CHEM 311 Fall 2010

10-1

The equivalence point occurs when the quantity of titrant added is exactly the stoichiometric amount needed for complete reaction with the analyte. The end point occurs at some abrupt physical change, such as change in pH or indicator color. For an accurate and meaningful data, indicators must be chosen such that they change color at a pH that corresponds as near as possible to the equivalence point.

10.2

Titrating a strong base with a strong acid 100.00 ml of 0.100 M NaOH with 1.00 M HBr

 $\text{mmol OH}_{\text{initial}} = (100.00 \text{ mL})^*(0.100 \text{ M}) = 10.0 \text{ mmol OH}^-$

@ 0.00 mL added

 $[OH^{-}] = 0.100 \text{ M}$ $[H_{3}O]^{+} = 1.00*10^{-13}$ pH = 13.00

@ 1.00 mL

 $[OH^{-}] = [(mmol OH^{-}_{initial}) - (1.00 mL HBr)(1.00 M H^{+})]/V_{t}$ = [(10.0 - 1.00)]/101.00] = 0.089 M [H₃O]^{+} = 1.1*10^{-13} pH = 12.95

@ 5.00 mL

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[OH^{-}] = [(mmol OH^{-}_{initial}) - (5.00 mL HBr)(1.00 M H^{+})]/V_{t}
= [(10.0 - 5.00)]/105.00] = 0.048 M
[H<sub>3</sub>O]^{+} = 2.1 *10^{-13}
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pH = 12.68
@ 9.00 mL
$$[OH^{-}] = [(mmol OH^{-}_{initial}) - 9.00 mL HBr)(1.00 M H^{+})]/V_{t}$$
$$= [(10.0 - 9.00)]/109.00] = 9.2*10^{-3} M$$
$$[H_{3}O]^{+} = 1.1*10^{-12}$$
$$pH = 11.96$$

@ 9.90 mL

@ 10.00 mL

 $[OH^{-}] = [(mmol OH^{-}_{initial}) - (9.90 mL HBr)(1.00 M H^{+})]/V_{t}$ = [(10.0 - 9.9)]/109.90] = 9.099*10⁻⁴ M [H₃O]⁺ = 1.1*10⁻¹¹ pH = 10.96

 $[OH^{-}] = [(mmol OH^{-}_{initial}) - (10.00 mL HBr)(1.00 M H^{+})]/V_{t}$ = [(10.0 - 1.00)]/110.00] = 0 (= 10⁻⁷ M from Kw rxn) [H₃O]⁺ = 10⁻⁷ pH = 7.00

(@ 10.10 mL After the equiv. point the excess H^+ is what controls the pH.

equiv. pt

 $[H^{+}] = [(10.10 \text{ mL HBr})(1.00 \text{ M H}^{+})-(\text{mmol OH}^{-}_{\text{initial}})]/V_{t}$ = [10.10 - 10.0) / (110.10) = 9 *10⁻⁴ M pH = 3.0

@ 12.00 mL After the equiv. point the excess H^+ is what controls the pH.

 $[H^{+}] = [(12.00 \text{ mL HBr})(1.00 \text{ M H}^{+}) - (\text{mmol OH}^{-}_{\text{initial}})]/V_{t}$ = [12.00 - 10.0) / (112.00) = 1.8*10⁻² M pH = 1.75



10-6

100.0 mL of a solution of 0.100 M weak acid, HA, is titrated with 1.00 M KOH. (Ka = $1.0*10^{-5}$)

@ 0 mL added

Ka = $[H^+]^2/0.1 = 1.0*10^{-5}$ [H⁺] = 1.0*10⁻³ pH = 3.00

@ 1.00 mL added

OH⁻ added = $(1.00 \text{ M})^*(1.00 \text{ mL}) = 1.00 \text{ mmol OH}^-$ HA + OH⁻ \rightarrow A⁻ + H₂O (to completion/or near to) pH = pKa +log(mol A⁻/mol HA) mol A⁻ = 1.00 mmol mol HA = (100.0 mL*0.100 M)- 1.00 mol = 9.00 mmol pH = 5.00 + log(1/9) = 4.05

