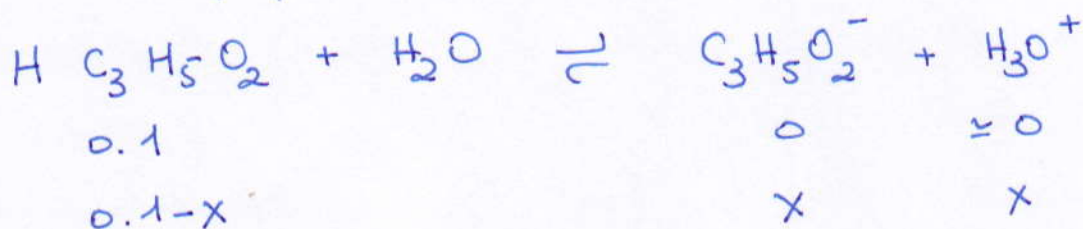


Chapter 15 - Acid-Base Equilibria

15.17

a. 0.100 M propanoic acid ($\text{HC}_3\text{H}_5\text{O}_2$, $K_a = 1.3 \times 10^{-5}$)

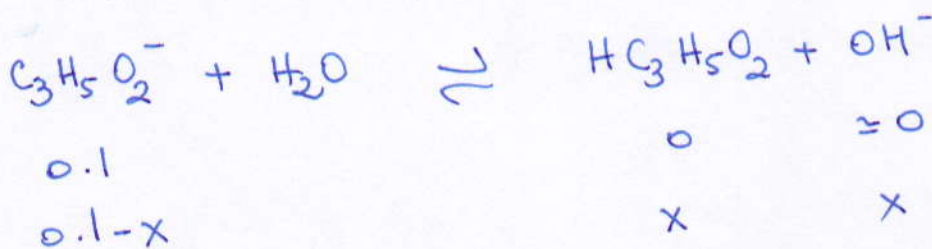


$$K_a = \frac{[\text{C}_3\text{H}_5\text{O}_2^-][\text{H}_3\text{O}^+]}{[\text{HC}_3\text{H}_5\text{O}_2]} = \frac{x^2}{0.1-x} \approx \frac{x^2}{0.1} \Rightarrow x = \sqrt{K_a \times 0.1}$$

$$\Rightarrow x = \sqrt{1.3 \times 10^{-5} \times 0.1} = 1.14 \times 10^{-3} \quad \text{app. accepted}$$

$$\Rightarrow [\text{H}_3\text{O}^+] = 1.14 \times 10^{-3} \text{ M} \Rightarrow \text{pH} = 2.94$$

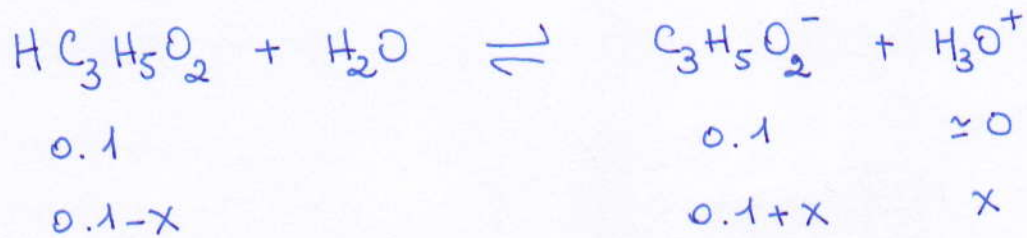
b. 0.100 M sodium propanoate ($\text{NaC}_3\text{H}_5\text{O}_2$)



$$\Rightarrow K_b = \frac{[\text{HC}_3\text{H}_5\text{O}_2][\text{OH}^-]}{[\text{C}_3\text{H}_5\text{O}_2^-]} = \frac{x^2}{0.1-x} \approx \frac{x^2}{0.1} \Rightarrow x = \sqrt{K_b \times 0.1}$$

$$\Rightarrow x = \sqrt{\frac{K_w}{K_a} \times 0.1} = \sqrt{\frac{10^{-14}}{1.3 \times 10^{-5}} \times 0.1} = 8.77 \times 10^{-6} \quad \text{app. accepted}$$

