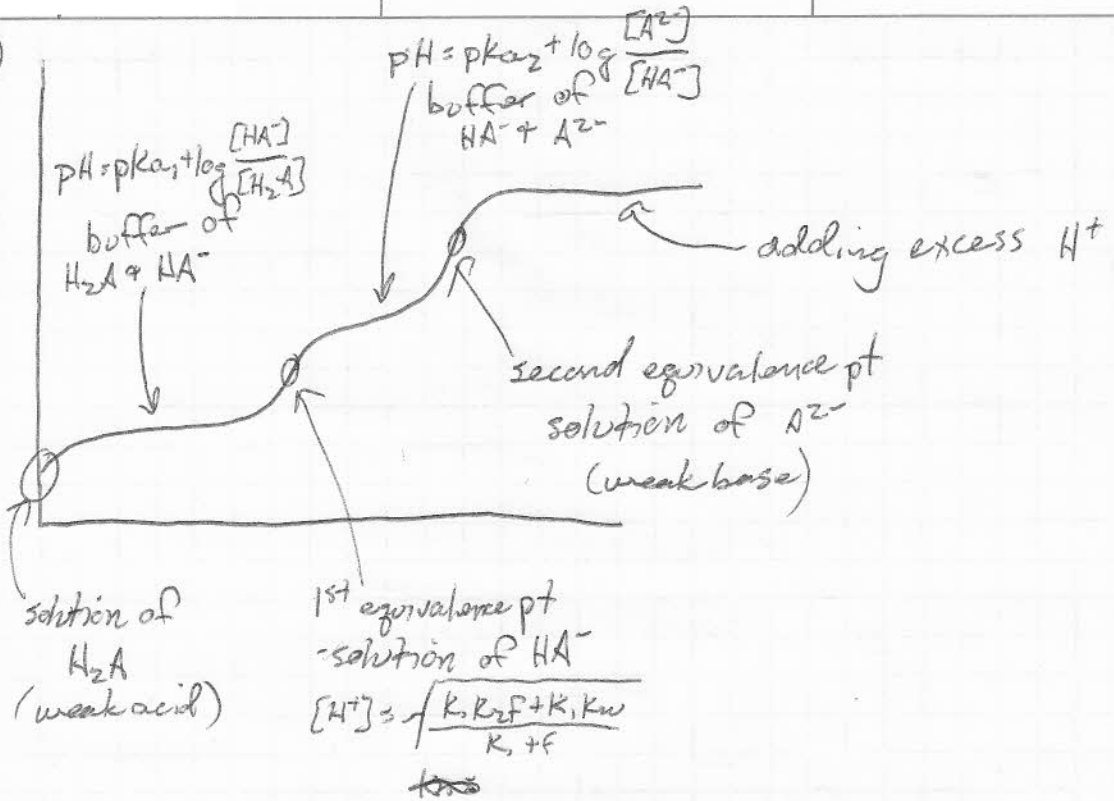


19



23. $V_a = 0 \text{ ml}$ $\frac{x^2}{0.100 - x} = 10^{-4}$
 $x^2 + 10^{-4}x - 10^{-5} = 0$
 $x = 0.00311 \text{ M} = [OH^-]$

$pH = -\log \left(\frac{10^{-14}}{3.11 \times 10^{-3}} \right) = 11.49$

$V_a = 1 \text{ ml}$ $100 \text{ ml} \left| \frac{0.100 \text{ mmol}}{1 \text{ mL}} \right| = 10.00 \text{ mmol } A^{2-}$
 $1 \text{ ml} \left| \frac{1 \text{ mmol } H^+}{1 \text{ mL}} \right| = 1 \text{ mmol } H^+$
 $pK_{a2} = 14 - pK_{b1} = 10$
 $10.00 - 1.00 = 9.00 \text{ mmol } A^{2-}$
 $1.00 \text{ mmol } HA^-$
 $pH = 10.00 + \log \frac{9}{1} = 10.95$

$V_a = 5 \text{ ml}$ $5 \text{ mmol } H^+$ $A^{2-} = 10 - 5 = 5 \text{ mmol}$
 $HA = 5$ $pH = 10.00 + \log \frac{5}{5} = 10.00$

$V_a = 9 \text{ mL}$ $9.00 \text{ mmol } H^+$ $A^{2-} = 10 - 9 = 1.00 \text{ mmol}$
 $HA = 9.00 \text{ mmol}$ $pH = 10.00 + \log \frac{1}{9} = 9.05$

$V_a = 10 \text{ mL}$ $10 \text{ mmol } H^+ \rightarrow$ 1st equivalence pt
 $[H^+] = \sqrt{\frac{(10^{-6})(10^{-10})(0.0909) + (10^{-6})(10^{-14})}{10^{-6} + 0.0909}}$ $F = \frac{10 \text{ mmol}}{110 \text{ mL}} = 0.0909 \text{ M}$
 $= 1.00 \times 10^{-8} \rightarrow pH = 8.00$

23 (cont)

$V_a = 11 \text{ ml}$ $11.00 \text{ mmol } H^+ \text{ (1.00 mmol past equiv. pt)}$ $pK_{a1} = 14 - pK_{b2}$
 $HA^- = 10 - 1 = 9.00 \text{ mmol}$ $pH = 6.00 + \log \frac{9}{1} = \boxed{6.95}$
 $H_2A = 1.00 \text{ mmol}$