@ 5.00 mL added

OH⁻ added = $(1.00 \text{ M})^*(5.00 \text{ mL}) = 5.00 \text{ mmol OH}^-$ HA + OH⁻ \rightarrow A⁻ + H₂O (to completion/or near to) pH = pKa +log(mol A⁻/mol HA) mol A⁻ = 5.00 mmol mol HA = (100.0 mL*0.500 M)- 5.00 mol = 5.00 mmol $pH = 5.00 + \log(5/5) = 5.00$

@ 9.00 mL added

 $OH^{-} added = (1.00 \text{ M})*(9.00 \text{ mL}) = 9.00 \text{ mmol OH}^{-}$ HA + OH⁻ \rightarrow A⁻ + H₂O (to completion/or near to) pH = pKa +log(mol A⁻/mol HA) mol A⁻ = 9.00 mmol mol HA = (100.0 mL*0.500 M)- 9.00 mol = 1.00 mmol pH = 5.00 + log(9/1) = 5.95

@ 9.90 mL added

OH⁻ added = $(1.00 \text{ M})^*(9.90 \text{ mL}) = 9.90 \text{ mmol OH}^-$ HA + OH⁻ \rightarrow A⁻ + H₂O (to completion/or near to) pH = pKa +log(mol A⁻/mol HA) mol A⁻ = 9.90 mmol mol HA = $(100.0 \text{ mL}^*0.500 \text{ M})$ - 9.90 mol = 0.10 mmol pH = $5.00 + \log(9.9/.1) = 7.00$

@ 10.00 mL added

 OH^- added = (1.00 M)*(10.00 mL) = 10.00 mmol OH^-HA + OH^- \rightarrow A⁻ + H₂O (to completion/or near to) pH = pKa +log(mol A⁻/mol HA) mol A⁻ = 10.00 mmol mol HA = (100.0 mL*0.500 M)- 10.0 mol = 0 mmol

This is the equivalence point. The appropriate equilibrium is the Kb reaction for A^{-} .

 $A^{-} + H_2O \leftrightarrow HA + OH^{-}$

$$\begin{split} F_{A-} &= (10.00 \text{ mmol})/(110.0 \text{ mL}) = 0.0909 \text{ M} \\ \text{Kb} &= \text{Kw/Ka} = 1.00*10^{-9} = [\text{HA}][\text{OH}^{-}]/(\text{F}_{A-}\text{-}[\text{HA}]) \\ \text{Assume [OH}^{-}] &= [\text{HA}], \text{ and let [HA]} = x \end{split}$$

Assume $F_{A-} \cong [A^-]$

$$1.00*10^{-9} = x^2/(0.0909)$$

x = [OH⁻] = $9.53*10^{-5}$ M
[H₃O]⁺ = $1.05*10^{-9}$
pH = 8.98

- @ 10.10 mL After the equiv. point the excess OH⁻ is what controls the pH.
- $$\begin{split} [OH^{-}] = & [(10.10 \text{ mL KOH})(1.00 \text{ M KOH})\text{-}(\text{mmol HA}_{\text{initial}})]/V_t \\ &= & [10.10 \text{ } 10.0) \ / \ (110.10) = 9 \ \text{*}10^{\text{-4}} \text{ M} \\ & pH = & 11.0 \end{split}$$
- @ 12.00 mL After the equiv. point the excess OH⁻ is what controls the pH.

$$\begin{split} [OH^{-}] &= \; [(12.00 \text{ mL KOH})(1.00 \text{ M OH}^{-})\text{-}(\text{mmol HA}_{\text{initial}})]/V_t \\ &= \; [12.00 \text{ - } 10.0) \; / \; (112.00) = 1.8 \text{*} 10^{\text{-2}} \text{ M} \\ pH &= \; 12.25 \end{split}$$



10-7 pH = pKa - 1, when $\log([A^-]/[HA]) = -1$ or $[A^-]/[HA] = 0.1$

$$\begin{aligned} \alpha_{VE@pH=PKa-1} &= [A^{-}]/F_{HA} &= [A^{-}]/\{[HA] + [A^{-}]\} \\ \text{Substitute [HA]} &= 10[A^{-}] \text{ to get} \\ \alpha_{VE@pH=PKa-1} &= [A^{-}]/F_{HA} &= [A^{-}]/\{0.1[A-] + [A^{-}]\} \\ &= [A^{-}]/11[A^{-}] = 0.0909 \text{Ve} \end{aligned}$$

pH = pKa + 1, when $log([A^-]/[HA]) = 1$ or $[A^-]/[HA] = 10$

 $\alpha = [A^{-}]/F_{HA} = [A^{-}]/\{[HA] + [A^{-}]\}$ Substitute [HA] = 0.1[A⁻] to get $\alpha_{VE@pH=PKa-1} = [A^{-}]/F_{HA} = [A^{-}]/\{0.1[A-] + [A^{-}]\}$ $= [A^{-}]/1.1[A^{-}] = 0.909Ve$