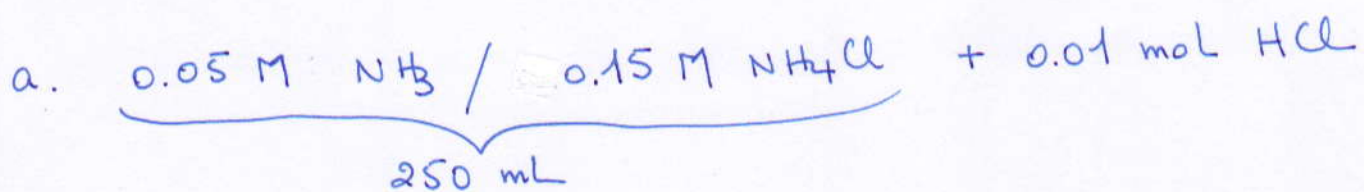
$$\Rightarrow [\text{OH}^-] = 8.77 \times 10^{-6} \text{ M} \Rightarrow [\text{H}_3\text{O}^+] = 1.14 \times 10^{-9} \text{ M} \Rightarrow \text{pH} = 8.94$$



$$K_a = \frac{[\text{C}_3\text{H}_5\text{O}_2^-][\text{H}_3\text{O}^+]}{[\text{HC}_3\text{H}_5\text{O}_2]} = \frac{(0.1+x)x}{0.1-x} \approx \frac{0.1x}{0.1} = x = 1.3 \times 10^{-5} \quad \text{app. accepted}$$

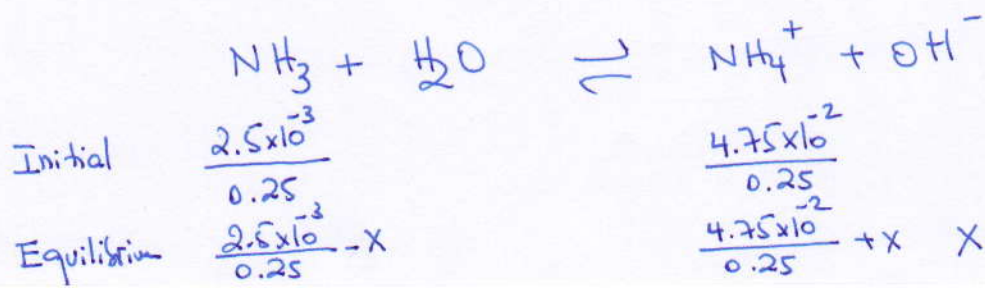
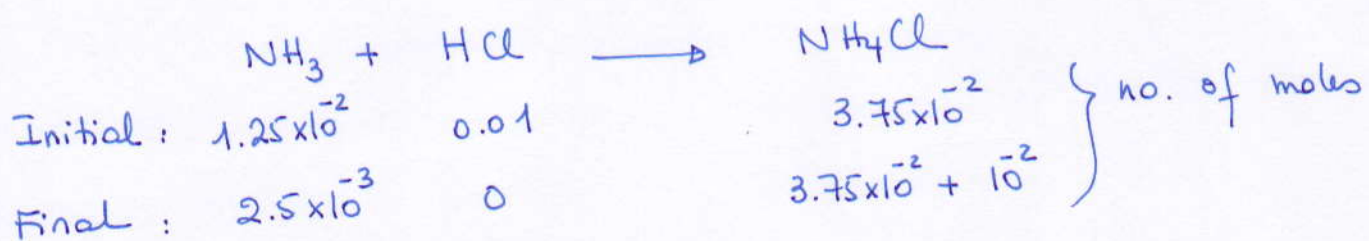
$$\Rightarrow [\text{H}_3\text{O}^+] = 1.3 \times 10^{-5} \text{ M} \Rightarrow \text{pH} = 4.89$$

15.35



$$n_{\text{NH}_3} = 0.05 \times 0.25 = 1.25 \times 10^{-2} \text{ mol}$$

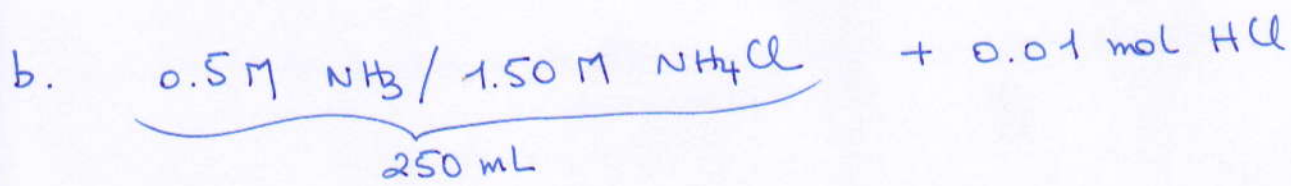
$$n_{\text{NH}_4^+} = 0.15 \times 0.25 = 3.75 \times 10^{-2} \text{ mol}$$



