## 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

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

@ 0.00 mL added

$$
\left[\mathrm{OH}^{-}\right]=0.100 \mathrm{M}
$$

$$
\left[\mathrm{H}_{3} \mathrm{O}\right]^{+}=1.00 * 10^{-13}
$$

$$
\mathrm{pH}=13.00
$$

@ 1.00 mL

$$
\begin{aligned}
& {\left[\mathrm{OH}^{-}\right] }=\left[\left(\mathrm{mmol} \mathrm{OH}_{\text {initial }}^{-}\right)-(1.00 \mathrm{~mL} \mathrm{HBr})\left(1.00 \mathrm{M} \mathrm{H}^{+}\right)\right] / \mathrm{V}_{\mathrm{t}} \\
&=[(10.0-1.00)] / 101.00]=0.089 \mathrm{M} \\
& {\left[\mathrm{H}_{3} \mathrm{O}\right]^{+} }=1.1^{*} 10^{-13} \\
& \mathrm{pH}=12.95
\end{aligned}
$$

@ 5.00 mL

$$
\begin{aligned}
{\left[\mathrm{OH}^{-}\right] } & =\left[\left(\mathrm{mmol} \mathrm{OH}_{\text {initial }}\right)-(5.00 \mathrm{~mL} \mathrm{HBr})\left(1.00 \mathrm{M} \mathrm{H}^{+}\right)\right] / \mathrm{V}_{\mathrm{t}} \\
& =[(10.0-5.00)] / 105.00]=0.048 \mathrm{M} \\
{\left[\mathrm{H}_{3} \mathrm{O}\right]^{+} } & =2.1 * 10^{-13}
\end{aligned}
$$

$$
\mathrm{pH}=12.68
$$

@ 9.00 mL

$$
\begin{aligned}
{\left[\mathrm{OH}^{-}\right] } & \left.=\left[\left(\mathrm{mmol} \mathrm{OH}_{\text {initial }}^{-}\right)-9.00 \mathrm{~mL} \mathrm{HBr}\right)\left(1.00 \mathrm{M} \mathrm{H}^{+}\right)\right] / \mathrm{V}_{\mathrm{t}} \\
& =[(10.0-9.00)] / 109.00]=9.2 * 10^{-3} \mathrm{M} \\
{\left[\mathrm{H}_{3} \mathrm{O}\right]^{+} } & =1.1^{*} 10^{-12} \\
\mathrm{pH}= & =11.96
\end{aligned}
$$

@ 9.90 mL

$$
\begin{aligned}
& {\left[\mathrm{OH}^{-}\right] }=\left[\left(\mathrm{mmol} \mathrm{OH}_{\text {initial }}\right)-(9.90 \mathrm{~mL} \mathrm{HBr})\left(1.00 \mathrm{M} \mathrm{H}^{+}\right)\right] / \mathrm{V}_{\mathrm{t}} \\
&=[(10.0-9.9)] / 109.90]=9.099 * 10^{-4} \mathrm{M} \\
& {\left[\mathrm{H}_{3} \mathrm{O}\right]^{+} }=1.1^{*} 10^{-11} \\
& \mathrm{pH}=10.96
\end{aligned}
$$

@ 10.00 mL equiv. pt

$$
\begin{aligned}
& {\left[\mathrm{OH}^{-}\right] }=\left[\left(\mathrm{mmol} \mathrm{OH}_{\text {initial }}^{-}\right)-\left(10.00 \mathrm{~mL} \mathrm{HBr}^{2}\left(1.00 \mathrm{M} \mathrm{H}^{+}\right)\right] / \mathrm{V}_{\mathrm{t}}\right. \\
&=[(10.0-1.00)] / 110.00]=0\left(=10^{-7} \mathrm{M} \text { from Kw rxn }\right) \\
& {\left[\mathrm{H}_{3} \mathrm{O}\right]^{+} }=10^{-7} \\
& \mathrm{pH}=7.00
\end{aligned}
$$

@ 10.10 mL After the equiv. point the excess $\mathrm{H}^{+}$is what controls the pH .

$$
\begin{aligned}
{\left[\mathrm{H}^{+}\right] } & =\left[(10.10 \mathrm{~mL} \mathrm{HBr})\left(1.00 \mathrm{M} \mathrm{H}^{+}\right)-\left(\mathrm{mmol} \mathrm{OH}_{\text {initial }}\right)\right] / \mathrm{V}_{\mathrm{t}} \\
& =[10.10-10.0) /(110.10)=9 * 10^{-4} \mathrm{M} \\
\mathrm{pH} & =3.0
\end{aligned}
$$

@ $12.00 \mathrm{~mL} \quad$ After the equiv. point the excess $\mathrm{H}^{+}$is what controls the pH .

$$
\begin{aligned}
{\left[\mathrm{H}^{+}\right] } & =\left[(12.00 \mathrm{~mL} \mathrm{HBr})\left(1.00 \mathrm{M} \mathrm{H}^{+}\right)-\left(\mathrm{mmol} \mathrm{OH}_{\text {initial }}\right)\right] / \mathrm{V}_{\mathrm{t}} \\
& =[12.00-10.0) /(112.00)=1.8^{*} 10^{-2} \mathrm{M} \\
\mathrm{pH} & =1.75
\end{aligned}
$$



10-6
100.0 mL of a solution of 0.100 M weak acid, HA, is titrated with $1.00 \mathrm{M} \mathrm{KOH} .\left(\mathrm{Ka}=1.0 * 10^{-5}\right)$
@ 0 mL added

$$
\begin{aligned}
& \mathrm{Ka}=\left[\mathrm{H}^{+}\right]^{2} / 0.1=1.0^{*} 10^{-5} \\
& {\left[\mathrm{H}^{+}\right]=1.0^{*} 10^{-3}} \\
& \mathrm{pH}=3.00
\end{aligned}
$$

