0	0		0.5 mmol

- $[NaAc] = \frac{n_{NaAc}}{V_{total}} = \frac{0.5 \text{ mmol}}{70 \text{ mL}} \frac{10^3 \text{ mL}}{\text{L}} \frac{\text{mol}}{10^3 \text{ mmol}}$

$= 0.00714 \text{ M}$

i.e. find pH of 0.00714 M NaAc

- $NaAc \rightarrow Na^+ + Ac^-$

$Ac^- + H_2O \rightleftharpoons HAc + OH^-$ K_b

I	0.00714		0	0
C	−x		+x	+x
E	0.00714 − x		x	x

- $K_b = \frac{K_w}{K_a} = \frac{[HAc][OH^-]}{[Ac^-]}$

$\frac{10^{-14}}{1.8 \cdot 10^{-5}} = \frac{x^2}{0.00714 - x} \approx \frac{x^2}{0.00714}$

$x = \sqrt{0.00714 \cdot 5.56 \cdot 10^{-10}} = 3.99 \cdot 10^{-6}$

- $pOH = -\log_{10}[OH^-] = -\log_{10}(3.99 \cdot 10^{-6}) = 5.70$

- $pH + pOH = 14$

$pH + 5.70 = 14$

$pH = 8.30$

$V_b = \frac{1}{2} V_{b,ep} = 10\ mL$

$n_{NaOH} = [NaOH]\, V_{NaOH}$

$= 25\ mmol/2 \cdot 10\ mL \cdot \frac{L}{10^3\ mL} = 0.25\ mmol\ NaOH$

- $NaOH + HAc \rightarrow H_2O + NaAc$

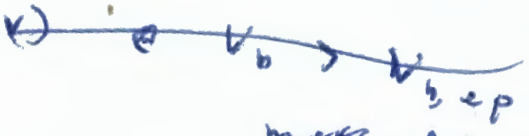
n I	0.25 mmol	0.5 mmol	/	0
n C	−0.25 mmol	−0.25 mmol	/	+0.25 mmol
n E	~~0.25 mmol~~ 0	0.25 mmol	/	0.25 mmol

- method 1: use HH eq.

$pH = pK_a + \log \frac{A^-}{HA}$ (1)

$pH = pK_a \quad @\ V_b = \frac{1}{2} V_{b,ep}$

$= -\log(1.8 \cdot 10^{-5}) = \underline{4.74}$



method 2: use ICE table

- $[HAc] = [NaAc] = \frac{n_{NaAc}}{V_{total}} = \frac{0.25\ mmol}{60\ mL} \cdot \frac{10^3\ mL}{L} \cdot \frac{mol}{10^3\ mmol}$

$= 0.00417\ M = [Ac^-]$

- $HAc + H_2O \rightleftharpoons H_3O^+ + Ac^-$

I	0.00417	/	0	0.00417
C	−x	/	+x	+x
E	0.00417 − x	/	x	0.00417 + x

- $K_a = \frac{[H_3O^+]\,[Ac^-]}{[HAc]}$

$1.8 \cdot 10^{-5} = \frac{x\,(0.00417 + x)}{0.00417 - x} \approx \frac{0.00417\,x}{0.00417}$

0.00406
0.0000178
$\uparrow 1.78 \cdot 10^{-5}$

- $\rightarrow pH = pK_a$

v) @ $V_b >> V_{b,eq}$ ⟶ pH → pH of base

rationale:

$$[OH^-] = \frac{n_{OH^-}}{V_{total}} \approx \frac{n_B - n_A}{V_A + V_B} = \frac{[B]V_B - [A]V_A}{V_A + V_B}$$

$[OH^-] = [B]$ using L'Hopital's rule

$V_b \to \infty$

- @ 50 $[OH^-] = [NaOH] = 25\,mM$

$$pOH = -\log[OH^-] = -\log(25 \cdot 10^{-3}) = 1.60$$

- $pH + pOH = 14$

$$pH + 1.60 = 14$$

$$pH = 12.4$$

(2) find pH . . .

(A) 25 mM NaOH

10 mM HAc
50 mL

i) $V_b = 5\,mL$

- $n_{HAc} = [\ ]V = 0.5\,mmol\ HAc$

$$n_{NaOH} = [\ ]V = 25\frac{mmol}{L} \cdot 5\,mL \cdot \frac{L}{10^3\,mL} = 0.125\,mmol$$

method: use ICE table

$$[OH^-] = \frac{n_{NaOH}}{V_{total}} = \frac{0.5\,mmol}{55\,mL} \cdot \frac{mol}{10^3\,mmol} \cdot \frac{10^3\,mL}{L}$$

- $HAc + NaOH \rightarrow H_2O + NaAc$

n_I	0.5 mmol	0.125 mmol	/	0
n_C	−0.125 mmol	−0.125 mmol	/	+0.125 mmol
n_E	0.375 mmol	0	/	0.125 mmol

• method 1: use ICE table

$HAc + H_2O \rightleftharpoons Ac^- + H_3O^+$

[I]	$\frac{0.375\ mmol}{55\ mL}$		$\frac{0.125\ mmol}{55\ mL}$	0
[C]	$-x$		$+x$	$+x$
[E]	$0.00682 - x$		$0.00227 + x$	

-0.00234
$\approx 5.245 \cdot 10^{-5}$ ✓

$$K_a = 1.8 \cdot 10^{-5} = \frac{(0.00227 + x)\,x}{0.00682 - x} \approx \frac{0.00227}{0.006}$$

$$x = 5.41 \cdot 10^{-5}\ M$$

• $pH = -\log [H^+] = -\log (5.41 \cdot 10^{-5}) = 4.27$

method 2: use HH eq.

$$pH = pK_a + \log \frac{Ac^-}{HAc}$$

$$= -\log (1.8 \cdot 10^{-5}) + \log \left(\frac{0.125\ mmol / 55\ mL}{0.375\ mmol / 55\ mL} \right)$$

$$= 4.27$$

ii) ✓ $V_b = 25\ mL$

• $n_{NaOH} = [NaOH]\, V_{NaOH} = 25\ \frac{mmol}{L}\ 25\ mL\ \frac{L}{10^3\ mL}$

$= 0.625\ mmol$

• $NaOH + HAc \longrightarrow NaAc + H_2O$

n I	0.625 mmol	0.5 mmol		
n C	−0.5	−0.5	+0.5	
n E	0.125 mmol	0		

• $[NaOH] = \frac{0.125\ mmol}{75\ mL} = 0.00167\ M = [OH^-]$

$[NaAc] = \frac{0.5\ mmol}{75\ mL} = 0.00667\ M = [Ac^-]$

- $Ac^- + H_2O \rightleftharpoons HAc + OH^-$ K_b

[I]	0.00667		0	0.00167
[C]	$-x$		$+x$	$+x$
[E]				

$$K_b = \frac{10^{-14}}{1.8 \cdot 10^{-5}} = 5.56 \cdot 10^{-10} = \frac{x(0.00167 + x)}{0.00667 - x}$$

$$[OH^-] = 0.00167 + x \approx 0.00167$$

$$\approx \frac{x\ 0.00167}{0.00667}$$

$$x = 2.22 \cdot 10^{-9}$$

- $pOH = -\log [OH^-] = -\log (2.22 \cdot 10^{-9})$

$$= 2.78$$

- $pH + pOH = 14$

$$pH + 2.78 = 14$$

$$pH = 11.22$$