$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{(0.19+x)x}{(0.01-x)} \approx \frac{0.19x}{0.01}$$

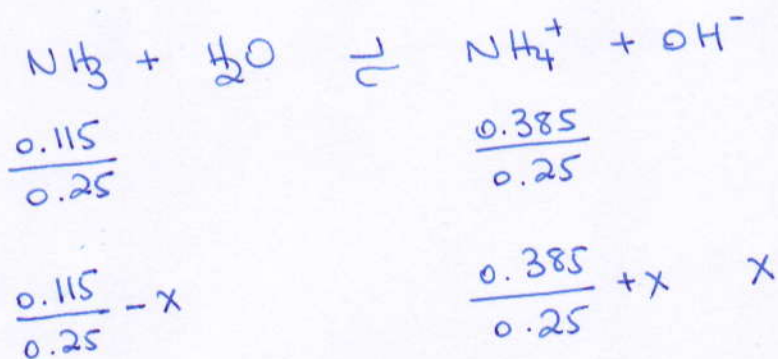
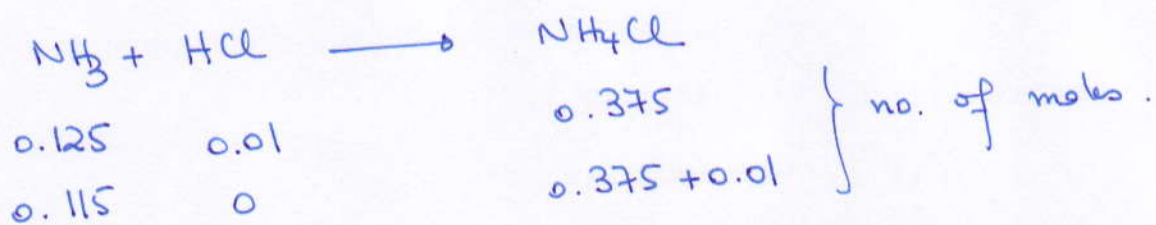
$$\Rightarrow x = \frac{K_b \times 0.1}{0.19} = \frac{1.8 \times 10^{-5} \times 0.01}{0.19} = 9.47 \times 10^{-7} \quad \text{app. accepted}$$

$$\Rightarrow [\text{OH}^-] = 9.47 \times 10^{-7} \text{ M} \Rightarrow [\text{H}_3\text{O}^+] = 1.06 \times 10^{-8} \text{ M} \Rightarrow \text{pH} = 7.97$$



$$n_{\text{NH}_3} = 0.125 \text{ mol}$$

$$n_{\text{NH}_4^+} = 0.375 \text{ mol}$$



$$K_b = \dots = \frac{(1.54+x)x}{0.46-x} \approx \frac{1.54x}{0.46} \Rightarrow x = 5.38 \times 10^{-6} \quad \text{app. accepted}$$

$$\Rightarrow [\text{OH}^-] = 5.38 \times 10^{-6} \text{ M} \Rightarrow \text{pOH} = 5.27 \Rightarrow \text{pH} = 8.73$$

c. $\text{pH} = \text{p}K_a + \log \frac{\text{Base}}{\text{acid}} = 9.26 + \log \frac{[\text{NH}_3]}{[\text{NH}_4^+]}$

In both case $\frac{[\text{NH}_3]}{[\text{NH}_4^+]} = 0.333 \Rightarrow \text{pH is the same} = 8.78$

⇒ A buffer with high buffer capacity will have a better resistance to pH changes. The second solution has a higher buffer capacity.