@ 1.00 mL added
$\mathrm{OH}^{-}$added $=(1.00 \mathrm{M}) *(1.00 \mathrm{~mL})=1.00 \mathrm{mmol} \mathrm{OH}^{-}$
$\mathrm{HA}+\mathrm{OH}^{-} \rightarrow \mathrm{A}^{-}+\mathrm{H}_{2} \mathrm{O}$ (to completion/or near to)
$\mathrm{pH}=\mathrm{pKa}+\log \left(\mathrm{mol} \mathrm{A}^{-} / \mathrm{mol} \mathrm{HA}\right)$
$\mathrm{mol} \mathrm{A}=1.00 \mathrm{mmol}$
$\mathrm{mol} \mathrm{HA}=(100.0 \mathrm{~mL} * 0.100 \mathrm{M})-1.00 \mathrm{~mol}=9.00 \mathrm{mmol}$
$\mathrm{pH}=5.00+\log (1 / 9)=4.05$
@ 5.00 mL added
$\mathrm{OH}^{-}$added $=(1.00 \mathrm{M}) *(5.00 \mathrm{~mL})=5.00 \mathrm{mmol} \mathrm{OH}^{-}$
$\mathrm{HA}+\mathrm{OH}^{-} \rightarrow \mathrm{A}^{-}+\mathrm{H}_{2} \mathrm{O}$ (to completion/or near to)
$\mathrm{pH}=\mathrm{pKa}+\log \left(\mathrm{mol} \mathrm{A}^{-} / \mathrm{mol} \mathrm{HA}\right)$
$\mathrm{mol} \mathrm{A}=5.00 \mathrm{mmol}$
$\mathrm{mol} \mathrm{HA}=(100.0 \mathrm{~mL} * 0.500 \mathrm{M})-5.00 \mathrm{~mol}=5.00 \mathrm{mmol}$

$$
\mathrm{pH}=5.00+\log (5 / 5)=5.00
$$

@ 9.00 mL added
$\mathrm{OH}^{-}$added $=(1.00 \mathrm{M}) *(9.00 \mathrm{~mL})=9.00 \mathrm{mmol} \mathrm{OH}^{-}$ $\mathrm{HA}+\mathrm{OH}^{-} \rightarrow \mathrm{A}^{-}+\mathrm{H}_{2} \mathrm{O}$ (to completion/or near to)
$\mathrm{pH}=\mathrm{pKa}+\log \left(\mathrm{mol} \mathrm{A}^{-} / \mathrm{mol} \mathrm{HA}\right)$
$\mathrm{mol} \mathrm{A}=9.00 \mathrm{mmol}$
$\mathrm{mol} \mathrm{HA}=(100.0 \mathrm{~mL} * 0.500 \mathrm{M})-9.00 \mathrm{~mol}=1.00 \mathrm{mmol}$
$\mathrm{pH}=5.00+\log (9 / 1)=5.95$
@ 9.90 mL added
$\mathrm{OH}^{-}$added $=(1.00 \mathrm{M}) *(9.90 \mathrm{~mL})=9.90 \mathrm{mmol} \mathrm{OH}^{-}$ $\mathrm{HA}+\mathrm{OH}^{-} \rightarrow \mathrm{A}^{-}+\mathrm{H}_{2} \mathrm{O}$ (to completion/or near to) $\mathrm{pH}=\mathrm{pKa}+\log \left(\mathrm{mol} \mathrm{A}^{-} / \mathrm{mol} \mathrm{HA}\right)$
$\mathrm{mol} \mathrm{A}^{-}=9.90 \mathrm{mmol}$
$\mathrm{mol} \mathrm{HA}=(100.0 \mathrm{~mL} * 0.500 \mathrm{M})-9.90 \mathrm{~mol}=0.10 \mathrm{mmol}$
$\mathrm{pH}=5.00+\log (9.9 / .1)=7.00$
@ 10.00 mL added
$\mathrm{OH}^{-}$added $=(1.00 \mathrm{M}) *(10.00 \mathrm{~mL})=10.00 \mathrm{mmol} \mathrm{OH}^{-}$ $\mathrm{HA}+\mathrm{OH}^{-} \rightarrow \mathrm{A}^{-}+\mathrm{H}_{2} \mathrm{O}$ (to completion/or near to) $\mathrm{pH}=\mathrm{pKa}+\log \left(\mathrm{mol} \mathrm{A}^{-} / \mathrm{mol} \mathrm{HA}\right)$ $\mathrm{mol} \mathrm{A}^{-}=10.00 \mathrm{mmol}$ $\mathrm{mol} \mathrm{HA}=(100.0 \mathrm{~mL} * 0.500 \mathrm{M})-10.0 \mathrm{~mol}=0 \mathrm{mmol}$

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

$$
\begin{aligned}
& \mathrm{A}^{-}+\mathrm{H}_{2} \mathrm{O} \leftrightarrow \mathrm{HA}+\mathrm{OH}^{-} \\
& \mathrm{F}_{\mathrm{A}-}=(10.00 \mathrm{mmol}) /(110.0 \mathrm{~mL})=0.0909 \mathrm{M} \\
& \mathrm{~Kb}= \mathrm{Kw} / \mathrm{Ka}=1.00^{*} 10^{-9}=[\mathrm{HA}]\left[\mathrm{OH}^{-}\right] /\left(\mathrm{F}_{\mathrm{A}^{-}}-[\mathrm{HA}]\right) \\
& \text { Assume }\left[\mathrm{OH}^{-}\right]=[\mathrm{HA}], \text { and let }[\mathrm{HA}]=\mathrm{x}
\end{aligned}
$$

$$
\text { Assume } \mathrm{F}_{\mathrm{A}-} \cong\left[\mathrm{A}^{\top}\right]
$$

$$
\begin{aligned}
& 1.00^{*} 10^{-9}=\mathrm{x}^{2} /(0.0909) \\
& \mathrm{x}=\left[\mathrm{OH}^{-}\right]=9.53 * 10^{-5} \mathrm{M} \\
& {\left[\mathrm{H}_{3} \mathrm{O}\right]^{+}=1.05 * 10^{-9}} \\
& \mathrm{pH}=8.98
\end{aligned}
$$

@ 10.10 mL After the equiv. point the excess $\mathrm{OH}^{-}$is what controls the pH .
$\left[\mathrm{OH}^{-}\right]=\left[(10.10 \mathrm{~mL} \mathrm{KOH})(1.00 \mathrm{M} \mathrm{KOH})-\left(\mathrm{mmol} \mathrm{HA}_{\text {initial }}\right)\right] / \mathrm{V}_{\mathrm{t}}$

$$
=[10.10-10.0) /(110.10)=9 * 10^{-4} \mathrm{M}
$$

$$
\mathrm{pH}=11.0
$$

@ 12.00 mL After the equiv. point the excess $\mathrm{OH}^{-}$is what controls the pH .

$$
\begin{aligned}
{\left[\mathrm{OH}^{-}\right] } & =\left[(12.00 \mathrm{~mL} \mathrm{KOH})\left(1.00 \mathrm{M} \mathrm{OH}^{-}\right)-\left(\mathrm{mmol} \mathrm{HA}_{\text {initial }}\right)\right] / \mathrm{V}_{\mathrm{t}} \\
& =[12.00-10.0) /(112.00)=1.8^{*} 10^{-2} \mathrm{M} \\
\mathrm{pH} & =12.25
\end{aligned}
$$