At $\frac{1}{2}$ Ve, $[A^{-}]/[HA] = 1$, $\log([A^{-}]/[HA]) = 0$ pH @ $\frac{1}{2}$ Ve = pKa

At 0 Ve, the appropriate equilibrium describing the solution is $HA + H_2O \leftrightarrow A^- + H_3O^+$

$$\begin{split} F_{HA} &= (10.00 \text{ mmol}) / (200.0 \text{ mL}) = 0.1000 \text{ M} \\ Ka &= 2.51*10^{-5} \\ \text{Assume } [H_3O^+] = [A^-], \text{ and let } [A^-] = x \\ \text{Assume } F_{HA} \cong [HA] \\ & 2.51*10^{-5} = x^2 / (0.100) \\ & x = [H_3O]^+ = 1.58*10^{-3} \\ & pH = 2.80 \end{split}$$

At Ve, all of the HA has been titrated to A⁻, the equiv point is reached, and the following equilibrium appropriately describes this solution

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

$$\begin{split} F_{A-} &= (10.00 \text{ mmol})/(200.0 \text{ mL}) = 0.0500 \text{ M} \\ Kb &= Kw/Ka = 10^{-14}/2.51*10^{-5} = 3.98*10^{-10} \\ Assume \ [OH^-] &= [HA], \text{ and let } [HA] = x \\ Assume \ F_{A-} &\cong [A^-] \\ & 3.98*10^{-10} = x^2/(0.0500) \\ x &= [OH^-] = 4.44*10^{-6} \text{ M} \\ [H_3O]^+ &= 2.25*10^{-9} \\ pH &= 8.65 \end{split}$$

@ 1.2 Ve excess OH⁻ is what controls the pH. Ve = 100.0 mL [OH⁻] = [(120.0 mL NaOH)(0.10 M OH⁻)-(mmol HA_{initial})]/V_t = [12.00 - 10.0) / (220.00) = $9.1*10^{-3}$ M pH = 11.96

pKa = 4.60 so

αVe	pН	
0	2.80	
0.0909Ve	3.60	
0.5Ve	4.60	
0.909Ve	5.60	
Ve	8.65	
1.2 Ve	11.96	



10-8

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

Let V = the initial volume of the weak acid. Because the concentration of the titrant, KOH, is half that of the analyte, it will take a volume of 2 V to get to the equivalence point. Therefore, the total volume of the solution at the equivalence point is 3V.

$$\begin{split} F_{A-} &= (F_{A-})^* V/(3V) = 0.0333 \text{ M} \\ Kb &= Kw/Ka = 10^{-14}/1.48^* 10^{-4} = 6.76^* 10^{-11} \\ Assume \ [OH^-] &= [HA], \text{ and let } [HA] = x \\ Assume \ F_{A-} &\cong [A^-] = 0.0333M \\ 6.76^* 10^{-11} &= x^2/(0.0333) \\ x &= [OH^-] = 1.50^* 10^{-6} \text{ M} \\ [H_3O]^+ &= 6.67^* 10^{-9} \\ pH &= 8.18 \end{split}$$

10.13

At the equivalence point exactly all of the weak base has been converted to its conjugate acid, and the hydrolysis of any weak acid produces a solution having a pH < 7.

10-15

Maximum buffer capacity is reached when enough acid has been added to convert exactly $\frac{1}{2}$ of the weak base to its conjugate acid. At this point [B] = [BH⁺].