$V_a = 15 \text{ ml}$ $HA^- = 10 - 5 = 5 \text{ mmol}$ $pH = 6.00 + \log \frac{5}{5} = \boxed{6.00}$
 $H_2A = 5 \text{ mmol}$

$V_a = 19 \text{ ml}$ $HA^- = 10 - 9 = 1 \text{ mmol}$ $pH = 6.00 + \log \frac{1}{9} = \boxed{5.05}$
 $H_2A = 9 \text{ mmol}$

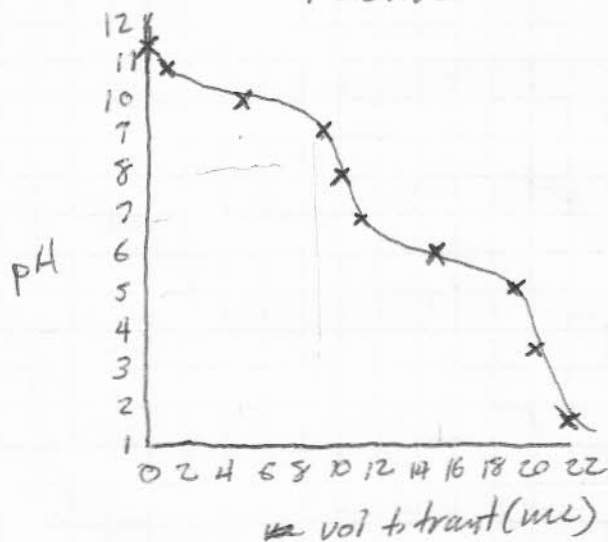
$V_a = 20 \text{ ml}$ $20.00 \text{ mmol } H^+ = 2^{\text{nd}}$ equivalence pt. solution of H_2A
 $[H_2A] = \frac{10 \text{ mmol}}{120 \text{ ml}} = 8.33 \times 10^{-2} M$

$$\frac{x^2}{8.33 \times 10^{-2} - x} = 10^{-6}$$

$pH = \boxed{3.54}$

$$x = \frac{3.46 \times 10^{-3} M}{2.89 \times 10^{-4}} = [H^+]$$

$V_a = 22 \text{ ml}$ $\frac{2 \text{ excess mmol } H^+}{122 \text{ ml}} = 0.0164 M H^+$ $pH = \boxed{1.79}$



26) $\frac{25.0 \text{ mL} / 0.0200 \text{ mmol}}{1 \text{ mL}} = 0.500 \text{ mmol base (intermediate form)}$
 $\frac{-0.1635}{0.500} = 0.3365 \text{ mmol base}$
 $\frac{10.9 \text{ mL} / 0.0150 \text{ mmol H}^+}{1 \text{ mL}} = 0.1635 \text{ mmol H}^+ \rightarrow \text{mmol acid}$
 $\text{pH} = 4.70 + \log \frac{0.3365}{0.1635} = \boxed{5.01}$

29) $\frac{0.0100 \text{ M}}{0.00400 \text{ M}} = 2.5 \text{ times more H}^+$
 equivalence pt conc. = $\frac{0.0100}{3.5} = 2.86 \times 10^{-3} \text{ M}$
 $\frac{x^2}{2.86 \times 10^{-3} - x} = 3.9 \times 10^{-3}$
 $x^2 + 3.9 \times 10^{-3}x - 1.11 \times 10^{-5} = 0$
 $x = 1.91 \times 10^{-3} = [\text{H}^+]$
 $\text{pH} = \boxed{2.72}$

31) oxalic acid $\text{pK}_{a2} = 4.266$ acid = $\frac{20.0 \text{ mL} / 0.800 \text{ mmol}}{1 \text{ mL}} = 16 \text{ mmol}$
 $4.40 = 4.266 + \log \frac{\text{base}}{\text{acid}}$ total oxalate = $16 + 21.76 = 37.8 \text{ mmol oxalate}$
 $\frac{\text{base}}{\text{acid}} = 1.36$ $\frac{\text{base}}{16} = 1.36$
 base = 21.76
 $\frac{37.8 \text{ mmol} / 166.22 \times 10^{-3} \text{ g}}{1 \text{ mmol}} = \boxed{6.28 \text{ g}}$

36) when $\text{pH} = \text{pK}_a$, there are equal ~~forms~~^{amounts} of acid and base forms. When $\text{pH} = \text{pK}_a \pm 1$ there is 10 times more of one or the other form. This should be sufficient to see a definite color change

41) a. red b. orange c. yellow

43) No, the pH at the equivalence pt will be above 7.

47) $\frac{14.22 \text{ mL} / 0.1063 \text{ mmol H}^+}{1 \text{ mL}} / \frac{1 \text{ mmol NH}_3}{1 \text{ mmol H}^+} / \frac{17.031 \text{ mg NH}_3}{1 \text{ mmol NH}_3} = \frac{25.74 \text{ mg NH}_3}{4.373 \times 10^{-3} \text{ mg soln}} \times 100$
 dilution factor = $\frac{10.231}{10.231 + 39.466} = 0.206$
 $\frac{0.589\%}{0.206} = \boxed{2.86\%} = 0.589\% \text{ in diluted soln}$