10-7
$\mathrm{pH}=\mathrm{pKa}-1$, when $\log \left(\left[\mathrm{A}^{-}\right] /[\mathrm{HA}]\right)=-1$ or $\left[\mathrm{A}^{-}\right] /[\mathrm{HA}]=0.1$
$\alpha_{\text {VE@ } @_{\text {PH }}=\text { PKa }-1}=\left[\mathrm{A}^{-}\right] / \mathrm{F}_{\mathrm{HA}}=\left[\mathrm{A}^{-}\right] /\left\{[\mathrm{HA}]+\left[\mathrm{A}^{-}\right]\right\}$
Substitute $[\mathrm{HA}]=10\left[\mathrm{~A}^{*}\right]$ to get

$$
\begin{aligned}
\alpha_{\mathrm{VE} @ \mathrm{pH}=\mathrm{PKa}-1}=\left[\mathrm{A}^{-}\right] / \mathrm{F}_{\mathrm{HA}} & =\left[\mathrm{A}^{-}\right] /\left\{0.1\left[\mathrm{~A}^{-}\right]+\left[\mathrm{A}^{-}\right]\right\} \\
& =\left[\mathrm{A}^{-}\right] / 11\left[\mathrm{~A}^{-}\right]=0.0909 \mathrm{Ve}
\end{aligned}
$$

$\mathrm{pH}=\mathrm{pKa}+1$, when $\log \left(\left[\mathrm{A}^{-}\right] /[\mathrm{HA}]\right)=1$ or $\left[\mathrm{A}^{-}\right] /[\mathrm{HA}]=10$
$\alpha=\left[\mathrm{A}^{-}\right] / \mathrm{F}_{\mathrm{HA}}=\left[\mathrm{A}^{-}\right] /\left\{[\mathrm{HA}]+\left[\mathrm{A}^{-}\right]\right\}$
Substitute $[\mathrm{HA}]=0.1\left[\mathrm{~A}^{-}\right]$to get

$$
\begin{aligned}
\alpha_{\mathrm{VE} @ \mathrm{pH}=\mathrm{PKa}-1}=\left[\mathrm{A}^{-}\right] / \mathrm{F}_{\mathrm{HA}} & =\left[\mathrm{A}^{-}\right] /\left\{0.1\left[\mathrm{~A}^{-}\right]+\left[\mathrm{A}^{-}\right]\right\} \\
& =\left[\mathrm{A}^{-}\right] / 1.1\left[\mathrm{~A}^{-}\right]=0.909 \mathrm{Ve}
\end{aligned}
$$

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

At 0 Ve , the appropriate equilibrium describing the solution is $\mathrm{HA}+\mathrm{H}_{2} \mathrm{O} \leftrightarrow \mathrm{A}^{-}+\mathrm{H}_{3} \mathrm{O}^{+}$
$\mathrm{F}_{\mathrm{HA}}=(10.00 \mathrm{mmol}) /(200.0 \mathrm{~mL})=0.1000 \mathrm{M}$ $\mathrm{Ka}=2.51 * 10^{-5}$
Assume $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\left[\mathrm{A}^{-}\right]$, and let $\left[\mathrm{A}^{-}\right]=\mathrm{x}$
Assume $\mathrm{F}_{\mathrm{HA}} \cong[\mathrm{HA}]$

$$
\begin{aligned}
& 2.51 * 10^{-5}=\mathrm{x}^{2} /(0.100) \\
& \mathrm{x}=\left[\mathrm{H}_{3} \mathrm{O}\right]^{+}=1.58 * 10^{-3} \\
& \mathrm{pH}=2.80
\end{aligned}
$$

At Ve , all of the HA has been titrated to $\mathrm{A}^{-}$, the equiv point is reached, and the following equilibrium appropriately describes this solution

$$
\mathrm{A}^{-}+\mathrm{H}_{2} \mathrm{O} \leftrightarrow \mathrm{HA}+\mathrm{OH}^{-}
$$

$$
\mathrm{F}_{\mathrm{A}-}=(10.00 \mathrm{mmol}) /(200.0 \mathrm{~mL})=0.0500 \mathrm{M}
$$

$$
\mathrm{Kb}=\mathrm{Kw} / \mathrm{Ka}=10^{-14} / 2.51 * 10^{-5}=3.98 * 10^{-10}
$$

$$
\text { Assume }\left[\mathrm{OH}^{-}\right]=[\mathrm{HA}] \text {, and let }[\mathrm{HA}]=x
$$

$$
\text { Assume } \mathrm{F}_{\mathrm{A}_{-}} \cong\left[\mathrm{A}^{-}\right]
$$

$$
\begin{aligned}
& 3.98 * 10^{-10}=\mathrm{x}^{2} /(0.0500) \\
& \mathrm{x}=\left[\mathrm{OH}^{-}\right]=4.44^{*} 10^{-6} \mathrm{M} \\
& {\left[\mathrm{H}_{3} \mathrm{O}\right]^{+}=2.25 * 10^{-9}} \\
& \mathrm{pH}=8.65
\end{aligned}
$$

@ 1.2 Ve excess $\mathrm{OH}^{-}$is what controls the pH .

$$
\mathrm{Ve}=100.0 \mathrm{~mL}
$$

$$
\left[\mathrm{OH}^{-}\right]=\left[(120.0 \mathrm{~mL} \mathrm{NaOH})\left(0.10 \mathrm{M} \mathrm{OH}^{-}\right)-\left(\mathrm{mmol} \mathrm{HA}_{\text {initial }}\right)\right] / \mathrm{V}_{\mathrm{t}}
$$

$$
=[12.00-10.0) /(220.00)=9.1 * 10^{-3} \mathrm{M}
$$

$$
\mathrm{pH}=11.96
$$

$\mathrm{pKa}=4.60$
so

| $\alpha \mathrm{Ve}$ | pH |
| :--- | :--- |
| 0 | 2.80 |
| 0.0909 Ve | 3.60 |
| 0.5 Ve | 4.60 |
| 0.909 Ve | 5.60 |
| Ve | 8.65 |
| 1.2 Ve | 11.96 |



10-8
$\mathrm{A}^{-}+\mathrm{H}_{2} \mathrm{O} \leftrightarrow \mathrm{HA}+\mathrm{OH}^{-}$
Let $\mathrm{V}=$ 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 3 V .

$$
\begin{aligned}
& \mathrm{F}_{\mathrm{A}-}=\left(\mathrm{F}_{\mathrm{A}-}\right) * \mathrm{~V} /(3 \mathrm{~V})=0.0333 \mathrm{M} \\
& \mathrm{~Kb}=\mathrm{Kw} / \mathrm{Ka}=10^{-14} / 1.48 * 10^{-4}=6.76 * 10^{-11} \\
& \text { Assume }\left[\mathrm{OH}^{-}\right]=[\mathrm{HA}], \text { and let }[\mathrm{HA}]=\mathrm{x} \\
& \quad \text { Assume } \mathrm{F}_{\mathrm{A}-} \cong\left[\mathrm{A}^{-}\right]=0.0333 \mathrm{M}
\end{aligned}
$$

$$
\begin{aligned}
& 6.76 * 10^{-11}=\mathrm{x}^{2} /(0.0333) \\
& \mathrm{x}=\left[\mathrm{OH}^{-}\right]=1.50^{*} 10^{-6} \mathrm{M} \\
& {\left[\mathrm{H}_{3} \mathrm{O}^{+}=6.67 * 10^{-9}\right.} \\
& \mathrm{pH}=8.18
\end{aligned}
$$

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 $\mathrm{pH}<7$.

