

14

EQUILIBRIA IN ACID-BASE SOLUTIONS

PROBLEMS

1. (a) $\text{NH}_3(aq) + \text{HF}(aq) \rightleftharpoons \text{NH}_4^+(aq) + \text{F}^-(aq)$ (b) $\text{H}^+(aq) + \text{OH}^-(aq) \rightleftharpoons \text{H}_2\text{O}$
 (c) $\text{SO}_3^{2-}(aq) + \text{H}^+(aq) \rightleftharpoons \text{HSO}_3^-(aq)$ (d) $\text{H}^+(aq) + \text{OH}^-(aq) \rightleftharpoons \text{H}_2\text{O}$
3. (a) $\text{SO}_3^{2-}(aq) + \text{H}^+(aq) \rightleftharpoons \text{HSO}_3^-(aq)$ (b) $\text{H}^+(aq) + \text{OH}^-(aq) \rightleftharpoons \text{H}_2\text{O}$
 (c) $\text{C}_7\text{H}_5\text{O}_2^-(aq) + \text{H}^+(aq) \rightleftharpoons \text{HC}_7\text{H}_5\text{O}_2(aq)$
5. (a) $\text{NH}_3(aq) + \text{H}^+(aq) \rightleftharpoons \text{NH}_4^+(aq)$ $1/K_a = 1/(5.6 \times 10^{-10})$
 $\text{HF}(aq) \rightleftharpoons \text{H}^+(aq) + \text{F}^-(aq)$ $K_a = 6.9 \times 10^{-4}$
 $\text{NH}_3(aq) + \text{HF}(aq) \rightleftharpoons \text{NH}_4^+(aq) + \text{F}^-(aq)$ $K = 1.2 \times 10^6$
 (b) $K = 1/K_w = 1.0 \times 10^{14}$
 (c) $K = 1/K_a \text{HSO}_3^- = 1/(6.0 \times 10^{-8}) = 1.7 \times 10^7$
 (d) $K = 1/K_w = 1.0 \times 10^{14}$
7. (a) $K = 1/K_a \text{HSO}_3^- = 1/(6.0 \times 10^{-8}) = 1.7 \times 10^7$
 (b) $K = 1/K_w = 1.0 \times 10^{14}$
 (c) $K = 1/K_a \text{HC}_7\text{H}_5\text{O}_2 = 1/(6.6 \times 10^{-5}) = 1.5 \times 10^4$
9. $[\text{H}^+] = K_a \times \frac{[\text{HLac}]}{[\text{Lac}^-]}$; $[\text{H}^+] = 1.4 \times 10^{-4} \times \frac{[\text{HLac}]}{[\text{Lac}^-]}$
 (a) $[\text{H}^+] = 1.4 \times 10^{-4} \times \frac{0.250}{0.250}$; $[\text{H}^+] = 1.4 \times 10^{-4}$; pH = 3.85
 (b) $[\text{H}^+] = 1.4 \times 10^{-4} \times \frac{0.250}{0.125}$; $[\text{H}^+] = 2.8 \times 10^{-4}$; pH = 3.55
 (c) $[\text{H}^+] = 1.4 \times 10^{-4} \times \frac{0.250}{0.0800}$; $[\text{H}^+] = 4.4 \times 10^{-4}$; pH = 3.36
 (d) $[\text{H}^+] = 1.4 \times 10^{-4} \times \frac{0.250}{0.0500}$; $[\text{H}^+] = 7.0 \times 10^{-4}$; pH = 3.15

$$11. [\text{H}^+] = K_a \times \frac{n_{\text{HA}}}{n_{\text{A}^-}}; \quad [\text{H}^+] = K_a \times \frac{\text{mol HNO}_2}{\text{mol NO}_2^-}; \quad [\text{H}^+] = 6.0 \times 10^{-4} \times \frac{(0.2500 \text{ L})(0.0410 \text{ mol/L})}{0.0250 \text{ mol}}$$

$$[\text{H}^+] = 2.5 \times 10^{-4}; \quad \text{pH} = 3.61$$

$$13. \text{(a) mol HC}_2\text{H}_3\text{O}_2 = \frac{12.50 \text{ g}}{60.05 \text{ g/mol}} = 0.2082; \quad \text{mol C}_2\text{H}_3\text{O}_2^- = \frac{15.00 \text{ g}}{82.0 \text{ g/mol}} = 0.1829$$

$$[\text{H}^+] = 1.8 \times 10^{-5} \times \frac{0.208}{0.1829} = 2.0 \times 10^{-5}; \quad \text{pH} = 4.69$$

(b) pH = 4.69

$$15. \text{ Find } K_b: \quad \text{pOH} = 4.78; \quad [\text{OH}^-] = 1.7 \times 10^{-5} \text{ M} \rightarrow K_b = \frac{(1.7 \times 10^{-5})^2}{0.206} = 1.34 \times 10^{-9}$$

$$\text{Find } K_a: \quad K_a = (1.0 \times 10^{-14}) / (1.34 \times 10^{-9}) = 7.48 \times 10^{-6}$$

$$[\text{H}^+] = 7.48 \times 10^{-6} \times \frac{0.368}{0.413} = 6.7 \times 10^{-6} \rightarrow \text{pH} = 5.18$$

$$17. \text{ mol SnF}_2 = (0.250 \text{ L})(0.150 \text{ mol/L}) = 0.0375; \quad \text{mol F}^- = 2(\text{mol SnF}_2) = 0.0750$$

(a) 0.0750 mol F⁻ + 0.100 mol H⁺; no buffer; all the F⁻ is used up

(b) 0.060 mol H⁺ produces 0.060 mol HF and uses up 0.0150 mol F⁻

Resulting solution: 0.060 mol HF + 0.0150 mol F⁻ → Solution is a buffer.