10-17 50.0 mL of a solution of 0.0319 M benzylamine, B, is titrated with 0.0500 M HCl. (Ka = $4.5*10^{-10}$)

@ 0 mL added $B + H_2O \leftrightarrow HB^+ + OH^ F_{\rm B} = 0.0319 \, {\rm M}$ $\overline{\text{Kb}} = \text{Kw}/\text{Ka} = 10^{-14}/4.5*10^{-10} = 2.22*10^{-5}$ Assume $[OH^-] = [HB^+]$, and let $[HB^+] = x$ Assume $F_{A_{-}} \cong [B] = 0.0319 \text{ M}$ $2.22*10^{-5} = x^2/(0.0319)$ $x = [OH^{-}] = 8.42 * 10^{-4} M$ $[H_3O]^+ = 1.19*10^{-11}$ pH = 10.93@ 12.00 mL added pKa =9.35 H^+ added = (0.0500M)*(12.00 mL) = 0.600 mmol H⁺ $B + H_3O^+ \rightarrow BH^+ + H_2O$ (to completion/or near to) $pH = pKa + log(mol A^{-}/mol HA)$ $mol BH^+ = 0.600 mmol$

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mol B = (50.0 \text{ ml}*0.0319 \text{ M}) - 0.600 \text{ mol}
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$$= 0.995 \text{ mmol}$$

pH = 9.35+ log(0.995/.600) = 9.57
@ ¹/₂ Ve or (50.0 mL B)(0.0319 M B)/(0.050 M HCl)/2 = 16.0 mL
pH = pKa =9.35
@ 30.00 mL added
pKa =9.35
H⁺ added = (0.0500M)*(30.00 mL) = 1.500 mmol H⁺
B + H₃O⁺ \rightarrow BH⁺ + H₂O (to completion/or near to)
pH = pKa +log(mol A⁻/mol HA)
mol BH⁺ = 1.500 mmol
mol B = (50.0 ml*0.0319 M)- 1.500 mol
= 0.095 mmol
pH = 9.35+ log(0.095/1.500) = 8.15

@ Ve or 31.9 mL (the equivalence point)

This is the equivalence point. The appropriate equilibrium is the Ka reaction for HB^+ .

 $HB^+ + H_2O \leftrightarrow B + H_3O^+$

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\begin{split} F_{BH+} &= (50.0 \text{ ml}*0.0319 \text{ M})/(81.9 \text{ ml}) = 0.0195 \text{ M} \\ Ka &= 4.5*10^{-10} = [B][H^+]/(F_{BH+}\text{-}[B]) \\ \text{Assume } [H_3O^+] &= [B], \text{ and let } [B] = x \\ \text{Assume } F_{B+} &\cong [BH^+] \\ & 4.5*10^{-10} = x^2/(0.0195) \\ x &= [OH^-] = 2.96*10^{-6} \text{ M} \\ pH &= 5.53 \end{split}
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@ 35.0 mL

Excess mol of
$$H^+ = (35.0 \text{mL} - 31.9 \text{ mL})*(.0500)/(35 \text{ mL} + 50 \text{ mL})$$

= 0.0182 M
or
 $H^+ = [(35.0 \text{ mL})*(.0500 \text{ M}) - (0.0319 \text{ M}*50.00 \text{mL})]/(85 \text{ mL})$
= 0.0182 M

pH = 2.74

10.18

- $mmol CN^{-} = 5.00 mmol (4.20mL)(.438 M) = 3.16 mmol$ a. mmol HCN = (4.20mL)(.438 M) = 1.84 mmol pH = pKa(HCN) + log (mmol CN/mmol HCN)pH = 9.21 + log(3.16/1.84) = 9.44
- mmol HCN = (11.82mL)(.438 M) = 5.18 mmolb. excess $H^+ = 0.18$ mmol $[H^+] = 0.0028_{66} M$ pH = 2.54
- $K_{a1} = x^2/(F-x) = 6.2 \cdot 10^{-10}, F = 5.00/(11.42+50.00) =$ c. 0.0814 M $[H^+] = 7.105 \cdot 10^{-6}$ pH = 5.148

10.22 a) Ka = $10^{-2.86}$ HA + H₂O \leftrightarrow H₃O⁺ + A⁻ $Kb = 10^{-3.36}$ $B + H_2O \leftrightarrow OH^- + BH^+$ $1/Kw = 10^{13.99}$ $\mathrm{H_{3}O^{+}+OH^{-}\leftrightarrow 2H_{2}O}$ $HA + B \leftrightarrow BH^+ + A^-$

 $K = 10^{7.78}$

b) For the diprotic titration 3/2 Ve represents half-way to the second equivalence point where $[HA^-] = [A^{2-}]$. From H-H, pH = pKa2.