10-15
Maximum buffer capacity is reached when enough acid has been added to convert exactly $1 / 2$ of the weak base to its conjugate acid. At this point $[B]=\left[\mathrm{BH}^{+}\right]$.

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

$$
\mathrm{B}+\mathrm{H}_{2} \mathrm{O} \leftrightarrow \mathrm{HB}^{+}+\mathrm{OH}^{-}
$$

$\mathrm{F}_{\mathrm{B}}=0.0319 \mathrm{M}$
$\mathrm{Kb}=\mathrm{Kw} / \mathrm{Ka}=10^{-14} / 4.5 * 10^{-10}=2.22 * 10^{-5}$
Assume $\left[\mathrm{OH}^{-}\right]=\left[\mathrm{HB}^{+}\right]$, and let $\left[\mathrm{HB}^{+}\right]=x$ Assume $\mathrm{F}_{\mathrm{A}} \cong[\mathrm{B}]=0.0319 \mathrm{M}$

$$
\begin{aligned}
& 2.22^{*} 10^{-5}=\mathrm{x}^{2} /(0.0319) \\
& \mathrm{x}=\left[\mathrm{OH}^{-}\right]=8.42 * 10^{-4} \mathrm{M} \\
& {\left[\mathrm{H}_{3} \mathrm{O}\right]^{+}=1.19 * 10^{-11}} \\
& \mathrm{pH}=10.93
\end{aligned}
$$

@ 12.00 mL added

$$
\begin{aligned}
& \mathrm{pKa}=9.35 \\
& \mathrm{H}^{+} \text {added }=(0.0500 \mathrm{M}) *(12.00 \mathrm{~mL})=0.600 \mathrm{mmol} \mathrm{H} \\
& \left.\mathrm{~B}+\mathrm{H}_{3} \mathrm{O}^{+} \rightarrow \mathrm{BH}^{+}+\mathrm{H}_{2} \mathrm{O} \text { (to completion } / \text { or near to }\right) \\
& \mathrm{pH}=\mathrm{pKa}^{+}+\log (\mathrm{mol} \mathrm{~A} / 2 / \mathrm{mol} \mathrm{HA}) \\
& \quad \text { mol BH }
\end{aligned}
$$

$$
\begin{gathered}
=0.995 \mathrm{mmol} \\
\mathrm{pH}=9.35+\log (0.995 / .600)=9.57
\end{gathered}
$$

@ $1 / 2 \mathrm{Ve}$ or $(50.0 \mathrm{~mL} \mathrm{~B})(0.0319 \mathrm{M} \mathrm{B}) /(0.050 \mathrm{M} \mathrm{HCl}) / 2=16.0 \mathrm{~mL}$ $\mathrm{pH}=\mathrm{pKa}=9.35$
@ 30.00 mL added

$$
\mathrm{pKa}=9.35
$$

$$
\mathrm{H}^{+} \text {added }=(0.0500 \mathrm{M})^{*}(30.00 \mathrm{~mL})=1.500 \mathrm{mmol} \mathrm{H}^{+}
$$

$$
\mathrm{B}+\mathrm{H}_{3} \mathrm{O}^{+} \rightarrow \mathrm{BH}^{+}+\mathrm{H}_{2} \mathrm{O} \text { (to completion/or near to) }
$$

$$
\mathrm{pH}=\mathrm{pKa}+\log \left(\mathrm{mol} \mathrm{~A}^{2} / \mathrm{mol} \mathrm{HA}\right)
$$

$$
\mathrm{mol} \mathrm{BH}^{+}=1.500 \mathrm{mmol}
$$

$$
\mathrm{mol} \mathrm{~B}=(50.0 \mathrm{ml} * 0.0319 \mathrm{M})-1.500 \mathrm{~mol}
$$

$$
=0.095 \mathrm{mmol}
$$

$$
\mathrm{pH}=9.35+\log (0.095 / 1.500)=8.15
$$

@ Ve or 31.9 mL (the equivalence point)
This is the equivalence point. The appropriate equilibrium is the Ka reaction for $\mathrm{HB}^{+}$.

$$
\begin{aligned}
& \mathrm{HB}^{+}+\mathrm{H}_{2} \mathrm{O} \leftrightarrow \mathrm{~B}+\mathrm{H}_{3} \mathrm{O}^{+} \\
& \mathrm{F}_{\mathrm{BH}+}=\left(50.0 \mathrm{ml}^{*} 0.0319 \mathrm{M}\right) /(81.9 \mathrm{ml})=0.0195 \mathrm{M} \\
& \mathrm{Ka}=4.5^{*} 10^{-10}=[\mathrm{B}]\left[\mathrm{H}^{+}\right] /\left(\mathrm{F}_{\mathrm{BH}+}-[\mathrm{B}]\right) \\
& \text { Assume }\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=[\mathrm{B}], \text { and let }[\mathrm{B}]=\mathrm{x} \\
& \text { Assume } \mathrm{F}_{\mathrm{B}+} \cong\left[\mathrm{BH}^{+}\right] \\
& 4.5^{*} 10^{-10}=\mathrm{x}^{2} /(0.0195) \\
& \mathrm{x}=\left[\mathrm{OH}^{-}\right]=2.96^{*} 10^{-6} \mathrm{M} \\
& \mathrm{pH}=5.53
\end{aligned}
$$

@ 35.0 mL

Excess mol of $\mathrm{H}^{+}=(35.0 \mathrm{~mL}-31.9 \mathrm{~mL}) *(.0500) /(35 \mathrm{~mL}+50 \mathrm{~mL})$ $=0.0182 \mathrm{M}$
or

$$
\begin{gathered}
\mathrm{H}^{+}=\left[(35.0 \mathrm{~mL})^{*}(.0500 \mathrm{M})-(0.0319 \mathrm{M} * 50.00 \mathrm{~mL})\right] /(85 \mathrm{~mL}) \\
\\
=0.0182 \mathrm{M}
\end{gathered}
$$

$$
\mathrm{pH}=2.74
$$

10.18
 $\mathrm{mmol} \mathrm{HCN}=(4.20 \mathrm{~mL})(.438 \mathrm{M})=1.84 \mathrm{mmol}$ $\mathrm{pH}=\mathrm{pKa}(\mathrm{HCN})+\log (\mathrm{mmol} \mathrm{CN} / \mathrm{mmol} \mathrm{HCN})$ $\mathrm{pH}=9.21+\log (3.16 / 1.84)=9.44$
b. $\quad \mathrm{mmol} \mathrm{HCN}=(11.82 \mathrm{~mL})(.438 \mathrm{M})=5.18 \mathrm{mmol}$ excess $\mathrm{H}^{+}=0.18 \mathrm{mmol}$