(c) 0.040 mol H⁺ produces 0.040 mol HF and uses up 0.040 mol F⁻.

Resulting solution: 0.040 mol HF + 0.0350 mol F⁻. → Solution is a buffer.

(d) No. The resulting solution has a strong base, NaOH and a weak base F⁻.

(e) Yes. The resulting solution has 0.040 mol HF and 0.0750 mol F⁻.

$$19. \text{ mol HOBr} = (2.50 \text{ g})(1 \text{ mol}/96.9 \text{ g}) = 0.0258$$

$$\text{mol OH}^- = \text{mol KOH} = (0.750 \text{ g})(1 \text{ mol}/56.1 \text{ g}) = 0.0134$$

The reaction between HOBr and KOH produces 0.0134 mol OBr⁻ and leaves 0.0124 mol HOBr.

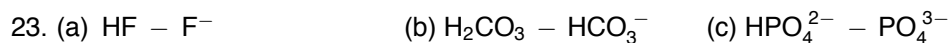
$$[\text{H}^+] = 2.5 \times 10^{-9} \times \frac{0.0124}{0.0134} = 2.3 \times 10^{-9}; \quad \text{pH} = 8.64$$

$$21. \text{ mol HBut} = (49.0 \text{ mL})(0.9595 \text{ g/mL})(1 \text{ mol}/88.1 \text{ g}) = 0.534 \text{ mol}$$

mol OH⁻ = mol KOH = (6.15 g)(1 mol/56.11 g) = 0.110 mol; OH⁻ is limiting and used up.

mol HBut remaining = 0.534 mol - 0.110 mol = 0.424 mol; mol But⁻ = 0.110

$$[\text{H}^+] = 1.54 \times 10^{-5} \times \frac{0.424}{0.110} = 5.94 \times 10^{-5}; \quad \text{pH} = 4.23$$



25. $\text{pH} = 9.40$; $[\text{H}^+] = 4.0 \times 10^{-10} \text{ M}$

(a) $4.0 \times 10^{-10} = 4.7 \times 10^{-11} \times \frac{[\text{HCO}_3^-]}{[\text{CO}_3^{2-}]}$; $\text{ratio} = \frac{4.0 \times 10^{-10}}{4.7 \times 10^{-11}} = 8.5$

(b) $\text{mol CO}_3^{2-} = \text{mol Na}_2\text{CO}_3 = (1.00 \text{ L})(0.225 \text{ mol/L}) = 0.225$

$$\frac{[\text{HCO}_3^-]}{[\text{CO}_3^{2-}]} = \frac{\text{mol HCO}_3^-}{\text{mol CO}_3^{2-}} ; \quad 8.5 = \frac{\text{mol HCO}_3^-}{0.225} ; \quad \text{mol HCO}_3^- = 1.9$$

(c) $\text{mol HCO}_3^- = (0.475 \text{ L})(0.336 \text{ mol/L}) = 0.160$

$$8.5 = \frac{0.160}{\text{mol CO}_3^{2-}} ; \quad \text{mol CO}_3^{2-} = 0.0188 ; \quad \text{mol Na}_2\text{CO}_3 = \text{mol CO}_3^{2-}$$

$$\text{mass Na}_2\text{CO}_3 = (0.0188 \text{ mol})(106 \text{ g/mol}) = 2.0 \text{ g}$$

(d) $\text{mol CO}_3^{2-} = \text{mol Na}_2\text{CO}_3 = (0.735 \text{ L})(0.139 \text{ mol/L}) = 0.102$

$$8.5 = \frac{\text{mol HCO}_3^-}{0.102} ; \quad \text{mol HCO}_3^- = 0.86 ; \quad \text{mol Na}_2\text{CO}_3 = \text{mol CO}_3^{2-}$$

$$V = 0.86 \text{ mol} \times \frac{1 \text{ L}}{0.200 \text{ mol}} = 4.3 \text{ L}$$

| 27. | Base | Acid |
|-----|---------|----------|
| (a) | 0.250 M | 0.250 M |
| (b) | 0.250 M | 0.125 M |
| (c) | 0.250 M | 0.0800 M |
| (d) | 0.250 M | 0.0500 M |

29. $\text{mol H}_2\text{PO}_4^- = \text{mol KH}_2\text{PO}_4 = (0.300 \text{ L})(0.500 \text{ mol/L}) = 0.150$

$$\text{mol HPO}_4^{2-} = \text{mol K}_2\text{HPO}_4 = (0.300 \text{ L})(0.317 \text{ mol/L}) = 0.0951$$