For the lower curve, at Ve all of the HA has been converted to A^- , and all of the weak base added is now in the BH⁺ form. The weak base added past this point does not react with anything. At 2Ve moles of B present equals the moles of BH⁺ formed at Ve, SO Ph = pKa of the titrant.

11.23

$$V_{1*}^{*} = 10.00 \text{ mL}$$

 $V_{2}^{*} = 20.00 \text{ mL}$
 $pKa1 = 4.00$
 $pKa2 = 10.00$
 $Va = 0.00 \text{ mL}$
 $Case 2$
 $K_{b1} = x^{2}/(0.1-x)$
 $x = [OH] =$
 $pH = 11.50$
 $Va = 1.00 \text{ mL}$
 $pH = 10.00 + \log(10-1)/(1)) = 10.95$
 $Va = 5.00 \text{ mL}$, $\frac{1}{2}$ way to 1^{st} equiv. pt.
 $pH = 10.00$
 $Va = 9.00 \text{ mL}$
 $pH = 6.00 + \log((10-9)/9) = 9.05$
 $Va = 10.00 \text{ mL}$
 At the equiv pt
 $pH = \frac{1}{2}(pK_{a1}+pK_{a2}) = 8.00$

- Va = 11.00 mL pH = 6.00 + log((10-1)/1) = 6.95Va = 15.00 mL, halfway to second equiv pt. pH = 6.00
- Va = 19.0 mLpH = 10.00 + log((10-9)/9) = 5.05
- Va = 20.00 mL; We have reached the second equivalence point. The solution consists of the primarily most basic species and water.

$$\begin{split} K_{a1} &= [OH^{-}]^{2} / (F_{A2}-[OH^{-}]) \\ F_{A2}- &= (0.100 \cdot 100 \text{ mL}) / (120 \text{ mL}) = 0.0833 \text{ M} \\ [H_{3}O^{+}] &= 0.00289 \text{ M} \\ pH &= 3.54 \end{split}$$

Va = 22.00 mL

pH based on moles of HCl added beyond the second equiv. pt.

$$[H_3O^+] = (1.00)(2.00 \text{ mL})/(122 \text{ mL}) = 0.00164 \text{ M}$$

pH = 2.785

10.25

Titrate 40.0 mL of a 0.100 M peperazine (P) solution with 0.1 M HCl

Peperazine is a diprotic base

P + H₂O ↔ HP⁺ + OH⁻
Kb₁= Kw/Ka₂ =
$$10^{-14}/1.86*10^{-10} = 5.38*10^{-5}$$

$$\begin{split} HP^{+} &+ H_{2}O \leftrightarrow H_{2}P^{2+} + OH^{-} \\ Kb_{2} &= Kw/Ka_{1} = 10^{-14}/4.65^{*}10^{-6} = 2.15^{*}10^{-9} \\ \hlineleftwidthinkpartial @ 0 mL added \\ P + H_{2}O \leftrightarrow HP^{+} + OH^{-} \\ F_{B} &= 0.100 \text{ M} \\ Assume [OH^{-}] &= [HP^{+}], \text{ and let } [HP^{+}] = x \\ Assume F_{A.} &\cong [P] = 0.100 \text{ M} \\ \\ &5.38^{*}10^{-5} = x^{2}/(0.100) \\ x &= [OH^{-}] = 2.32^{*}10^{-3} \text{ M} \\ [H_{3}O]^{+} &= 4.31^{*}10^{-12} \\ pH &= 11.37 \\ \hlineleftwidthinkpartial @ 10.00 \text{ mL added} \\ pKa_{2} &= 9.731 \\ H^{+} added &= (0.100M)^{*}(10.00 \text{ mL}) = 1.00 \text{ mmol } H^{+} \\ P + H_{3}O^{+} &\rightarrow PH^{+} + H_{2}O \text{ (to completion/or near to)} \\ pH &= pKa + log(mol P/mol HP^{+}) \\ mol PH^{+} &= 1.00 \text{ mmol} \\ mol P &= (40.0 \text{ ml}^{*}0.100 \text{ M}) - 1.00 \text{ mol} \\ &= 3.00 \text{ mmol} \\ pH &= 9.731 + \log(3/1) = 10.208 \\ \hlineleftwidthinkpartial phase statement{} \\ \end{matrix}$$

