

## Chapter 10 Homework

**10-6.**

$V_b$	0	1	5	9	9.9	10	10.1	12
pH	3.00	4.05	5.00	5.95	7.00	8.98	10.96	12.25

Representative calculations:

0 mL: 
$$\text{HA} = \text{H}^+ + \text{A}^-$$

$$\frac{x^2}{0.100 - x} = 10^{-5.00} \Rightarrow x = 9.95 \times 10^{-4} \text{ M}$$

$$\Rightarrow \text{pH} = 3.00$$

1 mL: 
$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]} = 5.00 + \log \frac{1}{9} = 4.05$$

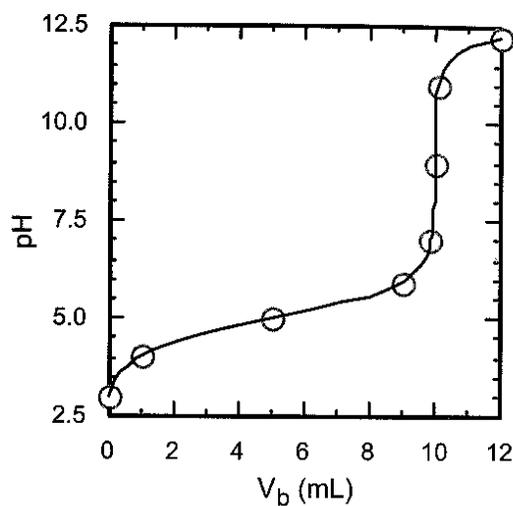
10 mL: 
$$\text{A}^- + \text{H}_2\text{O} = \text{HA} + \text{OH}^-$$

$$\frac{x^2}{0.0909 - x} = \frac{K_w}{K_a}$$

$$\Rightarrow x = 9.53 \times 10^{-6}$$

$$\Rightarrow [\text{H}^+] = \frac{K_w}{x} \Rightarrow \text{pH} = 8.98$$

10.1 mL: 
$$[\text{OH}^-] = \left(\frac{0.1}{110.1}\right)(1.00) = 9.08 \times 10^{-4} \text{ M} \Rightarrow \text{pH} = 10.96$$



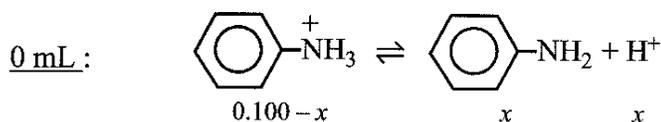
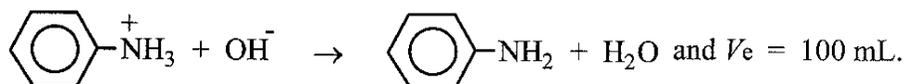
10-7.  $\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$        $\text{p}K_a - 1 = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]} \Rightarrow \frac{[\text{A}^-]}{[\text{HA}]} = \frac{1}{10}$

If the ratio  $\frac{[\text{A}^-]}{[\text{HA}]}$  is to be  $\frac{1}{10}$ , then  $\frac{1}{11}$  of the initial HA must remain as HA.

At this point,  $[\text{A}^-]/[\text{HA}] = (1/11)/(10/11) = 1/10$ . So  $\text{pH} = \text{p}K_a - 1$  when  $V_b = V_e/11$ .

In a similar manner,  $\text{pH} = \text{p}K_a + 1$  when  $V_b = 10V_e/11$ .

For anilinium ion,  $\text{p}K_a = 4.601$ . For the titration of 100 mL of 0.100 M anilinium ion with 0.100 M  $\text{OH}^-$ , the reaction is



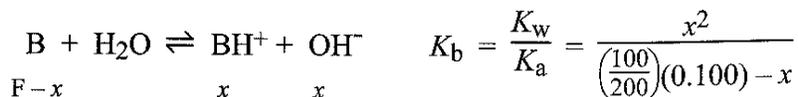
$$\frac{x^2}{0.100 - x} = K_a = 10^{-4.60} \Rightarrow x = 1.57 \times 10^{-3} \Rightarrow \text{pH} = 2.80$$

