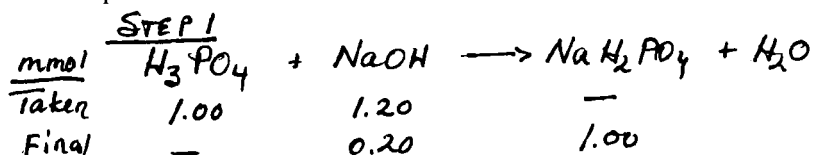


Useful Information:

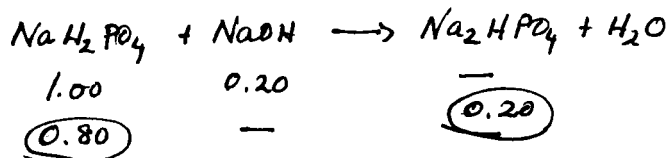
Acid	K_{a1}	K_{a2}	K_{a3}	Base	K_b
Acetic acid	1.8×10^{-5}			Ammonia	1.8×10^{-5}
Malonic Acid	1.4×10^{-4}	2.0×10^{-6}		Methylamine	4.3×10^{-4}
Phosphoric Acid	7.1×10^{-3}	6.3×10^{-8}	4.5×10^{-13}		

Part I (48 points). Show your work. Evaluation based on correctness, completeness and clarity. Use appropriate number of significant figures in your final result.

1. (16) A solution is prepared by addition of 12.0 mL of 0.100 M NaOH to 10.0 mL of 0.100 M phosphoric acid.
 a) Write the net stepwise reaction(s) and calculate the formal concentrations of the principal phosphate species in the solution.



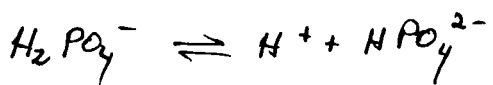
STEP 2



$$C_{NaH_2PO_4} = \frac{0.80 \text{ mmol}}{22.0 \text{ mL}} = 0.0364 \text{ M}$$

$$C_{Na_2HPO_4} = \frac{0.20 \text{ mmol}}{22 \text{ mL}} = 0.0091 \text{ M}$$

- b) Calculate the pH of the solution. Show the principle equilibrium reaction controlling the pH and develop your solution from the corresponding K_a expression.



$$K_{a2} = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]}$$

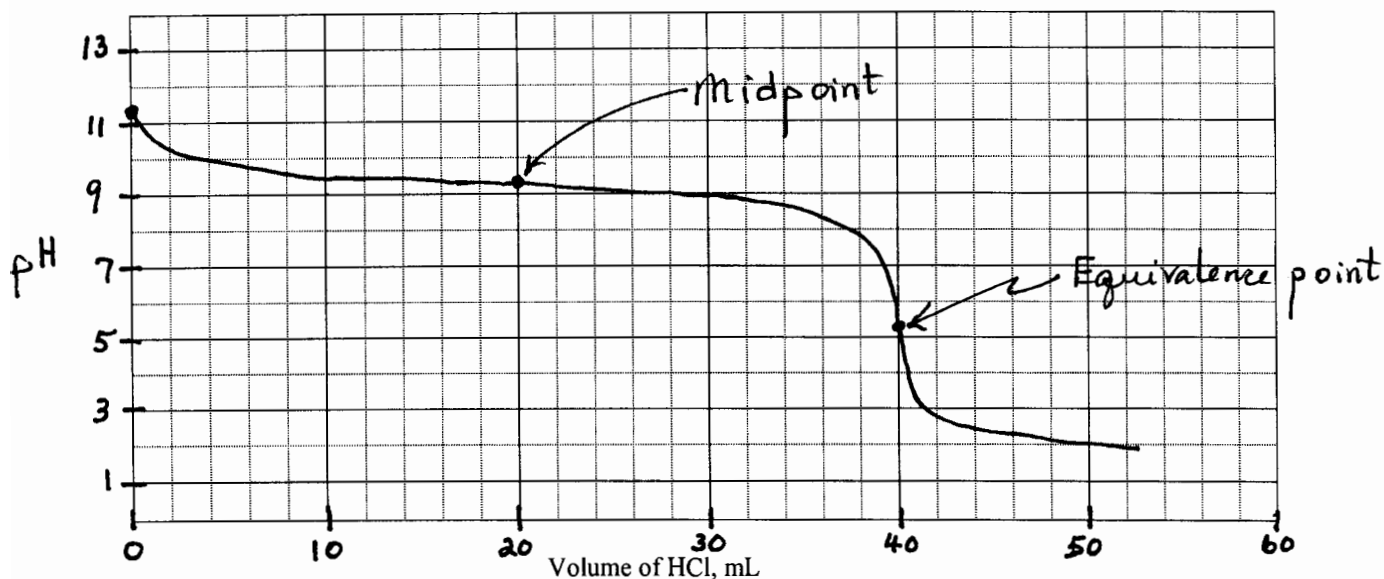
$$[H^+] = K_a \frac{[H_2PO_4^-]}{[HPO_4^{2-}]} \approx K_a \frac{\eta_{H_2PO_4}}{\eta_{HPO_4}}$$

