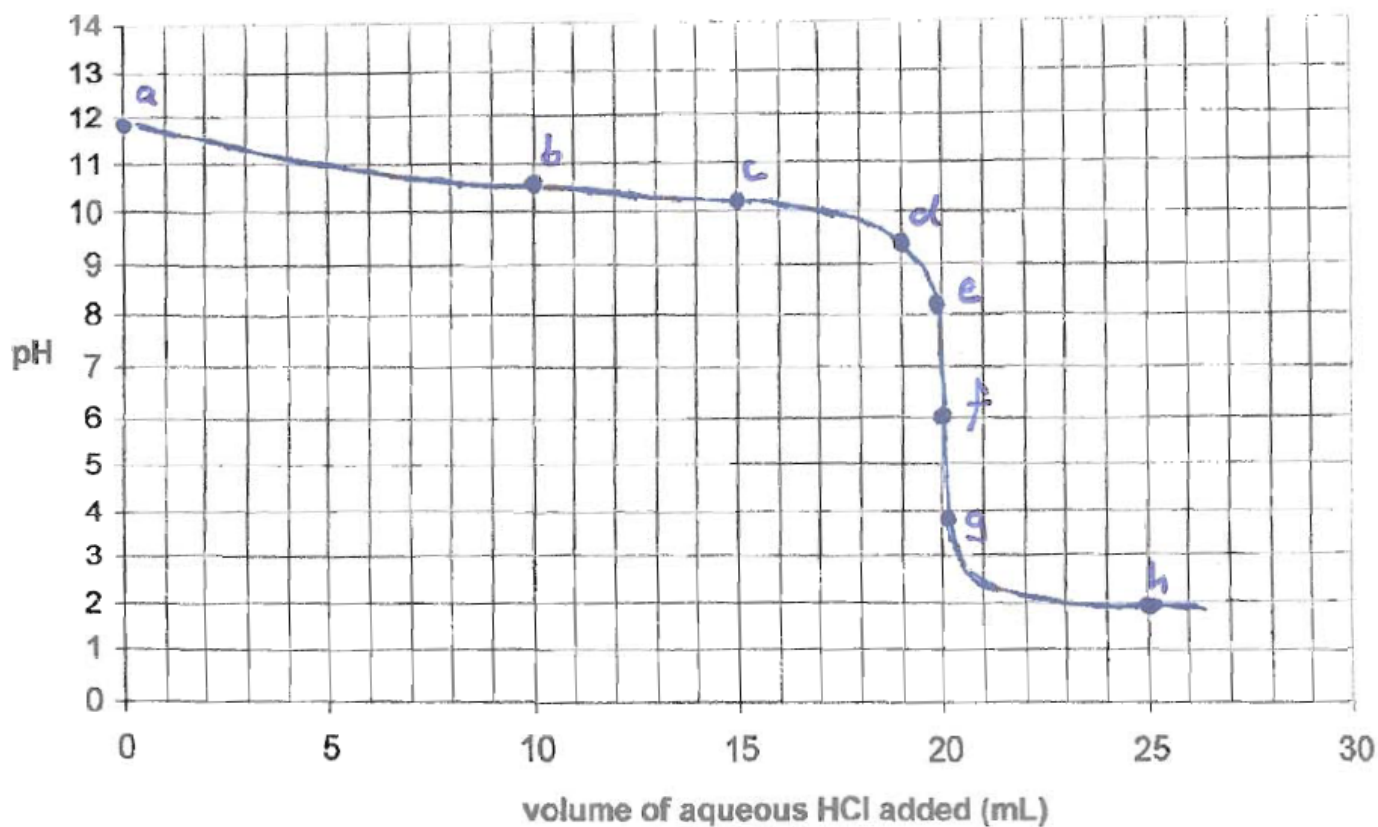


### Practice Exercise: Titration of a Weak Base with a Strong Acid – Solutions

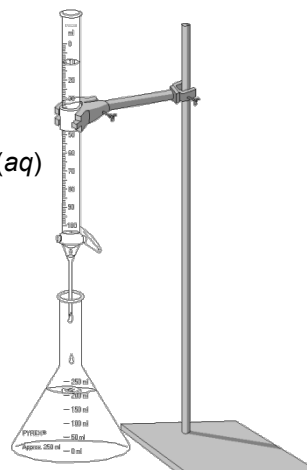
A 20.00-mL sample of 0.1000 M  $\text{N}(\text{CH}_2\text{CH}_3)_3$  is titrated with 0.1000 M HCl.  $K_b$  for  $\text{N}(\text{CH}_2\text{CH}_3)_3$  is  $5.3 \times 10^{-4}$ , so the  $K_a$  for  $\text{HN}(\text{CH}_2\text{CH}_3)_3^+$  is  $1.9 \times 10^{-11}$  and  $\text{p}K_a = 10.72$ . Determine the pH after the following volumes of HCl are added:

- 0 mL
- 10.00 mL
- 15.00 mL
- 19.00 mL
- 19.95 mL
- 20.00 mL
- 20.05 mL
- 25.00 mL
- 30.00 mL

and draw a smooth line on the grid below illustrating the titration curve you would expect for this titration. Circle the "buffer region." The  $K_a$  of  $\text{HN}(\text{CH}_2\text{CH}_3)_3^+$  is  $1.9 \times 10^{-11}$ .



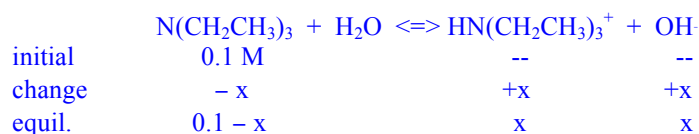
0.1000 M HCl(aq)



20 mL  
0.1000 M N(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>(aq)

a. 0 mL of 0.1000 M HCl(aq) added

This is a  $K_b$  problem



Solving

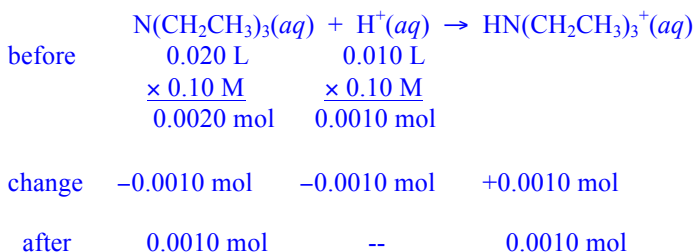
$$5.3 \times 10^{-4} = \frac{x^2}{0.10 - x}$$