(a) $[\text{H}^+] = 6.2 \times 10^{-8} \times \frac{\text{mol H}_2\text{PO}_4^-}{\text{mol HPO}_4^{2-}} = 6.2 \times 10^{-8} \times \frac{0.150}{0.0951} = 9.8 \times 10^{-8}$; $\text{pH} = 7.01$

(b) $\text{HCl} (\text{H}^+)$ reacts with HPO_4^{2-} to use up 0.0500 mol HPO_4^{2-} and make 0.0500 mol H_2PO_4^- .

$$\text{mol H}_2\text{PO}_4^- = 0.150 + 0.0500 = 0.200 ; \quad \text{mol HPO}_4^{2-} = 0.0951 - 0.0500 = 0.0451$$

$$[\text{H}^+] = 6.2 \times 10^{-8} \times \frac{\text{mol H}_2\text{PO}_4^-}{\text{mol HPO}_4^{2-}} = 6.2 \times 10^{-8} \times \frac{0.200}{0.0451} = 2.7 \times 10^{-7} ; \quad \text{pH} = 6.56$$

(c) NaOH (OH^-) reacts with H_2PO_4^- to use up 0.0500 mol H_2PO_4^- and make 0.0500 mol HPO_4^{2-} .

$$\text{mol H}_2\text{PO}_4^- = 0.150 - 0.0500 = 0.100; \quad \text{mol HPO}_4^{2-} = 0.0951 + 0.0500 = 0.1451$$

$$[\text{H}^+] = 6.2 \times 10^{-8} \times \frac{\text{mol H}_2\text{PO}_4^-}{\text{mol HPO}_4^{2-}} = 6.2 \times 10^{-8} \times \frac{0.100}{0.1451} = 4.3 \times 10^{-8}; \quad \text{pH} = 7.37$$

31. (a) mol H_2PO_4^- = mol KH_2PO_4 = (10.0 L)(0.500 mol/L) = 5.00

$$\text{mol HPO}_4^{2-} = \text{mol K}_2\text{HPO}_4 = (10.0 \text{ L})(0.317 \text{ mol/L}) = 3.17$$

$$[\text{H}^+] = 6.2 \times 10^{-8} \times \frac{\text{mol H}_2\text{PO}_4^-}{\text{mol HPO}_4^{2-}} = 6.2 \times 10^{-8} \times \frac{5.00}{3.17} = 9.8 \times 10^{-8}; \quad \text{pH} = 7.01$$

(b) Before dilution (from Problem 29):

$$\text{mol H}_2\text{PO}_4^- = \text{mol KH}_2\text{PO}_4 = (0.300 \text{ L})(0.500 \text{ mol/L}) = 0.150$$

$$\text{mol HPO}_4^{2-} = \text{mol K}_2\text{HPO}_4 = (0.300 \text{ L})(0.317 \text{ mol/L}) = 0.0951$$

After dilution to 10.0 L, and taking 0.600 L of the buffer:

$$\text{mol H}_2\text{PO}_4^- = \frac{0.150 \text{ mol}}{10.0 \text{ L}} \times 0.600 \text{ L} = 0.00900 \text{ mol}$$

$$\text{mol HPO}_4^{2-} = \frac{0.0951 \text{ mol}}{10.0 \text{ L}} \times 0.600 \text{ L} = 0.00571 \text{ mol}$$

H^+ added = 0.0500 mol; HPO_4^{2-} is limiting and used up. Mol H^+ left = 0.0500 - 0.00571 = 0.0443

$$[\text{H}^+] = 0.0443 \text{ mol}/0.600 \text{ L} = 0.0738 \text{ M}; \quad \text{pH} = 1.13$$

(c) as in (b): mol H_2PO_4^- = 0.00900; mol HPO_4^{2-} = 0.00571

mol OH^- added = 0.0500; H_2PO_4^- is limiting and used up.

$$\text{mol OH}^- \text{ left} = 0.0500 - 0.0090 = 0.0410$$

$$[\text{OH}^-] = 0.0410 \text{ mol}/0.600 \text{ L} = 0.0683 \text{ M}; \quad \text{pOH} = 1.17; \quad \text{pH} = 12.83$$

(d) (a) is the same; (b) and (c) vary.

(e) Dilution does not change the pH of a buffer but reduces buffer capacity.

$$33. (a) [\text{H}^+] = K_a \text{H}_2\text{PO}_4^- \times \frac{[\text{H}_2\text{PO}_4^-]}{[\text{HPO}_4^{2-}]} = 6.2 \times 10^{-8} \times 3.0 = 1.86 \times 10^{-7}; \quad \text{pH} = 6.73$$

(b) ratio of acid to base is 3:1. Using up 15% of base (HPO_4^{2-}) means:

$$\text{mol HPO}_4^{2-} = 1 - (0.15 \times 1) = 0.85; \quad \text{mol H}_2\text{PO}_4^- = 3 + (0.15 \times 1) = 3.15$$

$$[\text{H}^+] = 6.2 \times 10^{-8} \times \frac{3.15}{0.85} = 2.30 \times 10^{-7} \text{ M}; \quad \text{pH} = 6.64$$

$$(c) [\text{H}^+] = 1.0 \times 10^{-7} \text{ M}; \quad 1.0 \times 10^{-7} = 6.2 \times 10^{-8} \times \frac{[\text{H}_2\text{PO}_4^-]}{[\text{HPO}_4^{2-}]}; \quad \frac{[\text{H}_2\text{PO}_4^-]}{[\text{HPO}_4^{2-}]} = 1.6$$