$$= 6.3 \times 10^{-8} \left(\frac{0.80}{0.20} \right) = 2.5 \times 10^{-7} \text{ mol/L}$$

$$pH = 6.60$$

2. (24) Consider the titration of 40.0 mL of 0.100 M ammonia with 0.100 M HCl.

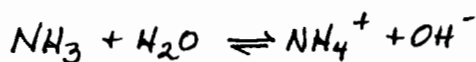
- a) After performing the calculations indicated in the following section, sketch the titration curve on the graph provided here. Label the midpoint and equivalence point.



b) Report the following data for given points in the titration.

- i) The initial pH of the ammonia solution (0 mL of acid added). Show your work.

$$C_{\text{NH}_3} = 0.100 \text{ M}$$



$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} \approx \frac{[\text{OH}^-]^2}{C_{\text{NH}_3}}$$

$$\begin{aligned} [\text{OH}^-] &\approx \sqrt{K_b C_{\text{NH}_3}} \\ &= \sqrt{(1.8 \times 10^{-5})(0.100)} \\ &= 1.34 \times 10^{-3} \end{aligned}$$

$$\text{pOH} = 2.87; \text{pH} = 14 - 2.87 = 11.13$$

Your results for i): pH = 11.13

- ii) At the midpoint: The volume of acid added and the pH of the solution. No calculations required.

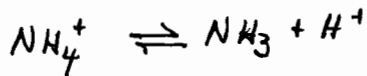
$$\text{pOH} = \text{p}K_b = -\log(1.8 \times 10^{-5}) = 4.74$$

$$\text{pH} = 14 - \text{pOH} = 9.26$$

Your results for ii): Volume of acid (mL) = 20; pH = 9.26

- iii) At the equivalence point: The volume of acid added and the pH of the solution. Show your work for calculation of pH.

$$\text{At } 40 \text{ mL, } C_{\text{NH}_4^+} = 0.100 \left(\frac{40}{80} \right) = 0.0500 \text{ M}$$



$$K_a = \frac{K_w}{K_b} = \frac{[\text{NH}_3][\text{H}^+]}{[\text{NH}_4^+]} \approx \frac{[\text{H}^+]^2}{C_{\text{NH}_4^+}}$$

$$\begin{aligned} [\text{H}^+] &\approx \sqrt{\frac{K_w}{K_b} C_{\text{NH}_4^+}} = \sqrt{\frac{1.00 \times 10^{-14}}{1.8 \times 10^{-5}} (0.0500)} = 5.3 \times 10^{-6} \\ \text{pH} &= 5.28 \end{aligned}$$

Your results for iii): Volume of acid (mL) = 40; pH = 5.28

(8) A 1.206-g sample of wheat flour was analyzed by the Kjeldahl method. The ammonia formed by addition of concentrated base after digestion with H_2SO_4 was distilled into 25.00 mL of 0.05000 M HCl. The excess HCl was then back-titrated with 6.20 mL of 0.04000 M NaOH. Calculate the percent nitrogen in the flour. Atomic mass of N = 14.00 g/mol.

$$n_N = n_{\text{NH}_3} = n_{\text{HCl}} - n_{\text{NaOH}} = M_{\text{HCl}} \text{ mL}_{\text{HCl}} - M_{\text{NaOH}} \text{ mL}_{\text{NaOH}}$$

$$\% \text{ N} = \frac{(M_{\text{HCl}} \text{ mL}_{\text{HCl}} - M_{\text{NaOH}} \text{ mL}_{\text{NaOH}}) (\text{m.w.}_N) 100}{\text{wt sample}}$$

$$= \frac{\{(0.05000)(25.00) - (0.04000)(6.20)\} \left(\frac{0.01400 \text{ g}}{\text{mmol}}\right) 100}{1.206 \text{ g}}$$

$$= 1.163 \% \text{ N}$$