gives  $x = 7.28 \times 10^{-3} = [OH^-]^* \Rightarrow pOH = 2.14 \Rightarrow pH = 11.86$

(\*should iterate to get a better answer; 2nd iteration,  $7.01 \times 10^{-3} = [OH^-] \Rightarrow pH = 11.85$ )

b. 10.00 mL of 0.1000 M HCl(aq) added

Between the no HCl added and the equivalence point (20 mL), so both  $N(CH_2CH_3)_3$  and  $HN(CH_2CH_3)_3^+$  present in solution. Therefore we can use the H-H equation.



The H-H equation gives

$$pH = pK_a + \log \frac{[B]}{[B-H^+]} = 10.72 + \log \frac{\text{mol B} / \cancel{\text{total vol}}}{\text{mol B-H}^+ / \cancel{\text{total vol}}} = 10.72 + \log \frac{0.0010}{0.0010} = 10.72 + 0 = 10.72$$

and  $pH = 10.72 = pK_a$  as expected for the half-equivalence point.

c. 15.00 mL of 0.1000 M HCl(aq) added

By analogy with part (b)

$$pH = pK_a + \log \frac{[B]}{[B-H^+]} = 10.72 + \log \frac{\text{mol B} / \cancel{\text{total vol}}}{\text{mol B-H}^+ / \cancel{\text{total vol}}} = 10.72 + \log \frac{0.0005}{0.0015} = 10.72 + (-0.477...) = 10.24$$

giving  $pH = 10.25$ . Note that the pH decreased with the addition of acid, as expected, but it did not decrease by much, also as expected because we are in the "buffer region."