$V_e/11 = 9.09 \text{ mL}$ :  $\text{pH} = \text{p}K_a - 1 = 3.60$

$V_e/2 = 50.0 \text{ mL}$ :  $\text{pH} = \text{p}K_a = 4.60$

$10V_e/11 = 90.91 \text{ mL}$ :  $\text{pH} = \text{p}K_a + 1 = 5.60$

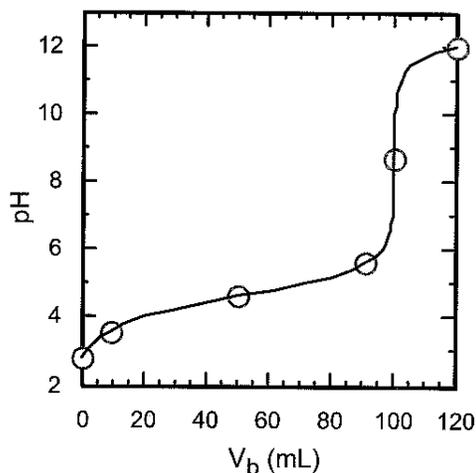
$V_e = 100.0 \text{ mL}$ :  $\text{BH}^+$  has been converted to B.



$$\Rightarrow x = 4.46 \times 10^{-6} \text{ M} \quad \text{pH} = -\log \frac{K_w}{x} = 8.65$$

$1.2V_e = 120.0 \text{ mL}$ : There are 20.0 mL of excess NaOH.

$$[\text{OH}^-] = \left(\frac{20}{220}\right)(0.100) = 9.09 \times 10^{-3} \text{ M} \Rightarrow \text{pH} = 11.96$$

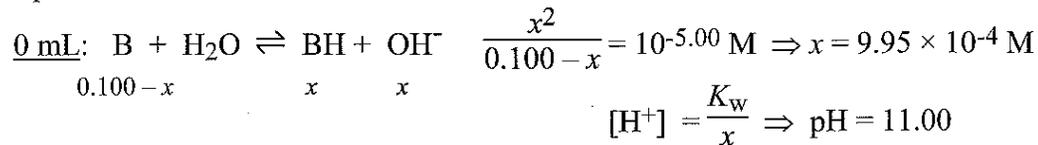


**10-13.** At the equivalence point, the weak base, B, is converted completely to the conjugate acid, BH<sup>+</sup>, which is necessarily acidic.

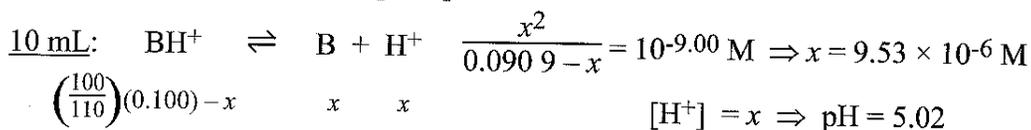
**10-14.**

$V_a$	0	1	5	9	9.9	10	10.1	12
pH	11.00	9.95	9.00	8.05	7.00	5.02	3.04	1.75

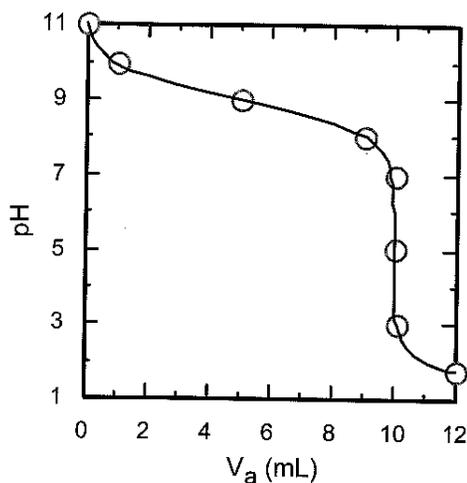
Representative calculations:



$$\underline{1 \text{ mL:}} \quad \text{pH} = \text{p}K_{\text{BH}^+} + \log \frac{[\text{B}]}{[\text{BH}^+]} = 9.00 + \log \frac{9}{1} = 9.95$$