15.51

40 mL 0.2 M HClO_4 + 0.1 M KOH

$$n_{\text{HClO}_4} = 0.2 \times 0.04 = 8 \times 10^{-3} \text{ mol}$$

a. 0 mL KOH added :

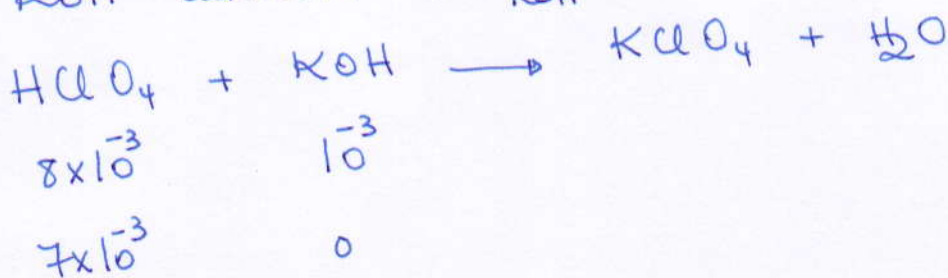


$$\Rightarrow n_{\text{H}_3\text{O}^+} \text{ produced} = 8 \times 10^{-3} \text{ mol} \Rightarrow [\text{H}_3\text{O}^+] = \frac{8 \times 10^{-3}}{0.04} = 0.2 \text{ M}$$

you can easily obtain this concentration from the original solution.

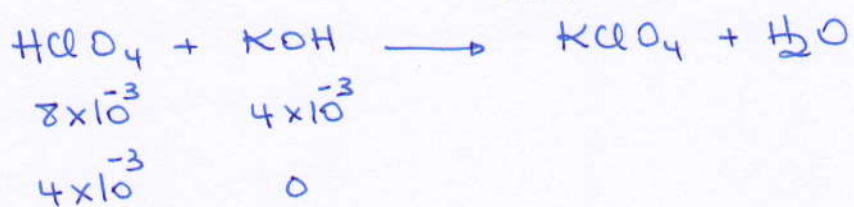
$$\Rightarrow \text{pH} = -\log[\text{H}_3\text{O}^+] = 0.70$$

b. 10 mL KOH added : $\Rightarrow n_{\text{KOH}} = 0.1 \times 0.01 = 10^{-3} \text{ mol}$



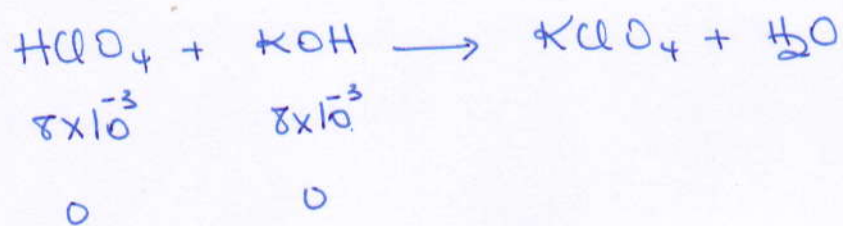
$$\Rightarrow [\text{HClO}_4] = \frac{7 \times 10^{-3}}{(0.04 + 0.01)} = 0.14 \text{ M} = [\text{H}_3\text{O}^+] \Rightarrow \text{pH} = 0.85$$

c. 40 mL KOH added $\Rightarrow n_{\text{KOH}} = 0.1 \times 0.04 = 4 \times 10^{-3} \text{ mol}$



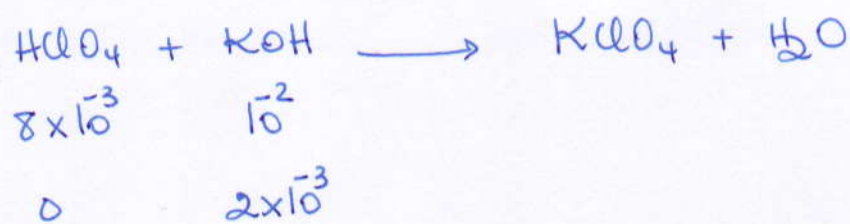
$$\Rightarrow [\text{HClO}_4] = \frac{4 \times 10^{-3}}{(0.04 + 0.04)} = 0.05 \text{ M} = [\text{H}_3\text{O}^+] \Rightarrow \text{pH} = 1.30$$

d. 80 mL KOH added $\Rightarrow n_{\text{KOH}} = 0.1 \times 0.08 = 8 \times 10^{-3} \text{ mol}$



\Rightarrow the only source of H_3O^+ in the solution is the autodissociation of water molecules $\Rightarrow \text{pH} = 7$
equivalence point

e. 100 mL KOH added $\Rightarrow n_{\text{KOH}} = 0.1 \times 0.1 = 10^{-2} \text{ mol}$



\Rightarrow KOH is in excess.

$$[\text{OH}^-] = \frac{2 \times 10^{-3}}{0.04 + 0.1} = 1.43 \times 10^{-2} \text{ M} \Rightarrow [\text{H}_3\text{O}^+] = 6.99 \times 10^{-13} \text{ M}$$