d. 19.00 mL of 0.1000 M HCl(aq) added

$$pH = pK_a + \log \frac{[B]}{[B-H^+]} = 10.72 + \log \frac{\text{mol B} / \cancel{\text{total vol}}}{\text{mol B-H}^+ / \cancel{\text{total vol}}} = 10.72 + \log \frac{0.0001}{0.0019} = 10.72 + (-1.278...) = 9.44$$

giving pH = 9.44.

e. 19.95 mL of 0.1000 M HCl(aq) added

$$pH = pK_a + \log \frac{[B]}{[B-H^+]} = 10.72 + \log \frac{\text{mol B} / \cancel{\text{total vol}}}{\text{mol B-H}^+ / \cancel{\text{total vol}}} = 10.72 + \log \frac{0.05 \times 10^{-4}}{19.95 \times 10^{-4}} = 8.12$$

giving pH = 8.12.

f. 20.00 mL of 0.1000 M HCl(aq) added

This volume takes us to the equivalence point, so all  $N(CH_2CH_3)_3$  has been converted to  $HN(CH_2CH_3)_3^+$ , and we essentially have a solution of  $HN(CH_2CH_3)_3^+$ . Therefore we must solve a  $K_a$  problem where we obtain  $K_a$  from  $K_b$

$K_a = K_w/K_b = (1.0 \times 10^{-14}/5.2 \times 10^{-4}) = 1.9 \times 10^{-11}$ . The total volume is 40 mL, so  $[HN(CH_2CH_3)_3^+] = (\frac{1}{2})0.10 \text{ M} = 0.050 \text{ M}$ . Solving

$$1.9 \times 10^{-11} = \frac{x^2}{0.05 - x}$$

gives  $x = 9.8 \times 10^{-7} = [H^+] \Rightarrow pH = 6.01$

g. 20.05 mL of 0.1000 M HCl(aq) added

This volume puts us past the equivalence point, so we must solve an excess  $H^+$  problem.

$$0.05 \text{ mL} = 5 \times 10^{-5} \text{ L} \times \text{OH}^- \times 0.10 \text{ mol/L} = 5 \times 10^{-6} \text{ mol } H^+$$

$$\text{volume} = 20.00 \text{ mL} + 20.05 \text{ mL} = 40.05 \text{ mL} = 0.04005 \text{ L}$$

$$(5 \times 10^{-6} \text{ mol}) / (0.04005 \text{ L}) = 0.00012 \text{ M } H^+(\text{aq}) \Rightarrow pH = 3.9$$

h. 25.00 mL of 0.1000 M HCl(aq) added

By analogy with part (g), 5.00 mL  $\times$ s  $OH^-$  past equivalence point

$$5.0 \text{ mL} = 5.0 \times 10^{-3} \text{ L} \times \text{OH}^- \times 0.10 \text{ mol/L} = 5.0 \times 10^{-4} \text{ mol } H^+$$

$$\text{volume} = 20.00 \text{ mL} + 25.00 \text{ mL} = 45.00 \text{ mL} = 0.045 \text{ L}$$

$$(5.0 \times 10^{-4} \text{ mol}) / (0.045 \text{ L}) = 0.011 \text{ M } H^+(\text{aq}) \Rightarrow pH = 1.95$$

i. 30.00 mL of 0.1000 M HCl(aq) added

10.00 mL  $\times$ s  $OH^-$  past equivalence point

$$10.0 \text{ mL} = 1.0 \times 10^{-2} \text{ L} \times \text{OH}^- \times 0.10 \text{ mol/L} = 1.0 \times 10^{-3} \text{ mol } H^+$$

$$\text{volume} = 20.00 \text{ mL} + 30.00 \text{ mL} = 50.00 \text{ mL} = 0.050 \text{ L}$$

$$(1.0 \times 10^{-3} \text{ mol}) / (0.050 \text{ L}) = 0.020 \text{ M } H^+(\text{aq}) \Rightarrow pH = 1.70$$