$$
\left[\mathrm{H}^{+}\right]=0.0028_{66} \mathrm{M}
$$

$$
\mathrm{pH}=2.54
$$

c. $\quad \mathrm{K}_{\mathrm{a} 1}=\mathrm{x}^{2} /(\mathrm{F}-\mathrm{x})=6.2 \cdot 10^{-10}, \mathrm{~F}=5.00 /(11.42+50.00)=$

$$
0.0814 \mathrm{M}
$$

$$
\left[\mathrm{H}^{+}\right]=7.105 \cdot 10^{-6}
$$

$$
\mathrm{pH}=5.148
$$

10.22
a)

$$
\begin{array}{ll}
\mathrm{HA}+\mathrm{H}_{2} \mathrm{O} \leftrightarrow \mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{A}^{-} & \mathrm{Ka}=10^{-2.86} \\
\mathrm{~B}+\mathrm{H}_{2} \mathrm{O} \leftrightarrow \mathrm{OH}^{-}+\mathrm{BH}^{+} & \mathrm{Kb}=10^{-3.36} \\
\mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{OH}^{-} \leftrightarrow 2 \mathrm{H}_{2} \mathrm{O} & 1 / \mathrm{Kw}=10^{13.99} \\
\hline
\end{array}
$$

$$
\mathrm{HA}+\mathrm{B} \leftrightarrow \mathrm{BH}^{+}+\mathrm{A}^{-} \quad \mathrm{K}=10^{7.78}
$$

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

For the lower curve, at Ve all of the HA has been converted to $\mathrm{A}^{-}$, and all of the weak base added is now in the $\mathrm{BH}^{+}$form. The weak base added past this point does not react with anything. At 2 Ve moles of B present equals the moles of $\mathrm{BH}^{+}$formed at $\mathrm{Ve}, \mathrm{SO} \mathrm{Ph}=$ pKa of the titrant.
11.23
$\mathrm{V}_{1}{ }^{*}=10.00 \mathrm{~mL}$
$\mathrm{V}_{2}{ }^{*}=20.00 \mathrm{~mL}$
$\mathrm{pKa} 1=4.00$
$\mathrm{pKa} 2=10.00$
$\mathrm{Va}=0.00 \mathrm{~mL}$
Case 2

$$
\mathrm{K}_{\mathrm{b} 1}=\mathrm{x}^{2} /(0.1-\mathrm{x})
$$

$$
\mathrm{x}=\left[\mathrm{OH}^{-}\right]=
$$

$$
\mathrm{pH}=11.50
$$

$$
\begin{aligned}
\mathrm{Va}= & 1.00 \mathrm{~mL} \\
& \mathrm{pH}=10.00+\log (10-1) /(1))=10.95
\end{aligned}
$$

$\mathrm{Va}=5.00 \mathrm{~mL}, 1 / 2$ way to $1^{\text {st }}$ equiv. pt. $\mathrm{pH}=10.00$
$\mathrm{Va}=9.00 \mathrm{~mL}$ $\mathrm{pH}=6.00+\log ((10-9) / 9)=9.05$
$\mathrm{Va}=10.00 \mathrm{~mL}$
At the equiv pt $\mathrm{pH}=1 / 2\left(\mathrm{pK}_{\mathrm{a} 1}+\mathrm{pK}_{\mathrm{a} 2}\right)=8.00$

$$
\begin{aligned}
\mathrm{Va}= & 11.00 \mathrm{~mL} \\
& \mathrm{pH}=6.00+\log ((10-1) / 1)=6.95 \\
\mathrm{Va}= & 15.00 \mathrm{~mL}, \text { halfway to second equiv } \mathrm{pt} . \\
& \mathrm{pH}=6.00
\end{aligned}
$$

$\mathrm{Va}=19.0 \mathrm{~mL}$

$$
\mathrm{pH}=10.00+\log ((10-9) / 9)=5.05
$$

$\mathrm{Va}=20.00 \mathrm{~mL}$; We have reached the second equivalence point. The solution consists of the primarily most basic species and water.

$$
\begin{aligned}
\mathrm{K}_{\mathrm{a} 1} & =\left[\mathrm{OH}^{-}\right]^{2} /\left(\mathrm{F}_{\mathrm{A} 2-}-\left[\mathrm{OH}^{-}\right]\right) \\
& \mathrm{F}_{\mathrm{A} 2-}=(0.100 \cdot 100 \mathrm{~mL}) /(120 \mathrm{~mL})=0.0833 \mathrm{M} \\
& {\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=0.00289 \mathrm{M} } \\
& \mathrm{pH}=3.54
\end{aligned}
$$

$\mathrm{Va}=22.00 \mathrm{~mL}$
pH based on moles of HCl added beyond the second equiv.
pt.

$$
\begin{aligned}
& {\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=(1.00)(2.00 \mathrm{~mL}) /(122 \mathrm{~mL})=0.00164 \mathrm{M}} \\
& \mathrm{pH}=2.785
\end{aligned}
$$

10.25

Titrate 40.0 mL of a 0.100 M peperazine $(\mathrm{P})$ solution with 0.1 M HCl

Peperazine is a diprotic base

$$
\begin{aligned}
& \mathrm{P}+\mathrm{H}_{2} \mathrm{O} \leftrightarrow \mathrm{HP}^{+}+\mathrm{OH}^{-} \\
& \mathrm{Kb}_{1}=\mathrm{Kw} / \mathrm{Ka}_{2}=10^{-14} / 1.86^{*} 10^{-10}=5.38 * 10^{-5}
\end{aligned}
$$

$$
\mathrm{HP}^{+}+\mathrm{H}_{2} \mathrm{O} \leftrightarrow \mathrm{H}_{2} \mathrm{P}^{2+}+\mathrm{OH}^{-}
$$

$$
\mathrm{Kb}_{2}=\mathrm{Kw} / \mathrm{Ka}_{1}=10^{-14} / 4.65 * 10^{-6}=2.15 * 10^{-9}
$$

@ 0 mL added

$$
\mathrm{P}+\mathrm{H}_{2} \mathrm{O} \leftrightarrow \mathrm{HP}^{+}+\mathrm{OH}^{-}
$$

$\mathrm{F}_{\mathrm{B}}=0.100 \mathrm{M}$
Assume $\left[\mathrm{OH}^{-}\right]=\left[\mathrm{HP}^{+}\right]$, and let $\left[\mathrm{HP}^{+}\right]=\mathrm{x}$
Assume $\mathrm{F}_{\mathrm{A}} \cong[\mathrm{P}]=0.100 \mathrm{M}$

$$
\begin{aligned}
& 5.38 * 10^{-5}=\mathrm{x}^{2} /(0.100) \\
& \mathrm{x}=\left[\mathrm{OH}^{-}\right]=2.32 * 10^{-3} \mathrm{M} \\
& {\left[\mathrm{H}_{3} \mathrm{O}\right]^{+}=4.31 * 10^{-12}} \\
& \mathrm{pH}=11.37
\end{aligned}
$$