@ 20 mL we are half way to the first equivalence point $pH = pKa_2 = 9.731$

@ 30 mL added $pKa_2 = 9.731$ H^+ added = (0.100M)*(30.00 mL) = 3.00 mmol H^+ $P + H_3O^+ \rightarrow PH^+ + H_2O$ (to completion/or near to) $pH = pKa + log(mol P/mol HP^+)$ $mol PH^+ = 3.00 mmol$

mol P =
$$(40.0 \text{ ml}*0.100 \text{ M})$$
- 3.00 mol
= 1.00 mmol
pH = $9.35 + \log(1/3) = 9.254$

@ 40 mL added we have reached the first equivalence point, and the dominant species is therefore BH⁺. This is an intermediate species that can act as both an acid and a base.

 $HP^+ + H_2O \leftrightarrow H_2P^{2+} + OH^ Kb_2 = Kw/Ka_1 = 10^{-14}/4.65*10^{-6} = 2.15*10^{-9}$ $\begin{array}{l} HP^+ + H_2O \leftrightarrow P + H_3O^+ \\ Ka_2 = 1.86*10^{-10} \end{array}$ $[H^{+}] = [(K_1K_2F + K_1Kw)/(K_1 + F)]^{0.5}$ F = (40 mL)(0.100)/(80 mL) = 0.05 M $K_1 = 4.65 * 10^{-6}$ $K_2 = 1.86 * 10^{-10}$ $Kw = 10^{-14}$ After simplifying $[H^+] = (K_1K_2)^{0.5} = 2.54*10^{-8} M$ pH = 7.53@ 50.00 mL added $pKa_1 = 5.333$ H^+ added(after eq pt) = (0.100M)*(10.00 mL) = 1.00 mmol $HP^+ + H_3O^+ \rightarrow H_2P^+ + H_2O$ (to completion/or near to) $pH = pKa_1 + log(mol HP^+/mol H_2P^+)$ mol $H_2 P^{2+} = 1.00$ mmol mol HP^+ = (40.0 ml*0.100 M)- 1.00 mol = 3.00 mmol $pH = 5.333 + \log(3/1) = 5.810$

@ 60 ml we are half way to the second equivalence point $pH = pKa_2 = 5.333$ @ 60.00 mL added

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@ 70 ml added
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 $\begin{array}{l} pKa_1 = 5.333 \\ H^+ \mbox{ added}(after \mbox{ eq pt}) = (0.100 \mbox{ M})^*(30.00 \mbox{ mL}) = 3.00 \mbox{ mmol} \\ HP^+ + H_3 O^+ \rightarrow H_2 P^+ + H_2 O \mbox{ (to completion/or near to)} \\ pH = pKa_1 \mbox{ + log}(mol \mbox{ HP}^+/mol \mbox{ H}_2 P_{+2}) \\ mol \mbox{ H}_2 P^{2+} = 1.00 \mbox{ mmol} \\ mol \mbox{ HP}^+ \mbox{ = (40.0 \mbox{ m})^* 0.100 \mbox{ M})^- 3.00 \mbox{ mol} \\ = 1.00 \mbox{ mmol} \\ pH = 5.333 \mbox{ + log}(1/3) = 4.856 \end{array}$

@ 80 ml we hit the second equivalence point. The dominant species is H_2P^{2+} . We can find the pH by examining the hydrolysis of this species.

 $H_2P^{2+} + H_2O \leftrightarrow HP^+ + H_3O^+$

$$\begin{split} F_{H2P2+} &= (40.0 \text{ mL}*0.100 \text{ M})/(120.0 \text{ mL}) = 0.0333 \text{ M} \\ Ka &= 4.65*10^{-6} = [HP^+][H^+]/(F_{H2P2+}-[HP^+]) \\ \text{Assume } [H_3O^+] &= [HP^+], \text{ and let } [HP^+] = x \\ \text{Assume } F_{B+} &\cong [H_2P^{2+}] \\ &\quad 4.65*10^{-6} = x^2/(0.0333) \\ &\quad x = [H_3O^+] = 3.94*10^{-6} \text{ M} \\ &\quad pH = 3.41 \end{split}$$

