

10-2. (a)  $\text{pH} = -\log [\text{H}^+] = -\log (1.0 \times 10^{-3}) = 3.00$

(b)  $[\text{H}^+] = K_w / [\text{OH}^-] = (1.0 \times 10^{-14}) / (1.0 \times 10^{-2}) = 1.0 \times 10^{-12} \text{ M}$   
 $\text{pH} = -\log [\text{H}^+] = 12.00$

10-3.  $[\text{H}^+] = [\text{OH}^-] + [\text{ClO}_4^-] \Rightarrow [\text{OH}^-] = [\text{H}^+] - 5.0 \times 10^{-8}$

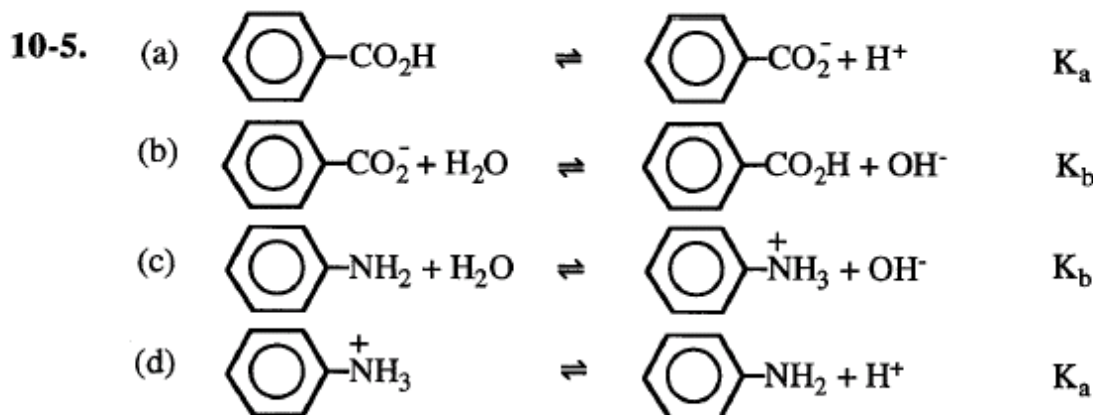
$$[\text{H}^+] [\text{OH}^-] = K_w$$

$$[\text{H}^+] ([\text{H}^+] - 5.0 \times 10^{-8}) = 1.0 \times 10^{-14} \Rightarrow [\text{H}^+] = 1.28 \times 10^{-7} \text{ M}$$

$$\text{pH} = -\log [\text{H}^+] = 6.89$$

$$[\text{OH}^-] = K_w / [\text{H}^+] = 7.8 \times 10^{-8} \text{ M} \Rightarrow [\text{H}^+] \text{ from } \text{H}_2\text{O} = 7.8 \times 10^{-8} \text{ M}$$

$$\text{Fraction of total } [\text{H}^+] \text{ from } \text{H}_2\text{O} = \frac{7.8 \times 10^{-8} \text{ M}}{1.28 \times 10^{-7} \text{ M}} = 0.61$$



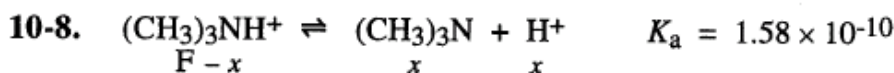
10-6. Let  $x = [\text{H}^+] = [\text{A}^-]$  and  $0.100 - x = [\text{HA}]$ .

$$\frac{x^2}{0.100 - x} = 1.00 \times 10^{-5} \Rightarrow x = 9.95 \times 10^{-4} \text{ M} \Rightarrow \text{pH} = -\log x = 3.00$$

$$\alpha = \frac{[\text{A}^-]}{[\text{A}^-] + [\text{HA}]} = \frac{9.95 \times 10^{-4}}{0.100} = 9.95 \times 10^{-3}$$

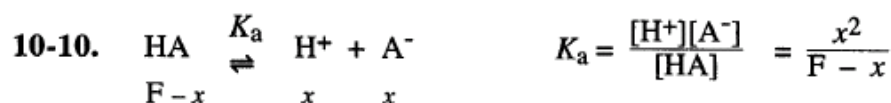


$$\frac{x^2}{0.100 - x} = 1.00 \times 10^{-10} \Rightarrow x = [\text{B}] = [\text{H}^+] = 3.16 \times 10^{-6} \text{ M} \Rightarrow \text{pH} = 5.50$$



$$\frac{x^2}{0.060 - x} = K_a \Rightarrow x = 3.08 \times 10^{-6} \Rightarrow \text{pH} = 5.51$$

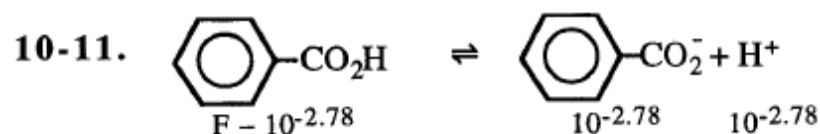
$$[(\text{CH}_3)_3\text{N}] = x = 3.1 \times 10^{-6} \text{ M}, \quad [(\text{CH}_3)_3\text{NH}^+] = F - x = 0.060 \text{ M}$$



