

1. A) Intermediate (HA^-) form

$$[\text{H}^+] = \sqrt{\frac{K_{a1}K_{a2}F + K_{a1}K_w}{K_{a1} + F}} = \sqrt{\frac{(1.41 \times 10^{-2})(3.60 \times 10^{-5})(0.205) + (1.41 \times 10^{-2})(1.0 \times 10^{-14})}{1.41 \times 10^{-2} + 0.205}}$$

$$[\text{H}^+] = 6.89 \times 10^{-4}$$

$$\text{pH} = 3.162$$

B) completely deprotonated (A^{2-}) form

$$\alpha_{\text{A}^{2-}} = \frac{K_{a1}K_{a2}}{[\text{H}^+]^2 + [\text{H}^+]K_{a1} + K_{a1}K_{a2}} = \frac{5.076 \times 10^{-7}}{4.75 \times 10^{-7} + 9.71 \times 10^{-6} + 5.076 \times 10^{-7}}$$

$$\alpha_{\text{A}^{2-}} = 0.0475 = 4.75\%$$

2. Start with 1.0×10^{-3} moles H_3Cit

want pH = 7.00

$\text{pK}_{a1} = 3.128$

$\text{pK}_{a2} = 4.762$

$\text{pK}_{a3} = 6.396$

use pK_a closest to desired pH

\therefore use pK_{a3}

K_{a3} reaction: $\text{HCit}^{2-} \leftrightarrow \text{Cit}^{3-} + \text{H}^+$

\therefore add 2 equivalents of base to convert all H_3Cit to HCit^{2-}

\therefore add $2 * 1.0 \times 10^{-3}$ moles = 2.0×10^{-3} moles NaOH

$$\text{pH} = \text{pK}_{a3} + \log \frac{\text{Cit}^{3-}}{\text{HCit}^{2-}}$$

$$7.00 = 6.396 + \log \frac{\text{Cit}^{3-}}{\text{HCit}^{2-}}$$

$$0.604 = \log \frac{Cit^{-3}}{HCit^{-2}}$$

$$4.018 = \frac{Cit^{-3}}{HCit^{-2}}$$

	HCit ⁻²	OH ⁻	Cit ⁻³
Initial	1.0x10 ⁻³	X	0
Final	1.0x10 ⁻³ - X	0	X

$$4.018 = \frac{X}{1.0 \times 10^{-3} - X}$$

$$X = 8.007 \times 10^{-4} \text{ moles NaOH}$$

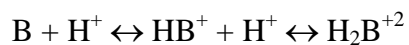
$$\therefore \text{total amount of base used} = 2.0 \times 10^{-3} + 8.007 \times 10^{-4} \text{ moles}$$

$$= 2.8007 \times 10^{-3} \text{ moles NaOH}$$

$$\frac{2.8007 \times 10^{-3} \text{ moles}}{1.00 \times 10^{-2} \text{ M}} = 0.280 \text{ L} = \mathbf{280 \text{ mL}}$$

3. The best drug to use is H₂L. Since the intermediate (singly protonated) state is desired, the pH should be between pK_{a1} and pK_{a2} in order to ensure that the major form is the intermediate form. Drug H₂L has pK_{a1} = 5.36 and pK_{a2} = 8.63 and is thus the best choice.

4. A. Triprolidine is a diprotic base



Use pK_{a2} because first proton on is related to last proton off

$$6.35 \times 10^{-2} \text{ M} * 0.250 \text{ L} = 1.5875 \times 10^{-2} \text{ moles B}$$

20.00 mL HCl * 0.500M = 0.0100 moles

	B	+	H⁺	→	HB⁺
Initial	0.015875		0.0100		0
Final	0.005875		0		0.01000

pKa2 = 9.301

$$\text{pH} = 9.301 + \log \frac{0.005875}{0.01000} = \mathbf{9.070}$$

B. 45.00 mL HCl * 0.500M = 0.0225 moles

Use 0.015875 moles H⁺ to convert 0.015875 moles B into 0.015875 moles HB⁺

∴ have 0.006625 moles H⁺ to react with HB⁺

Use pKa₁ because last proton on is related to first proton off

	HB⁺	+	H⁺	→	H₂B⁺²
Initial	0.015875		0.006625		0
Final	0.00925		0		0.006625

pKa1 = 3.600

$$\text{pH} = 3.600 + \log \frac{0.00925}{0.006625} = \mathbf{3.745}$$

5. A. want buffer pH as close to the pKa as possible

∴ for pH 4.50, use the second and third forms (B,C) or (H₂A and HA⁻)