35. $\text{pH} = 7.40$; $[\text{H}^+] = 4.0 \times 10^{-8}$

(a) $\frac{[\text{H}_2\text{CO}_3]}{[\text{HCO}_3^-]} = \frac{[\text{H}^+]}{K_a} = \frac{4.0 \times 10^{-8}}{4.4 \times 10^{-7}} = 0.091$

(b) $\frac{[\text{H}_2\text{CO}_3]}{[\text{HCO}_3^-]} = \frac{0.091}{1}$; Assume $[\text{HCO}_3^-] = 1.000 \text{ M}$, then $[\text{H}_2\text{CO}_3] = 0.091 \text{ M}$

$[\text{HCO}_3^-]$ after conversion to $\text{H}_2\text{CO}_3 = 1.000 - (0.15 \times 1.000) = 0.85 \text{ M}$

$[\text{H}_2\text{CO}_3]$ after conversion = $0.091 + (0.15 \times 1.000) = 0.241 \text{ M}$

$[\text{H}^+] = 4.4 \times 10^{-7} \times \frac{0.241}{0.85} = 1.25 \times 10^{-7} \text{ M}$; $\text{pH} = 6.90$

(c) From (a) assume $[\text{HCO}_3^-] = 1.000 \text{ M}$, then $[\text{H}_2\text{CO}_3] = 0.091 \text{ M}$

$[\text{H}_2\text{CO}_3]$ after conversion = $0.091 - (0.15 \times 0.091) = 0.077 \text{ M}$

$[\text{HCO}_3^-]$ after conversion = $1.000 + (0.15 \times 0.091) = 1.014 \text{ M}$

$[\text{H}^+] = 4.4 \times 10^{-7} \times \frac{0.077}{1.014} = 3.34 \times 10^{-8} \text{ M}$; $\text{pH} = 7.48$

37. (a) MO (b) PP (c) any (d) MO

39. (a) $\text{p}K_a = 8.2$; $K_a = 6.3 \times 10^{-9}$ (b) 7.2 – 9.2 (c) purple

41. (a) $\text{mol OH}^- = 2(\text{mol Sr(OH)}_2) = 2[(0.0584 \text{ L})(0.218 \text{ mol/L})] = 0.0255$

$\text{mol H}^+ = \text{mol HNO}_3 = \text{mol OH}^- = 0.0255$

$[\text{H}^+] = [\text{HNO}_3] = 0.0255 \text{ mol}/0.02500 \text{ L} = 1.02 \text{ M}$; $\text{pH} = 8.6 \times 10^{-3}$

(b) 7.00

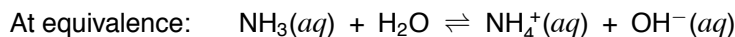
(c) $\text{mol NO}_3^- = \text{mol HNO}_3 = 0.0255$; $[\text{NO}_3^-] = \frac{0.0255 \text{ mol}}{(0.02500 + 0.0584) \text{ L}} = 0.305 \text{ M}$

$\text{mol Sr}^{2+} = \frac{1}{2}(\text{mol OH}^-) = \frac{0.0255}{2}$; $[\text{OH}^-] = \frac{(0.0255/2) \text{ mol}}{(0.02500 + 0.0584) \text{ L}} = 0.153 \text{ M}$

43. (a) $\text{mol NH}_4^+ = \text{mol NH}_4\text{Cl} = (25.00 \text{ g})(1 \text{ mol}/53.49 \text{ g}) = 0.467$

$\text{mol OH}^- = \text{mol KOH} = \text{mol NH}_4^+ = 0.467$; $V_{\text{KOH}} = (0.467 \text{ mol})(1 \text{ L}/0.114 \text{ mol}) = 4.10 \text{ L}$

$$(b) [\text{Cl}^-] = [\text{K}^+] = [\text{NH}_3] = \frac{0.467 \text{ mol}}{4.10 \text{ L} + 0.178 \text{ L}} = 0.109 \text{ M}$$

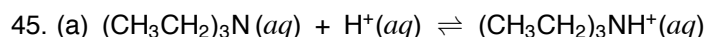


$$K_b = \frac{[\text{OH}^-]^2}{[\text{NH}_3] - [\text{OH}^-]} ; \quad \text{assume } [\text{OH}^-] \ll [\text{NH}_3]$$

$$1.8 \times 10^{-5} = \frac{[\text{OH}^-]^2}{0.109} ; \quad [\text{OH}^-] = 1.40 \times 10^{-3} ; \quad \% \text{ ionization} = 1.28 ; \quad \text{assumption valid}$$

$$\text{pOH} = 2.85 ; \quad \text{pH} = 11.15$$

(c) $\text{pH} = 7.00$



(b) $\text{mol H}^+ = \text{mol } (\text{CH}_3\text{CH}_2)_3\text{N} = (0.0200 \text{ L})(0.220 \text{ mol/L}) = 0.00440$

$$\text{mol HCl} = \text{mol H}^+ = 0.00440 ; \quad V_{\text{HCl}} = (0.00440 \text{ mol})(1 \text{ L}/0.544 \text{ mol}) = 0.00809 \text{ L}$$