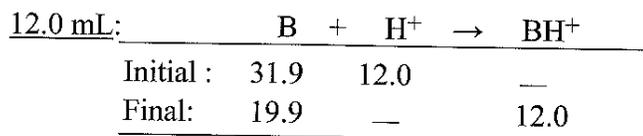


$$\underline{10.1 \text{ mL:}} \quad \text{[H}^+] = \left(\frac{0.1}{110.1}\right)(1.00) = 9.08 \times 10^{-4} \text{ M} \Rightarrow \text{pH} = 3.04$$



10-17. Titration reaction:  $B + H^+ \rightarrow BH^+$ . To find the equivalence point, we write  $(50.0)(0.0319) = (V_e)(0.0500) \Rightarrow V_e = 31.9 \text{ mL}$ .

$$\begin{array}{c} \text{0 mL: } B + H_2O \rightleftharpoons BH^+ + OH^- \\ \begin{array}{cccc} & & x^2 & \\ & & \frac{x^2}{0.0319-x} & = K_b = \frac{K_w}{K_a} = 2.22 \times 10^{-5} \\ 0.0319-x & & x & x \end{array} \\ \Rightarrow x = 8.31 \times 10^{-4} \text{ M} \Rightarrow \text{pH} = 10.92 \end{array}$$

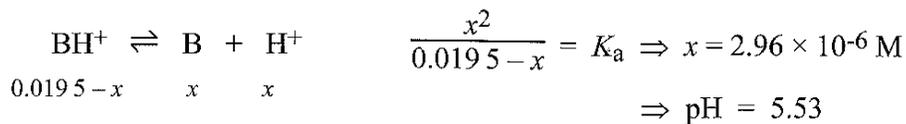


$$\text{pH} = \text{p}K_a + \log \frac{[B]}{[BH^+]} = 9.35 + \log \frac{19.9}{12.0} = 9.57$$

$\frac{1}{2}V_e$ :  $\text{pH} = \text{p}K_a = 9.35$

$\text{30 mL}$ :  $\text{pH} = \text{p}K_a + \log \frac{1.9}{30.0} = 8.15$

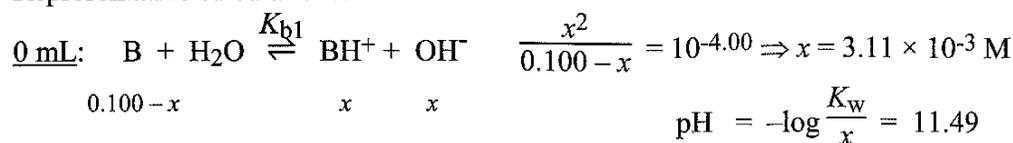
$V_e$ : B has been converted to  $BH^+$  at a concentration of  $\left(\frac{50.0}{81.9}\right)(0.0319)$   
 $= 0.0195 \text{ M}$



$\text{35.0 mL}$ :  $[H^+] = \left(\frac{3.1}{85.0}\right)(0.0500) = 1.82 \times 10^{-3} \text{ M} \Rightarrow \text{pH} = 2.74$

<b>10-23.</b>	$V_a$	0	1	5	9	10	11	15	19	20	22
	pH	11.49	10.95	10.00	9.05	8.00	6.95	6.00	5.05	3.54	1.79

Representative calculations:

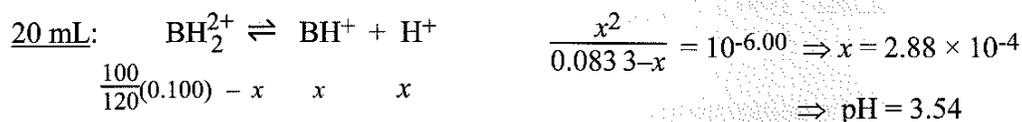


1 mL:  $pH = pK_{BH^+} + \log \frac{[B]}{[BH^+]} = 10.00 + \log \frac{9}{1} = 10.95$