B. pH = pKa when the two concentrations are equal

∴ at pH 1.991 the first form (H₃Asp⁺) and second form (H₂Asp) will have equal concentrations

C. isoelectric point (pI) is the average of the pKa values surrounding the neutral species

$$\mathbf{pI = (1.991 + 3.900)/2 = 2.946}$$

6. $385.0 \text{ mL} * 4.18 \times 10^{-3} \text{ M HA} = 1.609 \times 10^{-3} \text{ moles HA}$

$12.00 \text{ mL} * 0.105 \text{ M NaOH} = 1.26 \times 10^{-3} \text{ moles OH}^-$

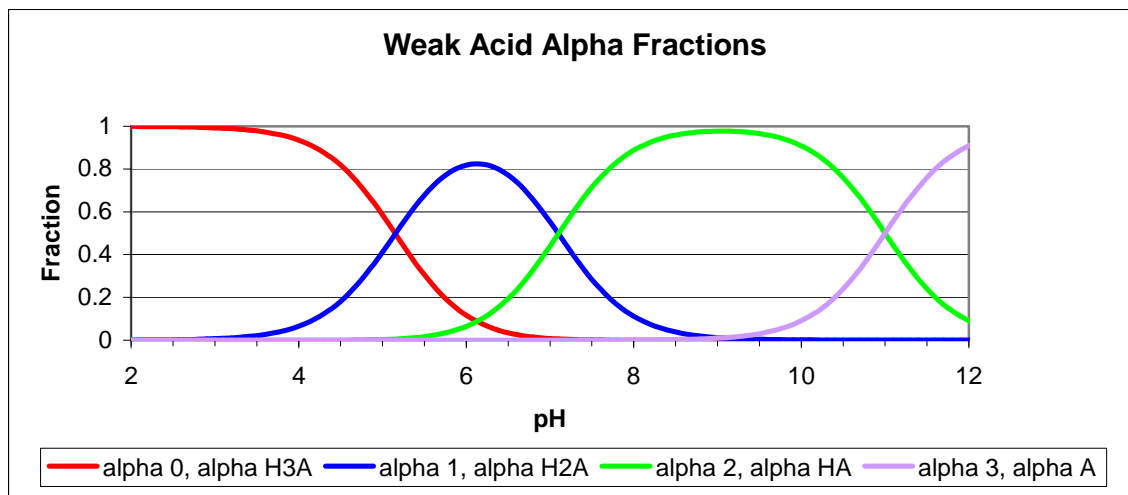
	HA	OH ⁻	A ⁻
Initial	0.001609	0.00126	0
Final	0.000349	0	0.00126

$$\text{pH} = \text{pK}_a + \log \frac{\text{A}^-}{\text{HA}}$$

$$6.285 = \text{pK}_a + \log \frac{0.00126}{0.000349}$$

$$\text{pK}_a = 5.728 \quad \mathbf{K}_a = \mathbf{1.87 \times 10^{-6}}$$

7. A.



B. Four alpha fractions indicates that there are 3 removable protons

∴ Triprotic species

C. $\text{pK}_a = \text{pH}$ when alpha fractions are equal

$$\therefore \text{pK}_{a1} \approx 5.1 \quad \text{pK}_{a2} \approx 7.1 \quad \text{pK}_{a3} \approx 11.0$$

D. buffer capacity is highest when there are equal concentrations of both acidic and basic forms

∴ buffer capacity is highest when $\text{pK}_a = \text{pH}$

∴ $\text{pH} \approx 7$

8. Final equivalence point is at ~ 35 mL

$$35 \text{ mL} * 0.1053 \text{ M} = 3.686 \times 10^{-3} \text{ moles acid added}$$

IF monoprotic:

3.686×10^{-3} moles acid added must have reacted with 3.686×10^{-3} moles base

$$\frac{0.7621 \text{ g}}{3.686 \times 10^{-3} \text{ moles}} = 206.8 \text{ g/mol} \quad \text{no monoprotics are listed with this molecular weight}$$

IF diprotic:

Each mole of base would react with 2 moles of acid

$$\therefore \text{there would be } \frac{3.686 \times 10^{-3}}{2} = 1.842 \times 10^{-3} \text{ moles of acid to begin with}$$

$$\frac{0.7621 \text{ g}}{1.842 \times 10^{-3} \text{ moles}} = 413.5 \text{ g/mol} \quad \text{this molecular weight corresponds to **base D**}$$