(c) $\text{mol Cl}^- = \text{mol H}^+ = \text{mol } (\text{CH}_3\text{CH}_2)_3\text{NH}^+ = 0.00440$

$$[\text{Cl}^-] = [(\text{CH}_3\text{CH}_2)_3\text{NH}^+] = \frac{0.00440 \text{ mol}}{(0.00809 + 0.0200) \text{ L}} = 0.157 \text{ M}$$

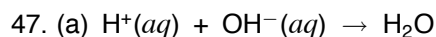
$$K_a (\text{CH}_3\text{CH}_2)_3\text{NH}^+ = \frac{1.0 \times 10^{-14}}{K_b} = \frac{1.0 \times 10^{-14}}{5.2 \times 10^{-4}} = 1.9 \times 10^{-11}$$

$$[\text{H}^+] = [(\text{CH}_3\text{CH}_2)_3\text{N}] ; \quad \text{assume } [\text{H}^+] \ll [(\text{CH}_3\text{CH}_2)_3\text{NH}^+]$$

$$1.9 \times 10^{-11} = \frac{[\text{H}^+]^2}{0.157} ; \quad [\text{H}^+] = 1.7 \times 10^{-6} ; \quad \% \text{ ionization} = 0.0011 ; \quad \text{assumption valid}$$

$$[\text{H}^+] = [(\text{CH}_3\text{CH}_2)_3\text{N}] = 1.7 \times 10^{-6} \text{ M}$$

(d) $\text{pH} = 5.77$



(b) $\text{Ba}^{2+}, \text{NO}_3^-$

(c) $\text{mol OH}^- = 2(\text{mol Ba}(\text{OH})_2) = 2[(0.0500 \text{ L})(0.237 \text{ mol/L})] = 0.0237$

$$\text{mol OH}^- = \text{mol H}^+ = \text{mol HNO}_3 = 0.0237 ; \quad V_{\text{HNO}_3} = (0.0237 \text{ mol})(1 \text{ L}/0.4000 \text{ mol}) = 0.0592 \text{ L}$$

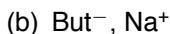
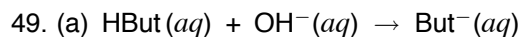
(d) $[\text{OH}^-] = 2[\text{Ba}(\text{OH})_2] = 2(0.237) = 0.474 \text{ M} ; \quad \text{pOH} = 0.324 ; \quad \text{pH} = 13.68$

(e) $\text{mol OH}^- \text{ (halfway)} = \frac{1}{2}(0.0237) = 0.01185$

$$V_{\text{tot}} \text{ (halfway)} = (0.05000)_{\text{from OH}^-} + \frac{1}{2}(0.0592)_{\text{from H}^+} = 0.0796 \text{ L}$$

$$[\text{OH}^-] \text{ (halfway)} = 0.01185 \text{ mol}/0.0796 \text{ L} = 0.149 ; \quad \text{pOH} = 0.827 ; \quad \text{pH} = 13.17$$

(f) 7.00



(c) $\text{mol OH}^- = \text{mol HBut} = (0.0500 \text{ L})(0.350 \text{ mol/L}) = 0.0175$

$\text{mol NaOH} = \text{mol OH}^- = 0.0175$; $V_{\text{NaOH}} = (0.0175 \text{ mol})(1 \text{ L}/0.225 \text{ mol}) = 0.0778 \text{ L}$

(d) $K_a = \frac{[\text{H}^+][\text{But}^-]}{[\text{HBut}] - [\text{H}^+]}$; $[\text{H}^+] = [\text{But}^-]$; assume $[\text{H}^+] \ll [\text{HBut}]$

$1.5 \times 10^{-5} = \frac{[\text{H}^+]^2}{0.350}$; $[\text{H}^+] = 2.29 \times 10^{-3}$; % ionization = 0.65 \ll 5%; pH = 2.64

(e) At half-equivalence: $[\text{H}^+] = K_a = 1.5 \times 10^{-5}$; pH = 4.82

(f) At the equivalence point: Solution has 0.0175 mol But^- and a volume of (0.0778 + 0.0500) L.

$[\text{But}^-] = 0.0175 \text{ mol} / 0.1278 \text{ L} = 0.137 \text{ M}$; $K_b = \frac{1.0 \times 10^{-14}}{1.5 \times 10^{-5}} = 6.7 \times 10^{-10}$

$K_b = \frac{[\text{HBut}][\text{OH}^-]}{[\text{But}^-] - [\text{OH}^-]}$; $[\text{HBut}] = [\text{OH}^-]$; assume $[\text{OH}^-] \ll [\text{But}^-]$

$6.7 \times 10^{-10} = \frac{[\text{OH}^-]^2}{0.137}$; $[\text{OH}^-] = 9.6 \times 10^{-6}$; % ionization \ll 5%; assumption valid

pOH = 5.02; pH = 8.98

51. (a) mass of solution = 30.0 g; mass HClO = (30.0 g)(0.10) = 3.00 g

$\text{mol HClO} = (3.00 \text{ g})(1 \text{ mol}/52.46 \text{ g}) = 0.0572$; $[\text{HClO}]_o = 0.0572 \text{ mol}/0.0300 \text{ L} = 1.91 \text{ M}$