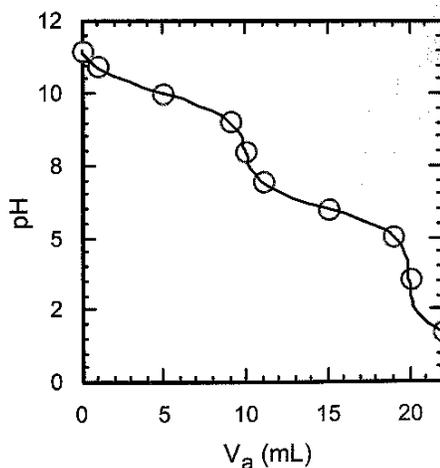
10 mL: Predominant form is  $BH^+$  with formal concentration  $\frac{100}{110}(0.100) = 0.0909 M$

$[H^+] \approx \sqrt{\frac{10^{-6.00} \cdot 10^{-10.00} (0.0909) + 10^{-6.00} \cdot 10^{-14.00}}{10^{-6.00} + 0.0909}}$   
 $= 1.00 \times 10^{-8} \Rightarrow pH = 8.00$

11 mL:  $pH = pK_{BH_2^+} + \log \frac{[BH^+]}{[BH_2^+]} = 6.00 + \log \frac{9}{1} = 6.95$

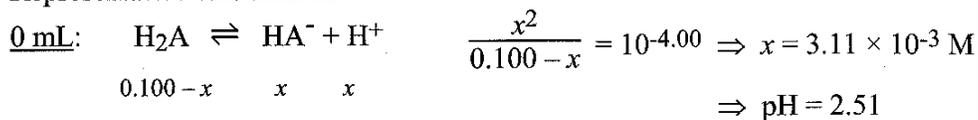


22 mL:  $[H^+] = \left(\frac{2}{122}\right)(1.00) = 1.64 \times 10^{-2} M \Rightarrow pH = 1.79$



<b>10-24.</b>	$V_b$	0	1	5	9	10	11	15	19	20	22
	pH	2.51	3.05	4.00	4.95	6.00	7.05	8.00	8.95	10.46	12.21

Representative calculations:



1 mL:  $\text{pH} = \text{p}K_1 + \log \frac{[\text{HA}^-]}{[\text{H}_2\text{A}]} = 4.00 + \log \frac{1}{9} = 3.05$

10 mL: Predominant form is  $\text{HA}^-$  with formal concentration  $\left(\frac{100}{110}\right)(0.100) = 0.0909 \text{ M}$ .

$$[\text{H}^+] \approx \sqrt{\frac{10^{-4.00} 10^{-8.00} (0.0909) + 10^{-4.00} 10^{-14.00}}{10^{-4.00} + 0.0909}}$$

$$= 9.99 \times 10^{-7} \Rightarrow \text{pH} = 6.00$$

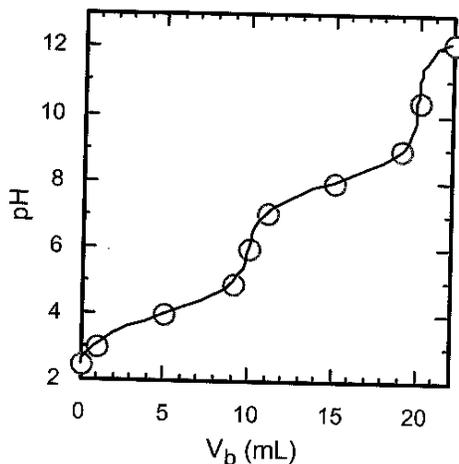
11 mL:  $\text{pH} = \text{p}K_2 + \log \frac{[\text{A}^{2-}]}{[\text{HA}^-]} = 8.00 + \log \frac{1}{9} = 7.05$

20 mL:  $\text{A}^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{HA}^- + \text{OH}^-$

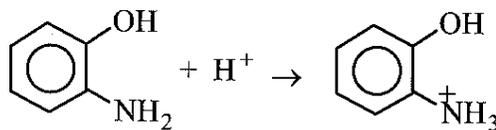
$$\frac{x^2}{\left(\frac{100}{120}\right)(0.100) - x} = \frac{K_w}{K_2} \Rightarrow x = 2.88 \times 10^{-4} \text{ M}$$

$$\text{pH} = -\log \frac{K_w}{x} = 10.46$$

22 mL:  $[\text{OH}^-] = \left(\frac{2}{122}\right)(1.00) = 1.64 \times 10^{-2} \text{ M} \Rightarrow \text{pH} = 12.21$



10-26.