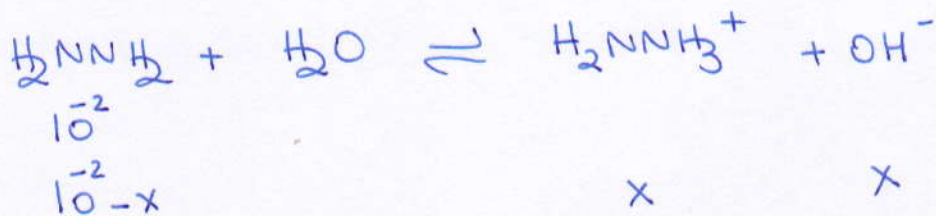
$$\Rightarrow \text{pH} = 12.16$$

15.54

100 mL 0.1 M H_2NNH_2 ($K_b = 3.0 \times 10^{-6}$) + 0.2 M HNO_3

$$n_{\text{H}_2\text{NNH}_2} = 0.1 \times 0.1 = 10^{-2} \text{ mol}$$

a. 0 mL HNO_3 added.

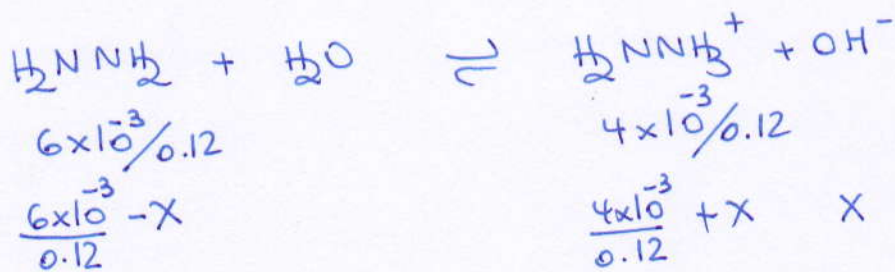
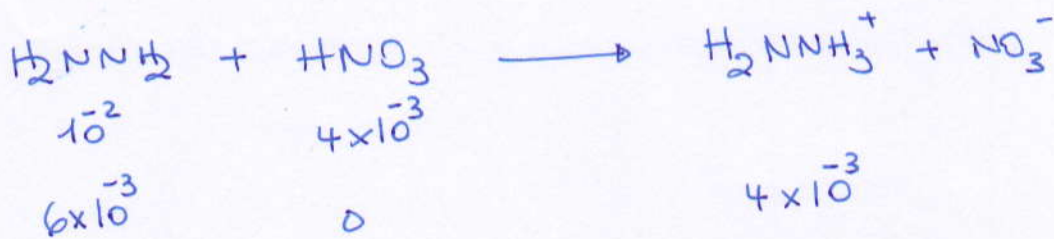


$$K_b = \frac{[\text{H}_2\text{NNH}_3^+][\text{OH}^-]}{[\text{H}_2\text{NNH}_2]} = \frac{x^2}{10^{-2} - x} \approx \frac{x^2}{10^{-2}} \Rightarrow x = \sqrt{K_b \times 10^{-2}}$$

$$\Rightarrow x = \sqrt{3.0 \times 10^{-6} \times 10^{-2}} = 1.73 \times 10^{-4} \quad \text{app. accepted}$$

$$\Rightarrow [\text{OH}^-] = 1.73 \times 10^{-4} \text{ M} \Rightarrow [\text{H}_3\text{O}^+] = 5.78 \times 10^{-11} \text{ M} \Rightarrow \text{pH} = 10.24$$