$K_a = \frac{[\text{H}^+][\text{ClO}^-]}{[\text{HClO}] - [\text{H}^+]}$; $[\text{H}^+] = [\text{ClO}^-]$; assume $[\text{H}^+] \ll [\text{HClO}]$

$2.8 \times 10^{-8} = \frac{[\text{H}^+]^2}{1.91}$; $[\text{H}^+] = 2.3 \times 10^{-4}$; % ionization \ll 5%; pH = 3.64

(b) At half-equivalence: $[\text{H}^+] = K_a = 2.8 \times 10^{-8}$; pH = 7.55

(c) $(\text{mol ClO}^-)_{\text{eq}} = (\text{mol HClO})_o = 0.0572$; $\text{mol KOH} = \text{mol OH}^- = \text{mol HClO} = 0.0572$

$V_{\text{KOH}} = (0.0572 \text{ mol})(1 \text{ L}/0.419 \text{ mol}) = 0.137 \text{ L}$; $V_{\text{tot}} = (0.137 + 0.030) \text{ L} = 0.167 \text{ L}$

$[\text{ClO}^-] = 0.0572 \text{ mol}/0.167 \text{ L} = 0.343 \text{ M}$

$K_b = \frac{[\text{HClO}][\text{OH}^-]}{[\text{ClO}^-] - [\text{OH}^-]}$; $[\text{HClO}] = [\text{OH}^-]$; assume $[\text{OH}^-] \ll [\text{ClO}^-]$

$3.6 \times 10^{-7} = \frac{[\text{OH}^-]^2}{0.343}$; $[\text{OH}^-] = 3.51 \times 10^{-4}$; % ionization = 0.102; assumption valid

pOH = 3.45; pH = 10.54

53. $\text{pH} = 4.50$; $[\text{H}^+] = 3.2 \times 10^{-5} \text{ M}$

$$\text{mol Lac}^- = \text{mol NaLac} = (250.0 \text{ g})(1 \text{ mol}/112.1 \text{ g}) = 2.230 \text{ mol}$$

$$[\text{H}^+] = K_a \frac{\text{mol HLac}}{\text{mol Lac}^-} ; \quad \text{mol HLac} = \frac{(3.2 \times 10^{-5})(2.230)}{1.4 \times 10^{-4}} = 0.51$$

$$\text{mass HLac} = (0.51 \text{ mol})(90.1 \text{ g/mol}) = 46 \text{ g} ; \quad \text{mass HLac solution} = \frac{46 \text{ g}}{0.73} = 63 \text{ g}$$

$$\text{Volume HLac solution} = (63 \text{ g})(1 \text{ mL}/1.20 \text{ g}) = 52 \text{ mL}$$

55. $\text{pH} = 2.95$; $[\text{H}^+] = 1.1 \times 10^{-3} \text{ M}$

$$K_a = \frac{[\text{H}^+][\text{Ac}^-]}{[\text{HAc}] - [\text{H}^+]}$$
 ; $[\text{H}^+] = [\text{Ac}^-]$; assume $[\text{H}^+] \ll [\text{HAc}]$

$$1.8 \times 10^{-5} = \frac{(1.1 \times 10^{-3})^2}{[\text{HAc}]}$$
 ; $[\text{HAc}] = 0.067 \text{ M}$; % ionization $\ll 5\%$; assumption valid

Assume 1000.0 mL of "vinegar" = 1050.0 g of "vinegar"

$$\text{mass HAc} = (0.067 \text{ mol})(60.0 \text{ g/mol}) = 4.02 \text{ g}$$

% HAc in "vinegar" = $(4.02/1050) \times 100\% = 0.38\%$. Solution *cannot* be called vinegar.

57. (a) $\text{mol OH}^- = \text{mol KOH} = (0.03262 \text{ L})(0.730 \text{ mol/L}) = 0.0238 \text{ mol}$

$$\text{mol HUric} = \text{mol OH}^- = 0.0238 ; \quad \text{MM HUric} = 4.00 \text{ g}/0.0238 \text{ mol} = 168 \text{ g/mol}$$

(b) $\text{pH} = 4.12$; $[\text{H}^+] = 7.6 \times 10^{-5} \text{ M}$; $\text{mol OH}^- = \text{mol KOH} = (0.01200 \text{ L})(0.730 \text{ mol/L}) = 0.00876$

$$\text{mol Uric}^- \text{ formed} = \text{mol OH}^- = 0.00876 ; \quad \text{mol HUric left} = 0.0238 - 0.00876 = 0.0150$$

$$[\text{H}^+] = K_a \frac{\text{mol HUric}}{\text{mol Uric}^-} ; \quad 7.6 \times 10^{-5} = K_a \frac{0.0150}{0.00876} ; \quad K_a = 4.4 \times 10^{-5}$$

59. $\Pi = MRT$; $M = \frac{1.287 \text{ atm}}{(0.0821 \text{ L} \cdot \text{atm}/\text{mol} \cdot \text{K})(298 \text{ K})} = 0.0526 \text{ mol/L}$

$$\text{pOH} = 14.00 - 8.94 = 5.06 \quad [\text{OH}^-] = 8.71 \times 10^{-6}$$

$$K_b = \frac{(8.71 \times 10^{-6})^2}{0.0526} = 1.44 \times 10^{-9} \quad \rightarrow \quad K_a = 6.9 \times 10^{-6}$$