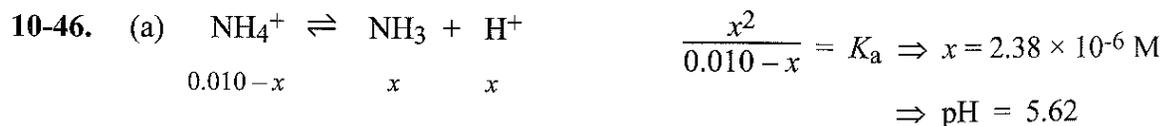


Initial mmol:	0.500	0.164	—
Final mmol:	0.336	—	0.164

$$\text{pH} = \text{p}K_1 + \log \frac{[\text{B}]}{[\text{BH}^+]} = 4.70 + \log \frac{0.336}{0.164} = 5.01$$

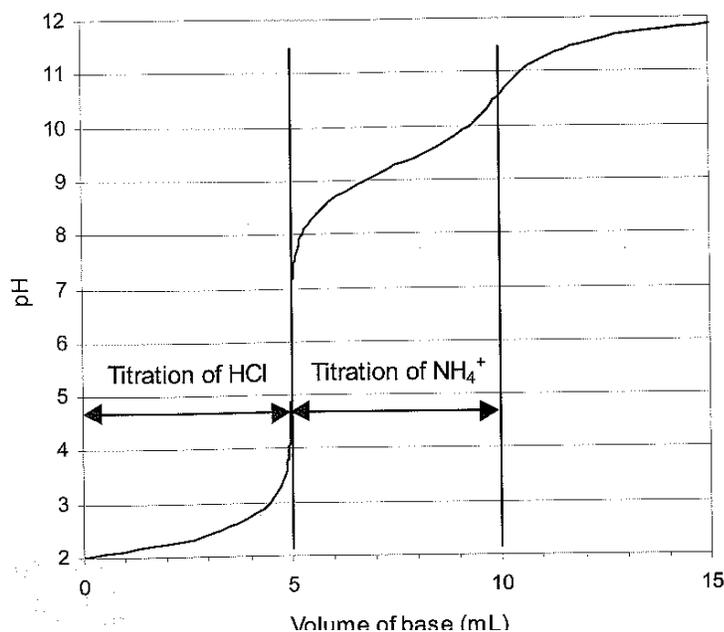
10-36. The quotient  $[\text{HIn}]/[\text{In}^-]$  changes from 10:1 when  $\text{pH} = \text{p}K_{\text{HIn}} - 1$  to 1:10 when  $\text{pH} = \text{p}K_{\text{HIn}} + 1$ . This change is generally sufficient to cause a complete color change.

**10-43.** No. When a weak acid is titrated with a strong base, the solution contains  $A^-$  at the equivalence point. A solution of  $A^-$  must have a pH above 7.



(b) One possible indicator is methyl red, using the yellow end point.

For a more complete analysis of this problem, we could compute the titration curve for a mixture of HCl and  $\text{NH}_4^+$ . For simplicity, we consider the mixture to be a “diprotic” acid with  $K_1 = 100$  (i.e., a “strong” acid) and  $K_2 = 5.7 \times 10^{-10}$  for the ammonium ion. We use the spreadsheet equation in Table 10-5 for titrating  $\text{H}_2\text{A}$  with strong base, taking  $C_a = 0.01 \text{ M}$  and  $C_b = 0.1 \text{ M}$ . An indicator with a color change in the range  $\sim 4.5\text{--}7.0$  would find the HCl end point without titrating a significant amount of  $\text{NH}_4^+$ .



**10-50.** The greater the equivalent mass, the more primary standard is required. There is less relative error in weighing a large mass of reagent than a small mass.

**10-55.**  $30 \text{ mL of } 0.05 \text{ M OH}^- = 1.5 \text{ mmol} = 0.31 \text{ g of potassium acid phthalate.}$