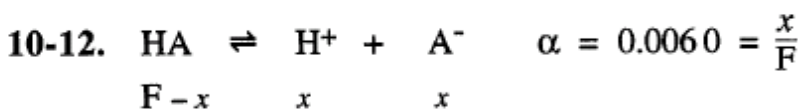
$$\text{For } F = \frac{K_a}{10}, \quad \frac{x^2}{\frac{K_a}{10} - x} = K_a \Rightarrow x = 0.092 K_a; \quad \alpha = \frac{x}{F} = \frac{0.092 K_a}{0.100 K_a} = 92\%$$

$$\text{For } F = 10 K_a, \quad \frac{x^2}{10K_a - x} = K_a \Rightarrow x = 2.7 K_a; \quad \alpha = \frac{x}{F} = \frac{2.7 K_a}{10 K_a} = 27\%$$

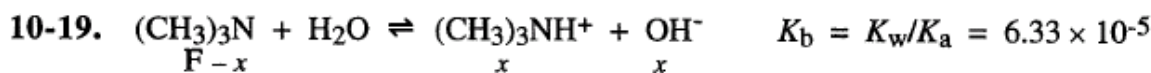
$$\text{For 99\% dissociation, } x = 0.99 F \Rightarrow K_a = \frac{(0.99 F)^2}{F - 0.99 F} \Rightarrow F = (0.0102) K_a$$



$$K_a = \frac{(10^{-2.78})^2}{0.0450 - 10^{-2.78}} = 6.4 \times 10^{-5} = pK_a = 4.19$$

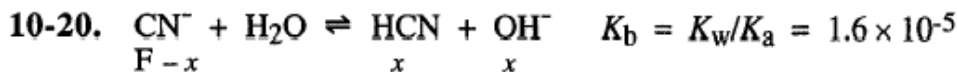


$$\text{Since } F = 0.0450 \text{ M, } x = 2.7 \times 10^{-4} \text{ M} \Rightarrow K_a = \frac{x^2}{F-x} = 1.6 \times 10^{-6} \Rightarrow pK_a = 5.79$$

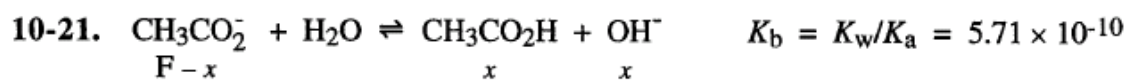


$$\frac{x^2}{0.060 - x} = K_b \Rightarrow x = 1.92 \times 10^{-3} \Rightarrow \text{pH} = -\log \frac{K_w}{x} = 11.28$$

$$[(\text{CH}_3)_3\text{NH}^+] = x = 1.92 \times 10^{-3} \text{ M}, \quad [(\text{CH}_3)_3\text{N}] = F - x = 0.058 \text{ M}$$



$$\frac{x^2}{0.050 - x} = K_b \Rightarrow x = 8.9 \times 10^{-4} \Rightarrow \text{pH} = -\log \frac{K_w}{x} = 10.95$$



$$\frac{x^2}{(1.00 \times 10^{-1}) - x} = K_b \Rightarrow x = 7.56 \times 10^{-6} \Rightarrow \alpha = \frac{x}{F} = 0.00756\%$$

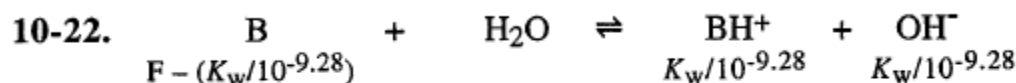
$$\frac{x^2}{(1.00 \times 10^{-2}) - x} = K_b \Rightarrow x = 2.39 \times 10^{-6} \Rightarrow \alpha = \frac{x}{F} = 0.0239\%$$

For  $1.00 \times 10^{-12}$  M sodium acetate, pH = 7.00 and we can say

$$[\text{HA}] = \frac{K_b[\text{A}^-]}{[\text{OH}^-]} = 5.71 \times 10^{-3} [\text{A}^-]$$

$$\alpha = \frac{[\text{HA}]}{[\text{HA}] + [\text{A}^-]} = \frac{5.71 \times 10^{-3} [\text{A}^-]}{(5.71 \times 10^{-3} + 1)[\text{A}^-]} = 0.568\%$$

The more dilute the solution, the greater is  $\alpha$ .



$$K_b = \frac{(K_w/10^{-9.28})^2}{F - (K_w/10^{-9.28})} = \frac{(K_w/10^{-9.28})^2}{0.10 - (K_w/10^{-9.28})} = 3.6 \times 10^{-9}$$

10-25. I would weigh out 0.0200 mol of acetic acid (= 1.201 g) and place it in a beaker with ~75 mL of water. While monitoring the pH with a pH electrode, I would add 3 M NaOH (~4 mL is required) until the pH is exactly 5.00. I would then pour the solution into a 100 mL volumetric flask and wash the beaker several times with a few milliliters of distilled water. Each washing would be added to the volumetric flask, to ensure quantitative transfer from the beaker to the flask. After swirling the volumetric flask to mix the solution, I would carefully add water up to the 100 mL mark, insert the cap, and invert 20 times to ensure complete mixing.