61. (a) 8 \square , 2 \circ

(b) 5 \square , 5 \circ (half-neutralization)

(c) 10 \circ

(d) 10 \circ , 2 \triangle

63. (a) weak

(b) at 25 mL, $\text{pH} \approx 3.3 = \text{p}K_a$; $K_a \approx 5 \times 10^{-4}$

(c) ≈ 8.5

65. (a) GT

(b) GT

(c) GT

(d) EQ

67. (a) False; $[\text{CHO}_2^-] = 0.1 \text{ M}$ only in 0.1 M NaCHO_2

(b) True

(c) False; combining a conjugate acid-base pair

(d) False; K_b for $\text{HCO}_3^- = 2.3 \times 10^{-8}$; K_b for $\text{CO}_3^{2-} = 2.1 \times 10^{-4}$

69. (a) acid (b) C (c) $\approx 10^{-8}$ (d) 0.1 (e) ≈ 5

70. at 1/3 neutralization, one mole of base is formed for every three moles of acid to be neutralized.

Thus two moles of acid are left.

$$[\text{H}^+] = 6.7 \times 10^{-4} \times \frac{2}{1} = 1.3 \times 10^{-3}; \quad \text{pH} = 2.9$$

71. $[\text{H}^+] = 6.3 \times 10^{-5}$; $\text{mol OH}^- = \text{mol Ac}^- = 0.1000 \text{ L} \times 1.25 \text{ M} = 0.125$

$$6.3 \times 10^{-5} = 1.8 \times 10^{-5} \times \frac{\text{mol HAc}}{0.125} \rightarrow \text{mol HAc in solution} = 0.44$$

mol HAc needed = 0.125 (to form Ac^-) + 0.44 (HAc needed in buffer) = 0.56

molarity of glacial acetic acid: Assume 100.0 g of glacial HAc \rightarrow 98.0 g HAc

mol HAc = 98.0 g / (60.05 g/mol) = 1.63

Volume of glacial acetic acid = 100.0 g / (1.0542 g/mL) = 94.86 mL

M of glacial acetic acid = 1.63 mol / 0.09486 L = 17 M

$V = 0.565 \text{ mol} / 17 \text{ M} = 33 \text{ mL}$

72. pH of original solution = 2.56; $[\text{H}^+] = 2.8 \times 10^{-3}$;

$K_a = 5.5 \times 10^{-5}$ At half-neutralization, pH = 4.25

$$5.5 \times 10^{-5} = \frac{(2.8 \times 10^{-3})^2}{[\text{HA}]}; \quad [\text{HA}] = 0.14 \text{ M}$$

mol HA = (0.14 mol/L)(0.250 L) = 0.034; $\text{MM HA} = (4.0 \text{ g}) / (0.034 \text{ mol}) = 1.2 \times 10^2 \text{ g/mol}$

73. pH is 6.50; $[\text{H}^+] = 3.16 \times 10^{-7}$

$$[\text{H}^+] = K_a \times \frac{\text{mol NH}_4^+}{\text{mol NH}_3}; \quad 3.16 \times 10^{-7} = 5.6 \times 10^{-10} \times \frac{\text{mol NH}_4^+}{\text{mol NH}_3}; \quad \frac{\text{mol NH}_4^+}{\text{mol NH}_3} = 565$$

One would need 500 times as much NH_4^+ as NH_3 .

74. (a) $\frac{[\text{H}^+]^2}{1.000} = 6.0 \times 10^{-4}$; $[\text{H}^+] = 2.4 \times 10^{-2} \text{ M}$; $\text{pH} = 1.61$

(b) $\text{pH} = \text{p}K_a = 3.22$

(c) $\text{mol NO}_2^- = (1.000 \text{ mol/L})(0.0500 \text{ L}) = 0.0500$; $V_{\text{NaOH}} = \frac{0.0500 \text{ mol}}{0.850 \text{ mol/L}} = 0.0588 \text{ L}$

$V_{\text{tot}} = 0.0500 \text{ L} + 0.0588 \text{ L} = 0.109 \text{ L}$; $[\text{NO}_2^-] = 0.0500 \text{ mol}/0.109 \text{ L} = 0.459 \text{ M}$

$\frac{[\text{OH}^-]^2}{0.459} = 1.7 \times 10^{-11}$; $[\text{OH}^-] = 2.8 \times 10^{-6} \text{ M}$; $\text{pOH} = 5.55$; $\text{pH} = 8.45$

(d) $\text{mol HNO}_2 \text{ left} = (1.0 \times 10^{-4} \text{ L})(0.850 \text{ mol/L}) = 8.50 \times 10^{-5}$

$[\text{H}^+] = 6.0 \times 10^{-4} \times \frac{8.50 \times 10^{-5}}{0.0500 - 8.5 \times 10^{-5}} = 1.0 \times 10^{-6} \text{ M}$; $\text{pH} = 6.00$

(e) $\text{mol OH}^- = (1.0 \times 10^{-4} \text{ L})(0.850 \text{ mol/L}) = 8.50 \times 10^{-5}$

$[\text{OH}^-] = \frac{8.50 \times 10^{-5} \text{ mol}}{0.109 \text{ L}} = 7.8 \times 10^{-4} \text{ M}$; $\text{pOH} = 3.11$; $\text{pH} = 10.89$

(f) Similar to Figure 14.10 but pH is somewhat lower because HNO_2 is a stronger acid than $\text{HC}_2\text{H}_3\text{O}_2$.