@ 90.0 mL

 $[H^+] = (10.0 \text{ mL})*(.100)/(90 \text{ mL} +40 \text{ mL})$ = 7.69*10⁻³ M pH = 2.114

@ 100.0 mL added

$$[H^+] = (20.0 \text{ mL})*(.100)/(90 \text{ mL} +50 \text{ mL})$$

= 1.43*10⁻² M
pH = 1.845



10.27

50 mL of 0.100 M sodium glycinate with 0.100 M HCl $K_{a1} = 4.47 \cdot 10^{-3}$ $K_{a2} = 1.67 \cdot 10^{-10}$ $V_{2nd eq point} = 100.0 mL$

 $K_{a1}=4.47{\cdot}10^{-3}=x^2/((.1)(50/150){-}x)\ \{assumption\ 2 \ not\ valid!!!\}\ x=[H_3O^+]=0.01017\ M\ pH=1.993$

@ Va = 90.0 mL using assumption that the acid reacts completely with the glycine gives

$$pH = pKa + \log(10/40) = 2.350 - 0.602 = 1.747$$

Unreasonable because it is lower than the equivalence point pH.

@ Va = 101.0, excess HCl is (1.0 mL)(0.1000)/151.0 = 0.00062 MpH = 3.18; Unreasonable because it is lower than the equivalence point pH. Most of the H⁺ comes from the dissociation of the weak acid because the K_{a1} is so large. We can not ignore it!!

10.29

tyrosine

0.0100 M tyrosine titrated with 0.00400 M HClO₄ $K_{a1} = 3.9 \cdot 10^{-3}$ $K_{a2} = 2.1 \cdot 10^{-9}$ $K_{a3}^{-} 9.8 \cdot 10^{-12}$ Tyrosine is H₂T (first intermediate species) At the eq. pt all of H2T has been converted to HT-, the second intermediate species. $V_{eq} = V_{tyr}(0.100 \text{ M})/(0.00400 \text{ M}) = 2.5 \text{ V}_{tyr}$ FHT- = (0.100 M)/(0.00400 M) = 2.5 V_{tyr} FHT- = (0.100 M)V_{try}/3.5V_{tyr} = 0.0286 M [H⁺] = [(K₂K₃F+K₂Kw)/(K₂+F)]^{0.5} ={[(2.1 \cdot 10^{-9})(9.8 \cdot 10^{-12})(.0286)+(2.1 \cdot 10^{-9})(1.01 \cdot 10^{-14})] / (0.0286 M+2.1 \cdot 10^{-9})}^{1/2}

After simplifying

$$[H^+] = (K_2K_3)^{0.5} = 1.4_3 \cdot 10^{-10} M$$

 $pH = 9.84$

10.30

Titrate 40.0 mL of a 0.0300 M K₂C solution with 0.0600 M HClO₄

cysteine is a triprotic base, and we a starting with the most basic species C^{2-} .

$$C^{2-} + H_2O \leftrightarrow HC^- + OH^-$$

$$HC^- + H_2O \leftrightarrow H_2C + OH^-$$

$$H_2C + H_2O \leftrightarrow H_3C^+ + OH^-$$

$$Ka_1 = 1.95*10^{-2}$$

$$Ka_2 = 4.4*10^{-9}$$

$$Ka_3 = 1.7*10^{-11}$$

Since the titrant is twice as concentrated as the analyte, it will take only 20.0 mL to reach the first equivalence point. Therefore,

$$F_{\text{HC-}}(\text{at } 1^{\text{st}} \text{ eq.pt.}) = (0.0300 \text{ M})(40.0 \text{ mL})/(60.0 \text{ mL}) = 0.0200 \text{ M}$$
$$[\text{H}^+] = [(\text{K}_1\text{K}_2\text{F} + \text{K}_1\text{Kw})/(\text{K}_1 + \text{F})]^{0.5}$$
$$[\text{H}^+] = = 2.8 * 10^{-10} \text{ M}$$
$$\text{pH} = 9.56$$

b) You are starting with the most acidic species, so this is the equilibrium that is dominant

$$\begin{array}{l} H_{3}C^{+} + H_{2}O \leftrightarrow H_{2}C + H3O^{+} \\ Ka_{1} &= 1.95*10^{-2} = [H_{2}C][H_{3}O^{+}]/H_{3}C^{+}] \\ &= x^{2}/.0500\text{-x} \text{ (use excel or the quadratic formula)} \\ x &= 0.0230 \text{ M} = [H_{3}O^{+}] \end{array}$$