@ 10.00 mL added

$$
\begin{aligned}
& \mathrm{pKa}_{2}=9.731 \\
& \mathrm{H}^{+} \text {added }=(0.100 \mathrm{M})^{*}(10.00 \mathrm{~mL})=1.00 \mathrm{mmol} \mathrm{H} \\
& \mathrm{P}^{+}+\mathrm{H}_{3} \mathrm{O}^{+} \rightarrow \mathrm{PH}^{+}+\mathrm{H}_{2} \mathrm{O}(\text { to completion } / \text { or near to }) \\
& \mathrm{pH}=\mathrm{pKa}+\log \left(\mathrm{mol} \mathrm{P} / \mathrm{mol} \mathrm{HP}^{+}\right)
\end{aligned} \quad \begin{aligned}
& \mathrm{mol} \mathrm{PH} \\
& \\
& \mathrm{~mol} \mathrm{P} \quad 1.00 \mathrm{mmol} \\
& \quad=(40.0 \mathrm{ml} * 0.100 \mathrm{M})-1.00 \mathrm{~mol} \\
& \quad=3.00 \mathrm{mmol}
\end{aligned} \quad \begin{aligned}
& \mathrm{pH}=9.731+\log (3 / 1)=10.208
\end{aligned}
$$

@ 20 mL we are half way to the first equivalence point $\mathrm{pH}=\mathrm{pKa}_{2}=9.731$
@ 30 mL added
$\mathrm{pKa}_{2}=9.731$
$\mathrm{H}^{+}$added $=(0.100 \mathrm{M})^{*}(30.00 \mathrm{~mL})=3.00 \mathrm{mmol} \mathrm{H}^{+}$
$\mathrm{P}+\mathrm{H}_{3} \mathrm{O}^{+} \rightarrow \mathrm{PH}^{+}+\mathrm{H}_{2} \mathrm{O}$ (to completion/or near to)
$\mathrm{pH}=\mathrm{pKa}+\log \left(\mathrm{mol} \mathrm{P} / \mathrm{mol} \mathrm{HP}^{+}\right)$ $\mathrm{mol} \mathrm{PH}+=3.00 \mathrm{mmol}$

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

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

$$
\begin{aligned}
& \mathrm{HP}^{+}+\mathrm{H}_{2} \mathrm{O} \leftrightarrow \mathrm{H}_{2} \mathrm{P}^{2+}+\mathrm{OH}^{-} \\
& \mathrm{Kb}_{2}=\mathrm{Kw} / \mathrm{Ka}_{1}=10^{-14} / 4.65^{*} 10^{-6}=2.15^{*} 10^{-9}
\end{aligned}
$$

$$
\mathrm{HP}^{+}+\mathrm{H}_{2} \mathrm{O} \leftrightarrow \mathrm{P}+\mathrm{H}_{3} \mathrm{O}^{+}
$$

$$
\mathrm{Ka}_{2}=1.86 * 10^{-10}
$$

$$
\left[\mathrm{H}^{+}\right]=\left[\left(\mathrm{K}_{1} \mathrm{~K}_{2} \mathrm{~F}+\mathrm{K}_{1} \mathrm{Kw}\right) /\left(\mathrm{K}_{1}+\mathrm{F}\right)\right]^{0.5}
$$

$$
\mathrm{F}=(40 \mathrm{~mL})(0.100) /(80 \mathrm{~mL})=0.05 \mathrm{M}
$$

$$
\mathrm{K}_{1}=4.65 * 10^{-6}
$$

$$
\mathrm{K}_{2}=1.86 * 10^{-10}
$$

$$
\mathrm{Kw}=10^{-14}
$$

After simplifying
$\left[\mathrm{H}^{+}\right]=\left(\mathrm{K}_{1} \mathrm{~K}_{2}\right)^{0.5}=2.54 * 10^{-8} \mathrm{M}$
$\mathrm{pH}=7.53$
@ 50.00 mL added
$\mathrm{pKa}_{1}=5.333$
$\mathrm{H}^{+}$added $($after eq pt $)=(0.100 \mathrm{M}) *(10.00 \mathrm{~mL})=1.00 \mathrm{mmol}$
$\mathrm{HP}^{+}+\mathrm{H}_{3} \mathrm{O}^{+} \rightarrow \mathrm{H}_{2} \mathrm{P}^{+}+\mathrm{H}_{2} \mathrm{O}$ (to completion/or near to)
$\mathrm{pH}=\mathrm{pKa}_{1}+\log \left(\mathrm{mol} \mathrm{HP}^{+} / \mathrm{mol} \mathrm{H}_{2} \mathrm{P}^{+}\right)$
$\mathrm{mol} \mathrm{H} \mathrm{P}^{2+}=1.00 \mathrm{mmol}$
$\mathrm{mol} \mathrm{HP}{ }^{+}=\left(40.0 \mathrm{ml}^{*} 0.100 \mathrm{M}\right)-1.00 \mathrm{~mol}$
$=3.00 \mathrm{mmol}$
$\mathrm{pH}=5.333+\log (3 / 1)=5.810$
@ 60 ml we are half way to the second equivalence point $\mathrm{pH}=\mathrm{pKa}_{2}=5.333 @ 60.00 \mathrm{~mL}$ added
@ 70 ml added

$$
\left.\begin{array}{l}
\mathrm{pKa}_{1}=5.333 \\
\mathrm{H}^{+} \text {added }(\text { after eq pt })=(0.100 \mathrm{M})^{*}(30.00 \mathrm{~mL})=3.00 \mathrm{mmol} \\
\mathrm{HP}^{+}+\mathrm{H}_{3} \mathrm{O}^{+} \rightarrow \mathrm{H}_{2} \mathrm{P}^{+}+\mathrm{H}_{2} \mathrm{O}(\text { to completion or near to }) \\
\mathrm{pH}= \\
\quad \mathrm{pKa}_{1}+\log (\mathrm{mol} \mathrm{HP} \\
\quad \mathrm{mol} \mathrm{H}_{2} \mathrm{P}^{2+}=1.00 \mathrm{~mol} \mathrm{Hol} \\
2
\end{array} \mathrm{P}_{+2}\right) .
$$