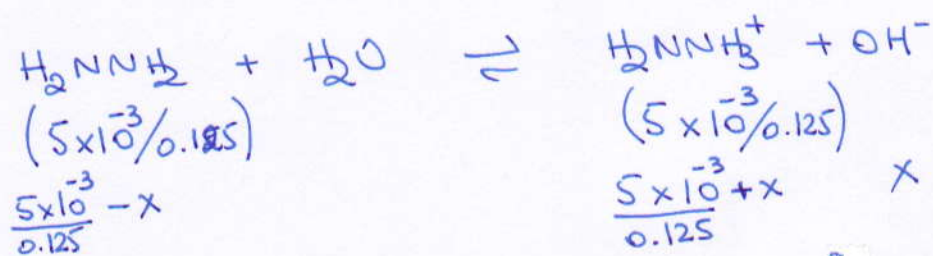
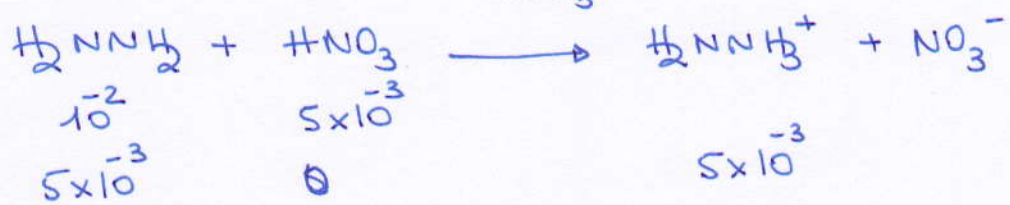
b. 20 mL HNO_3 added $\Rightarrow n_{\text{HNO}_3} = 0.2 \times 0.02 = 4 \times 10^{-3} \text{ mol}$



$$K_b = \frac{\left(\frac{4 \times 10^{-3}}{0.12} + x\right) x}{\left(\frac{6 \times 10^{-3}}{0.12} - x\right)} \approx \frac{\left(\frac{4 \times 10^{-3}}{0.12}\right) x}{\left(\frac{6 \times 10^{-3}}{0.12}\right)} \Rightarrow x = 4.5 \times 10^{-6} \quad \text{app. accepted}$$

$$\Rightarrow [\text{OH}^-] = 4.5 \times 10^{-6} \text{ M} \Rightarrow \text{pOH} = 5.35 \Rightarrow \text{pH} = 8.65$$

c. 25 mL HNO_3 added $\Rightarrow n_{\text{HNO}_3} = 5 \times 10^{-3}$ mol half-equiv.



$$\text{pH} = \text{p}K_a + \log \frac{\text{base}}{\text{acid}} = 8.48 + \log \frac{4 \times 10^{-2}}{4 \times 10^{-2}} = 8.48$$

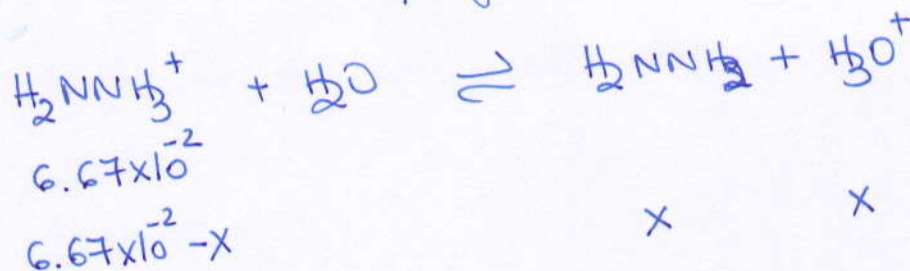
d. 40 mL HNO_3 added $\Rightarrow n_{\text{HNO}_3} = 8 \times 10^{-3}$ mol

Similar to part c

$$\text{pH} = \text{p}K_a + \log \frac{\text{base}}{\text{acid}} = 8.48 + \log \frac{2 \times 10^{-3} / 0.14}{8 \times 10^{-3} / 0.14} = 7.88$$

e. 50 mL HNO_3 added $\Rightarrow n_{\text{HNO}_3} = 10^{-2}$ mol equiv. point

$\Rightarrow \text{H}_2\text{NNH}_2$ reacts completely with HNO_3 to form H_2NNH_3^+ (10^{-2} mol)



$$K_a = \frac{K_w}{K_b} = \frac{x^2}{6.67 \times 10^{-2} - x} \approx \frac{x^2}{6.67 \times 10^{-2}} \Rightarrow x = 1.49 \times 10^{-5} \text{ app. accepted}$$

$$\Rightarrow [\text{H}_3\text{O}^+] = 1.49 \times 10^{-5} \text{ M} \Rightarrow \text{pH} = 4.83$$

