10-6. Given HA ($pK_a = 5.00$), 100.0 mL + 0.100 M conc.
Titrant = 1.00 M KOH; Calc. pH at $V_b$ = 1.00, ~~9.90~~, 10.00 and 10.10 mL

Work: First, calc. $V_e$ ⇒ $V_e = \frac{M_a V_a}{M_b} = \frac{(0.100\ M)(100.0\ mL)}{1.00\ M}$

$V_e = 10.00\ mL$

(a) $V_b = 1.00\ mL$ ⇒ before the equiv. point; since HA is a weak acid, reaction with $OH^-$ produces $A^-$
⇒ buffer region

Initial mol HA = 0.0100 ; mol $OH^-$ = 0.00100

| | HA | + | $OH^-$ | ⟶ | $A^-$ + $H_2O$ |
|---|---|---|---|---|---|
| Init. mol | 0.01 | | 0.001 | | 0 |
| change | −0.001 | | −0.001 | | +0.001 |
| Final mol | 0.009 | | 0 | | 0.001 |

$pH = pK_a + \log\left(\frac{mol\ A^-}{mol\ HA}\right) = 5.00 + \log\frac{0.001}{0.009}$

**pH = 4.05**

(b) $V_b = 10.00\ mL = V_e$ ; Only $A^-$ in water at the eq. pt.
mol $A^-$ formed = mol HA initially present = 0.0100

$F_{A^-} = \frac{0.0100\ mol}{0.110\ L} = 9.09 \times 10^{-2}\ M$ ← 100 mL + 10.00 mL

Since $A^-$ is a weak base, it will hydrolyze:

$A^- + H_2O \overset{K_b}{\rightleftharpoons} HA + OH^-$

F − y  y  y

$K_b = \frac{K_w}{K_a} = \frac{1\times10^{-14}}{1\times10^{-5}} = \frac{y^2}{(9.09\times10^{-2} - y)}$

$1.0\times10^{-9} = \frac{y^2}{9.09\times10^{-2} - y}$, $y \approx 0$   Assume $y << 9.09\times10^{-2}$

$y^2 = 9.09\times10^{-11}$ ⟶ $y = [OH^-] = 9.53\times10^{-6}$

pOH = 5.02 ; **pH = 8.98**   pH > 7 at the equiv. pt. because $A^-$ is a weak base