75. $\text{mol NaOH} = (0.0485 \text{ L})(0.425 \text{ mol/L}) = 0.0206 = \text{mol OH}^- = \text{mol H}^+$

$\text{mol H}_2\text{B} \cdot x\text{H}_2\text{O} = 0.0206 \text{ mol H}^+ \times \frac{1 \text{ mol H}_2\text{B}}{2 \text{ mol H}^+} = 0.103$

$M = 0.103 \text{ mol}/0.025 \text{ L} = 0.412$

$\text{mol H}_2\text{B} \cdot x\text{H}_2\text{O} \text{ in } 150.0 \text{ mL} = (0.412 \text{ mol/L})(0.150 \text{ L}) = 0.0618$

$\text{MM} = (10.00 \text{ g})/(0.0618 \text{ mol}) = 162 \rightarrow \text{MM H}_2\text{B} = 126 \rightarrow 162 - 126 = 36 \text{ g/mol} = \text{MM of } x\text{H}_2\text{O}$

$\text{MM H}_2\text{O} = 18 \rightarrow 36/18 = 2 \rightarrow x = 2$

76. (a) $[\text{H}^+] = 0.1500 \text{ M}$ $\text{pH} = 0.82$

(b) $0.011 = \frac{[\text{H}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]} = \frac{(0.1500 + x)(x)}{0.1500 - x}$

Solving for x using the quadratic equation, $x \approx 0.01$; $[\text{H}^+] = 0.16 \text{ M}$; $\text{pH} = 0.80$

77. $[\text{H}^+] = K_a \times \frac{[\text{HB}]}{[\text{B}^-]} = K_a \times \frac{7.00}{14.0}$; $K_a = 2[\text{H}^+] = 2(1.1 \times 10^{-9})$; $K_b = \frac{1.0 \times 10^{-14}}{2.2 \times 10^{-9}} = 4.5 \times 10^{-6}$

$$78. \text{ mol NH}_3 = (0.150 \text{ mol/L})(1.000 \text{ L}) = 0.150 ; \quad \text{ mol NH}_4^+ = \text{ mol NH}_4\text{Cl} = (10.0 \text{ g})(1 \text{ mol}/53.49 \text{ g}) = 0.187$$

$$[\text{H}^+] = 5.6 \times 10^{-10} \times \frac{0.187}{0.150} = 6.98 \times 10^{-10} ; \quad \text{pH} = 9.16$$

$$\text{new pH} = 9.16 + 1.00 = 10.16 ; \quad [\text{H}^+] = 6.98 \times 10^{-11}$$

Let x = mol OH^- that react with NH_3

$$6.98 \times 10^{-11} = 5.6 \times 10^{-10} \times \frac{0.187 - x}{0.150 + x} ; \quad x = 0.15 \text{ mol OH}^-$$

$$\text{mass NaOH} = (0.15 \text{ mol})(40.0 \text{ g/mol}) = 6.0 \text{ g}$$

$$79. \log_{10} [\text{H}^+] = \log_{10} K_a + \log_{10} \frac{[\text{HB}]}{[\text{B}^-]}$$

$$\text{Multiply by } (-1): \text{pH} = \text{p}K_a + \log_{10} \frac{[\text{B}^-]}{[\text{HB}]}$$

80. (a) Yes - there is an excess of OH^- in solution.

$$(b) \text{ mol KOH added} = \text{ mol OH}^- \text{ added} = (0.04235 \text{ L})(0.731 \text{ mol/L}) = 0.03096$$

$$M \text{ of solution from pH reading: } \text{pOH} = 14.00 - 12.39 = 1.61 \quad \rightarrow \quad [\text{OH}^-] = 0.02454$$

$$\text{Volume of solution after KOH addition} = 0.02500 \text{ L} + 0.04235 \text{ L} = 0.06735 \text{ L}$$

$$\text{mol OH}^- \text{ in solution} = (0.02454 \text{ mol/L})(0.06735 \text{ L}) = 0.00165$$

$$\begin{aligned} \text{mol OH}^- \text{ used to neutralize H}^+ &= \text{ moles OH}^- \text{ added} - \text{ moles OH}^- \text{ in solution when pH was taken} \\ &= 0.03096 - 0.00165 = 0.02931 \text{ mol} \end{aligned}$$

$$\text{mol OH}^- \text{ to neutralize} = \text{ mol H}^+ \text{ in solution} = 0.02931$$

$$[\text{H}^+] = (0.02931 \text{ mol})/(0.025 \text{ L}) = 1.172 \text{ mol/L} = 1.172 \text{ M}$$

$$(c) \text{ mol OH}^- \text{ in excess} = 0.00165$$

$$\text{volume added in excess} = (0.00165 \text{ mol})/(0.731 \text{ mol/L}) = 0.00226 \text{ L} = 2.26 \text{ mL}$$