f. 100 mL HNO_3 added $\Rightarrow n_{\text{HNO}_3} = 2 \times 10^{-2}$ mol

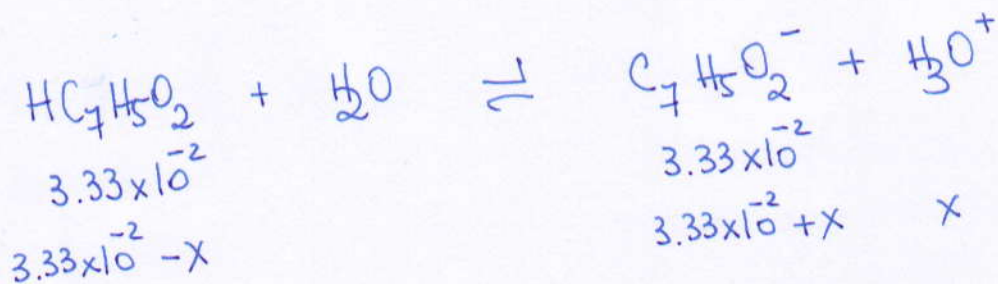
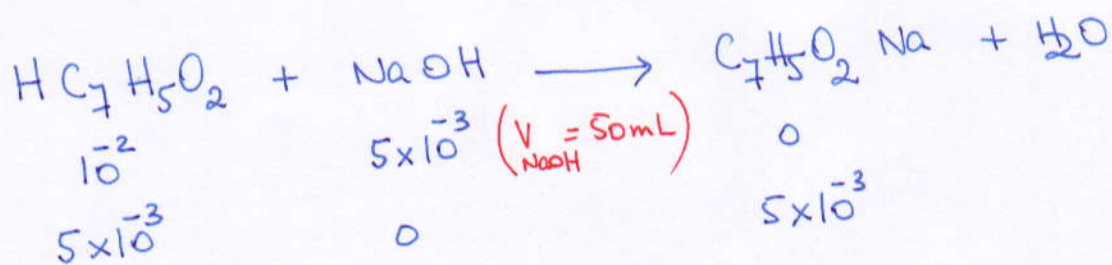
$\Rightarrow \text{HNO}_3$ in excess. (10^{-2} mol in excess).

At this stage, two sources of H_3O^+ exist in the solution which are the strong acid HNO_3 and the weak acid H_2NNH_3^+ . We consider (approximation) that the H_3O^+ comes only from the strong acid

$$\Rightarrow [\text{H}_3\text{O}^+] = \frac{10^{-2}}{0.2} = 5 \times 10^{-2} \text{ M} \Rightarrow \text{pH} = 1.30$$

15.59

a. 100 mL of 0.1 M $\text{HC}_7\text{H}_5\text{O}_2$ ($K_a = 6.4 \times 10^{-5}$) $\rightarrow n_{\text{HC}_7\text{H}_5\text{O}_2} = 10^{-2}$ mol
+ 0.1 M NaOH



$$\text{pH} = \text{p}K_a + \log \frac{[\text{C}_7\text{H}_5\text{O}_2^-]}{[\text{HC}_7\text{H}_5\text{O}_2]} = \text{p}K_a = 4.19 \quad \text{halfway point}$$

when the totality of $\text{HC}_7\text{H}_5\text{O}_2$ is titrated $\Rightarrow V_{\text{NaOH}} = 100 \text{ mL}$

$$\Rightarrow n_{\text{C}_7\text{H}_5\text{O}_2^-} = 10^{-2} \text{ mol}$$

b. The solution will start changing its color when the quantity of one form of the molecule is approximately $10 \times$ that of the other form.

$$\Rightarrow \frac{[\text{In}^-]}{[\text{HIn}]} = \frac{1}{10}$$

$$\Rightarrow \text{pH} = \text{pK}_a + \log \frac{1}{10} = \text{pK}_a - 1 = 8.$$

c. $n_{\text{HCl}} = 0.1 \times 0.1 = 10^{-2} \text{ mol}$
 $n_{\text{NaOH}} = 0.1 \times 0.2 = 2 \times 10^{-2} \text{ mol}$ } $\Rightarrow n_{\text{NaOH}}$ in excess after titration = 10^{-2} mol

$$\Rightarrow [\text{NaOH}] = \frac{10^{-2}}{0.3} = 3.33 \times 10^{-2} \text{ M} \Rightarrow \text{pH} = 12.52$$

$$\text{pH} = \text{pK}_a + \log \frac{[\text{In}^-]}{[\text{HIn}]} \Rightarrow \log \frac{[\text{In}^-]}{[\text{HIn}]} = 12.52 - 9 = 3.52$$

$$\Rightarrow \frac{[\text{In}^-]}{[\text{HIn}]} = 10^{3.52} = 3311 \Rightarrow \text{In}^- \text{ is dominant}$$

\Rightarrow the solution is blue