10-26. The pH of a buffer depends on the ratio of the concentrations of HA and  $\text{A}^-$  ( $\text{pH} = \text{p}K_a + \log [\text{A}^-]/[\text{HA}]$ ). When the volume of solution is changed, both concentrations are affected equally and their ratio does not change.

10-27. Buffer capacity measures the ability to maintain the original  $[\text{A}^-]/[\text{HA}]$  ratio when acid or base is added. A more concentrated buffer has more molecules of  $\text{A}^-$  and HA, so a smaller fraction of  $\text{A}^-$  or HA is consumed by the added acid or base and there is a smaller change in the ratio  $[\text{A}^-]/[\text{HA}]$ .

10-28. At very low or very high pH, there is so much acid or base in the solution already, that small additions of acid or base will hardly have any effect. At low pH the buffer is  $\text{H}_3\text{O}^+/\text{H}_2\text{O}$  and at high pH the buffer is  $\text{H}_2\text{O}/\text{OH}^-$ .

10-29. When  $\text{pH} = \text{p}K_a$ , the ratio of concentrations  $[\text{A}^-]/[\text{HA}]$  is unity. A given increment of added acid or base has the least effect on the ratio  $[\text{A}^-]/[\text{HA}]$  when the concentrations of  $\text{A}^-$  and HA are initially equal.

**10-32.**  $\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]} = 5.00 + \log \frac{0.050}{0.100} = 4.70$

**10-33.**  $\text{pH} = 3.745 + \log \frac{[\text{HCO}_2^-]}{[\text{HCO}_2\text{H}]}$

|   |       |       |       |
|---|-------|-------|-------|
| pH:   | 3.000 | 3.745 | 4.000 |
| $[\text{HCO}_2^-]/[\text{HCO}_2\text{H}]$ : | 0.180 | 1.00  | 1.80  |

**10-34.**  $\text{pH} = \text{p}K_a + \log \frac{[\text{NO}_2^-]}{[\text{HNO}_2]}$ , where  $\text{p}K_a = 14.00 - \text{p}K_b = 3.15$

(a) If  $\text{pH} = 2.00$ ,  $[\text{HNO}_2]/[\text{NO}_2^-] = 14$

(b) If  $\text{pH} = 10.00$ ,  $[\text{HNO}_2]/[\text{NO}_2^-] = 1.4 \times 10^{-7}$

- 10-35.**
1. Weigh out  $(0.250 \text{ L})(0.0500 \text{ M}) = 0.0125 \text{ mol}$  of HEPES and dissolve in ~200 mL.
  2. Adjust the pH to 7.45 with NaOH (HEPES is an acid).
  3. Dilute to 250 mL.

**10-38.** (a)  $\text{pH} = 2.865 + \log \frac{0.0400}{0.0800} = 2.56$

(b) Using Eqns. (10-20) and (10-21), and neglecting  $[\text{OH}^-]$ , we can write

$$K_a = 1.36 \times 10^{-3} = \frac{[\text{H}^+](0.0400 + [\text{H}^+])}{0.0800 - [\text{H}^+]} \Rightarrow [\text{H}^+] = 2.48 \times 10^{-3} \text{ M} \Rightarrow$$

$$\text{pH} = 2.61$$

(c) 0.080 mol of  $\text{HNO}_3$  + 0.080 mol of  $\text{Ca}(\text{OH})_2$  react completely, leaving an excess of 0.080 mol of  $\text{OH}^-$ . This much  $\text{OH}^-$  converts 0.080 mol of  $\text{ClCH}_2\text{CO}_2\text{H}$  into 0.080 mol of  $\text{ClCH}_2\text{CO}_2^-$ . The final concentrations are  $[\text{ClCH}_2\text{CO}_2^-] = 0.020 + 0.080 = 0.100 \text{ M}$  and  $[\text{ClCH}_2\text{CO}_2\text{H}] = 0.180 - 0.080 = 0.100 \text{ M}$ . So  $\text{pH} = \text{p}K_a = 2.86$ .



Initial moles:            0.0210             $x$             —

Final moles:             $0.0210 - x$             —             $x$

$$\text{pH} = 7.40 = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]} = 7.56 + \log \frac{x}{0.0210 - x} \Rightarrow x = 8.59 \times 10^{-3} \text{ mol.}$$

$$\text{volume} = \frac{8.59 \times 10^{-3} \text{ mol}}{0.626 \text{ M}} = 13.7 \text{ mL}$$