 $\begin{aligned} &Ka_3 = [C^{2-}][H_3O^+]/[HC^-] \\ &Ka_3/[H_3O^+] = [C^{2-}]/[HC^-] = (1.7*10^{-11})/.0230) = 7.4*10^{-10} \end{aligned}$

10.36 At $pK_{HIn} - 1$, [HIn] is 10x the concentration of [In⁻] At $pK_{HIn} + 1$, [In⁻] is 10x the concentration of [HIn] Therefore, because HIn and In⁻ absorb differently in the visible region, it is in this range that the color change is most detectable.

10.43

No! The pH at the equivalence point of a titration of a weak acid with a strong base is always greater than 7, because the pH is govern by a weak base hydrolysis reaction.

10.47

Total mass of diluted solution is 10.231+39.466 = 49.697 g Dilution factor = (49.697/4.373)Moles of ammonia in 4.373 g solution = (14.23 mL)(0.1063)

Weigh percent = $[(0.01423 \text{ L})(0.1063 \text{ M}) \cdot (49.697/4.373) \cdot (17.031 \text{ g/mol})/10.231 \text{ g solution}] \cdot 100 = 2.859_4 \%$

10.57 $CH_3O^- + H_2O \leftrightarrow CH_3OH + OH^ K_b$ of this reaction is $k_w/k_a = 1.82 \cdot 10^{-16}/2.88 \cdot 10^{-16} = 0.79$

 $CH_3CH_2O^- + H_2O \leftrightarrow CH_3CH_2OH + OH^-$ K_b of this reaction is $k_w/k_a = 1.82 \cdot 10^{-16}/1 \cdot 10^{-16} = 1.82$

These reactions essentially go to completion. The first one is about 90 % dissociated and the second is about 95 % dissociated. If one

uses 1.01e-14 for Kw instead than the difference is even less (99.8 % vs. 99.9 % dissociated).

101 = x2/(.1-x)x = 0.099901

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10.61
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a)

Use acetic acid. B is a much stronger base (greater extent of dissociation) in acetic acid than in water. It would be even weaker in pyridine than as in water.

b) A weak acid will be a stronger acid (greater extent of dissociation) in pyridine than in water. It would be even weaker in acetic acid than as in water.

11.60 in 7th Ed

Methanol is a weaker acid than water

```
CH_{3}OH + H_{2}O \leftrightarrow CH_{3}O^{-} + H_{3}O^{+}
k_{a} = 2.88 \cdot 10^{-16}
H_{2}O + H_{2}O \leftrightarrow OH^{-} + H_{3}O^{+}
k_{a} = 1.01 \cdot 10^{-14}
P + H_{2}O \leftrightarrow PH^{+} + OH^{-}
K_{b} = Kw/Ka = 1.6 \cdot 10^{-9}
K_{a} = 6.3 \cdot 10^{-6}
pKa = 5.2
add the following reaction
P + H_{2}O \leftrightarrow PH^{+} + OH^{-}
K_{b}(avrid)
```

 $\Theta H^{-} + H_{3}\Theta^{+} \leftrightarrow H_{2}\Theta + H_{2}\Theta^{-}$

 $\begin{array}{l} K_{b(pyridine \ in \ H2O)} = 1.6 {\cdot} 10^{-9} \\ 1/K_w = 9.9 {\cdot} 10^{13} \end{array}$

 $\begin{array}{rcl} CH_{3}OH &+ & H_{2}\Theta &\leftrightarrow & CH_{3}O^{-} &+ & H_{3}\Theta^{+} & k_{a} = 2.88 \cdot 10^{-16} \\ \hline \\ \hline P + CH_{3}OH &\leftrightarrow & PH^{+} + CH_{3}O^{-} & K_{b(pyridine \ in \ CH3OH)} = 4.6 \cdot 10^{-11} \end{array}$

Pyridine is a weaker base in this solution because methanol is a weaker acid than water. Therefore, the effective Kb is lower, and therefore, the effective Ka is greater (pKa is lower).