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

$$
\mathrm{H}_{2} \mathrm{P}^{2+}+\mathrm{H}_{2} \mathrm{O} \leftrightarrow \mathrm{HP}^{+}+\mathrm{H}_{3} \mathrm{O}^{+}
$$

$$
\begin{aligned}
& \mathrm{F}_{\mathrm{H} 2 \mathrm{P} 2+}=\left(40.0 \mathrm{~mL}^{*} 0.100 \mathrm{M}\right) /(120.0 \mathrm{~mL})=0.0333 \mathrm{M} \\
& \mathrm{Ka}= 4.65 * 10^{-6}=\left[\mathrm{HP}^{+}\right]\left[\mathrm{H}^{+}\right] /\left(\mathrm{F}_{\mathrm{H} 2 \mathrm{P} 2+}-\left[\mathrm{HP}^{+}\right]\right) \\
& \text {Assume }\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\left[\mathrm{HP}^{+}\right], \text {and let }\left[\mathrm{HP}^{+}\right]=\mathrm{x} \\
& \text { Assume } \mathrm{F}_{\mathrm{B}+} \cong\left[\mathrm{H}_{2} \mathrm{P}^{2+}\right] \\
& 4.65^{*} 10^{-6}=\mathrm{x}^{2} /(0.0333) \\
& \mathrm{x}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=3.94^{*} 10^{-6} \mathrm{M} \\
& \mathrm{pH}=3.41
\end{aligned}
$$

@ 90.0 mL

$$
\begin{aligned}
{\left[\mathrm{H}^{+}\right]=(10.0 \mathrm{~mL}) } & *(.100) /(90 \mathrm{~mL}+40 \mathrm{~mL}) \\
& =7.69^{*} 10^{-3} \mathrm{M} \\
\mathrm{pH} & =2.114
\end{aligned}
$$

@ 100.0 mL added

$$
\begin{aligned}
{\left[\mathrm{H}^{+}\right]=(20.0 \mathrm{~mL}) } & *(.100) /(90 \mathrm{~mL}+50 \mathrm{~mL}) \\
& =1.43 * 10^{-2} \mathrm{M} \\
\mathrm{pH}=1.845 &
\end{aligned}
$$


10.27

50 mL of 0.100 M sodium glycinate with 0.100 M HCl
$\mathrm{K}_{\mathrm{a} 1}=4.47 \cdot 10^{-3}$
$\mathrm{K}_{\mathrm{a} 2}=1.67 \cdot 10^{-10}$
$\mathrm{V}_{\text {2nd eq point }}=100.0 \mathrm{~mL}$
$\mathrm{K}_{\mathrm{a} 1}=4.47 \cdot 10^{-3}=\mathrm{x}^{2} /((.1)(50 / 150)-\mathrm{x})$ \{assumption 2 not valid!!!\}
$\mathrm{x}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=0.01017 \mathrm{M}$
$\mathrm{pH}=1.993$
$@ \mathrm{Va}=90.0 \mathrm{~mL}$ using assumption that the acid reacts completely with the glycine gives

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

Unreasonable because it is lower than the equivalence point pH.
@ $\mathrm{Va}=101.0$, excess HCl is $(1.0 \mathrm{~mL})(0.1000) / 151.0=0.00062 \mathrm{M}$ $\mathrm{pH}=3.18$; Unreasonable because it is lower than the equivalence point pH . Most of the $\mathrm{H}^{+}$comes from the dissociation of the weak acid because the $\mathrm{K}_{\mathrm{a} 1}$ is so large. We can not ignore it!!
10.29
tyrosine
0.0100 M tyrosine titrated with $0.00400 \mathrm{M} \mathrm{HClO}_{4}$
$\mathrm{K}_{\mathrm{a} 1}=3.9 \cdot 10^{-3}$
$\mathrm{K}_{\mathrm{a} 2}=2.1 \cdot 10^{-9}$
$\mathrm{K}_{\mathrm{a} 3}=9.8 \cdot 10^{-12}$
Tyrosine is $\mathrm{H}_{2} \mathrm{~T}$ (first intermediate species)
At the eq. pt all of H2T has been converted to HT-, the second intermediate species.

$$
\mathrm{V}_{\mathrm{eq}}=\mathrm{V}_{\mathrm{tyr}}(0.100 \mathrm{M}) /(0.00400 \mathrm{M})=2.5 \mathrm{~V}_{\mathrm{tyr}}
$$

FHT- $=(0.100 \mathrm{M}) \mathrm{V}_{\text {try }} / 3.5 \mathrm{~V}_{\text {tyr }}=0.0286 \mathrm{M}$

$$
\begin{aligned}
{\left[\mathrm{H}^{+}\right] } & =\left[\left(\mathrm{K}_{2} \mathrm{~K}_{3} \mathrm{~F}+\mathrm{K}_{2} \mathrm{Kw}\right) /\left(\mathrm{K}_{2}+\mathrm{F}\right)\right]^{0.5} \\
& =\left\{\left[\left(2.1 \cdot 10^{-9}\right)\left(9.8 \cdot 10^{-12}\right)(.0286)+\left(2.1 \cdot 10^{-9}\right)\left(1.01 \cdot 10^{-14}\right)\right] /\right. \\
& \left.\left(0.0286 \mathrm{M}+2.1 \cdot 10^{-9}\right)\right\}^{1 / 2} \\
& \text { After simplifying } \\
& {\left[\mathrm{H}^{+}\right]=\left(\mathrm{K}_{2} \mathrm{~K}_{3}\right)^{0.5}=1.43 \cdot 10^{-10} \mathrm{M} } \\
& \mathrm{pH}=9.84
\end{aligned}
$$

10.30

Titrate 40.0 mL of a $0.0300 \mathrm{M} \mathrm{K}_{2} \mathrm{C}$ solution with $0.0600 \mathrm{M} \mathrm{HClO}_{4}$
cysteine is a triprotic base, and we a starting with the most basic species $\mathrm{C}^{2-}$.

$$
\begin{aligned}
& \mathrm{C}^{2-}+\mathrm{H}_{2} \mathrm{O} \leftrightarrow \mathrm{HC}^{-}+\mathrm{OH}^{-} \\
& \mathrm{HC}^{-}+\mathrm{H}_{2} \mathrm{O} \leftrightarrow \mathrm{H}_{2} \mathrm{C}+\mathrm{OH}^{-} \\
& \mathrm{H}_{2} \mathrm{C}+\mathrm{H}_{2} \mathrm{O} \leftrightarrow \mathrm{H}_{3} \mathrm{C}^{+}+\mathrm{OH}^{-} \\
& \mathrm{Ka}_{1}=1.95^{*} 10^{-2} \\
& \mathrm{Ka}_{2}=4.4^{*} 10^{-9} \\
& \mathrm{Ka}_{3}=1.7 * 10^{-11}
\end{aligned}
$$

Since the titrant is twice as concentrated as the analyte, it will take only 20.0 mL to reach the first equivalence point. Therefore,
$\mathrm{F}_{\mathrm{HC}-}\left(\right.$ at $1^{\text {st }}$ eq.pt. $)=(0.0300 \mathrm{M})(40.0 \mathrm{~mL}) /(60.0 \mathrm{~mL})=0.0200 \mathrm{M}$

$$
\begin{aligned}
& {\left[\mathrm{H}^{+}\right]=\left[\left(\mathrm{K}_{1} \mathrm{~K}_{2} \mathrm{~F}+\mathrm{K}_{1} \mathrm{Kw}\right) /\left(\mathrm{K}_{1}+\mathrm{F}\right)\right]^{0.5}} \\
& {\left[\mathrm{H}^{+}\right]==2.8 * 10^{-10} \mathrm{M}} \\
& \mathrm{pH}=9.56
\end{aligned}
$$

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

$$
\begin{aligned}
& \mathrm{H}_{3} \mathrm{C}^{+}+\mathrm{H}_{2} \mathrm{O} \leftrightarrow \mathrm{H}_{2} \mathrm{C}+{\mathrm{H} 3 \mathrm{O}^{+}}^{\mathrm{Ka}_{1}} \begin{array}{l}
\left.=1.95 * 10^{-2}=\left[\mathrm{H}_{2} \mathrm{C}\right]\left[\mathrm{H}_{3} \mathrm{O}^{+}\right] / \mathrm{H}_{3} \mathrm{C}^{+}\right] \\
\quad=\mathrm{x}^{2} / .0500-\mathrm{x} \text { (use excel or the quadratic formula) } \\
\mathrm{x}=0.0230 \mathrm{M}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]
\end{array}
\end{aligned}
$$

$\mathrm{Ka}_{3}=\left[\mathrm{C}^{2-}\right]\left[\mathrm{H}_{3} \mathrm{O}^{+}\right] /\left[\mathrm{HC}^{-}\right]$
$\left.\mathrm{Ka}_{3} /\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\left[\mathrm{C}^{2-}\right] /\left[\mathrm{HC}^{-}\right]=\left(1.7 * 10^{-11}\right) / .0230\right)=7.4 * 10^{-10}$
10.36

At $\mathrm{pK}_{\mathrm{HIn}}-1,[\mathrm{HIn}]$ is 10 x the concentration of [ $\left.\mathrm{In}^{-}\right]$ At $\mathrm{pK}_{\mathrm{HIn}}+1,\left[\mathrm{In}^{n}\right]$ is 10 x the concentration of [HIn] Therefore, because HIn and ${ }^{-}$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 $10.231+39.466=49.697 \mathrm{~g}$
Dilution factor $=(49.697 / 4.373)$
Moles of ammonia in 4.373 g solution $=(14.23 \mathrm{~mL})(0.1063)$

```
Weigh percent \(=[(0.01423 \mathrm{~L})(0.1063 \mathrm{M}) \cdot(49.697 / 4.373) \cdot(17.031\) \(\mathrm{g} / \mathrm{mol}) / 10.231 \mathrm{~g}\) solution] \(\cdot 100=2.859_{4} \%\)
```

10.57
$\mathrm{CH}_{3} \mathrm{O}^{-}+\mathrm{H}_{2} \mathrm{O} \leftrightarrow \mathrm{CH}_{3} \mathrm{OH}+\mathrm{OH}^{-}$
$\mathrm{K}_{\mathrm{b}}$ of this reaction is $\mathrm{k}_{\mathrm{w}} / \mathrm{k}_{\mathrm{a}}=1.82 \cdot 10^{-16} / 2.88 \cdot 10^{-16}=0.79$
$\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{O}^{-}+\mathrm{H}_{2} \mathrm{O} \leftrightarrow \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{OH}+\mathrm{OH}^{-}$
$\mathrm{K}_{\mathrm{b}}$ of this reaction is $\mathrm{k}_{\mathrm{w}} / \mathrm{k}_{\mathrm{a}}=1.82 \cdot 10^{-16} / 1 \cdot 10^{-16}=1.82$
These reactions essentially go to completion. The first one is about $90 \%$ dissociated and the second is about $95 \%$ dissociated. If one
uses $1.01 \mathrm{e}-14$ for Kw instead than the difference is even less (99.8 \% vs. 99.9 \% dissociated).
$101=x 2 /(.1-x)$
$\mathrm{x}=0.099901$
10.61
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 $7^{\text {th }} \mathrm{Ed}$

Methanol is a weaker acid than water
$\mathrm{CH}_{3} \mathrm{OH}+\mathrm{H}_{2} \mathrm{O} \leftrightarrow \mathrm{CH}_{3} \mathrm{O}^{-}+\mathrm{H}_{3} \mathrm{O}^{+}$
$\mathrm{k}_{\mathrm{a}}=2.88 \cdot 10^{-16}$
$\mathrm{H}_{2} \mathrm{O}+\mathrm{H}_{2} \mathrm{O} \leftrightarrow \mathrm{OH}^{-}+\mathrm{H}_{3} \mathrm{O}^{+}$
$\mathrm{k}_{\mathrm{a}}=1.01 \cdot 10^{-14}$
$\mathrm{P}+\mathrm{H}_{2} \mathrm{O} \leftrightarrow \mathrm{PH}^{+}+\mathrm{OH}^{-}$
$\mathrm{K}_{\mathrm{b}}=\mathrm{Kw} / \mathrm{Ka}=1.6 \cdot 10^{-9}$
$K_{a}=6.3 \cdot 10^{-6}$
$\mathrm{pKa}=5.2$
add the following reaction

$$
\begin{array}{ll}
\mathrm{P}+\mathrm{H}_{2} \mathrm{O} \leftrightarrow \mathrm{PH}^{+}+\mathrm{OH}^{-} & \mathrm{K}_{\mathrm{b}(\text { pyridine in } \mathrm{H} 2 \mathrm{O})}=1.6 \cdot 10^{-9} \\
\mathrm{OH}^{-}+\mathrm{H}_{3} \mathrm{O}^{+} \leftrightarrow \mathrm{H}_{z} \Theta+\mathrm{H}_{2} \mathrm{O} & 1 / \mathrm{K}_{\mathrm{w}}=9.9 \cdot 10^{13}
\end{array}
$$

$\mathrm{CH}_{3} \mathrm{OH}+\mathrm{H}_{2} \mathrm{O} \leftrightarrow \mathrm{CH}_{3} \mathrm{O}^{-}+\mathrm{H}_{3} \mathrm{\theta}^{+} \quad \mathrm{k}_{\mathrm{a}}=2.88 \cdot 10^{-16}$
$\mathrm{P}+\mathrm{CH}_{3} \mathrm{OH} \leftrightarrow \mathrm{PH}^{+}+\mathrm{CH}_{3} \mathrm{O}^{-}$
$\mathrm{K}_{\mathrm{b} \text { (pyridine in } \mathrm{CH} 3 \mathrm{OH})}=4.6 \cdot 10^{-11}$
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).

