

Chapter 8 Homework

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

Mass balance is the same as charge balance.

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

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

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

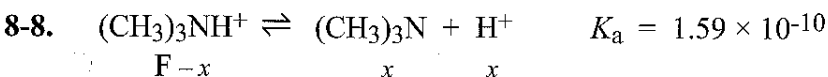
$[\text{OH}^-] = K_w/[\text{H}^+] = 7.8 \times 10^{-8} \text{ M} \Rightarrow [\text{H}^+] \text{ from } \text{H}_2\text{O} = 7.8 \times 10^{-8} \text{ M}$

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

8-6. Let $x = [\text{H}^+] = [\text{A}^-]$ and $0.100 - x = [\text{HA}]$.

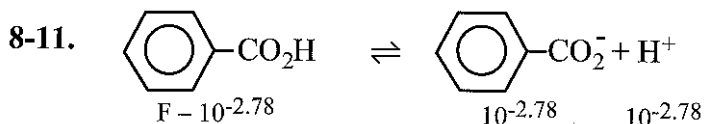
$\frac{x^2}{0.100 - x} = 1.00 \times 10^{-5} \Rightarrow x = 9.95 \times 10^{-4} \text{ M} \Rightarrow \text{pH} = -\log x = 3.00$

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

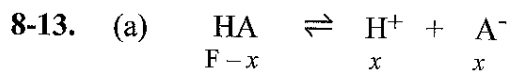


$\frac{x^2}{0.060 - x} = K_a \Rightarrow x = 3.09 \times 10^{-6} \Rightarrow \text{pH} = 5.51$

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



$K_a = \frac{(10^{-2.78})^2}{0.0450 - 10^{-2.78}} = 6.35 \times 10^{-5} = \text{p}K_a = 4.20$



$\frac{x^2}{F-x} = K_a \Rightarrow \frac{x^2}{0.010 - x} = 9.8 \times 10^{-5} \Rightarrow x = 9.4 \times 10^{-4}$

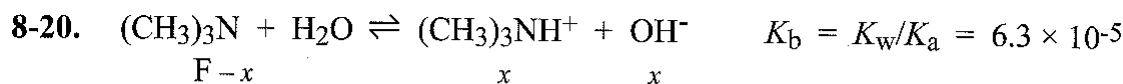
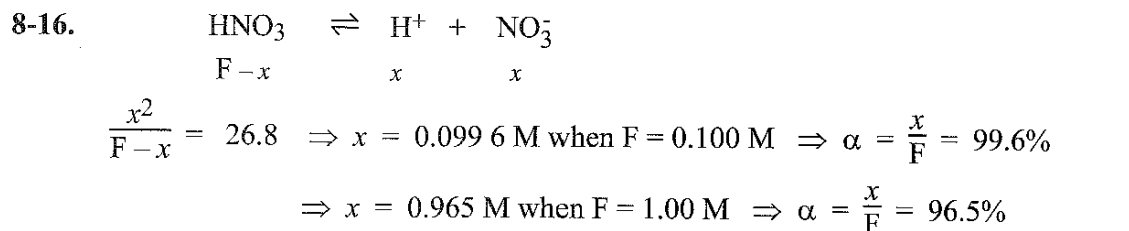
$\Rightarrow \text{pH} = 3.03$

$\alpha = \frac{[\text{A}^-]}{[\text{HA}] + [\text{A}^-]} = \frac{x}{F} = 9.4\%$

(b) $\text{pH} = 7.00$ because the acid is so dilute. From the K_a equilibrium we write

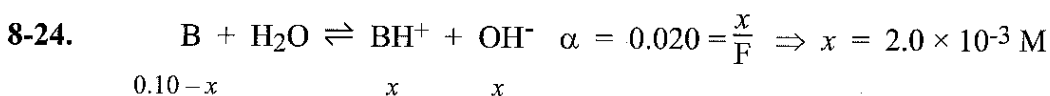
$[\text{A}^-] = \frac{K_a}{[\text{H}^+]}[\text{HA}] = \frac{9.8 \times 10^{-5}}{1.0 \times 10^{-7}}[\text{HA}] = 980 [\text{HA}]$

$\alpha = \frac{[\text{A}^-]}{[\text{HA}] + [\text{A}^-]} = \frac{980 [\text{HA}]}{[\text{HA}] + 980 [\text{HA}]} = \frac{980}{981} = 99.9\%$



$$\frac{x^2}{0.060-x} = K_b \Rightarrow x = 1.91 \times 10^{-3} \Rightarrow \text{pH} = -\log \frac{K_w}{x} = 11.28$$

$$[(\text{CH}_3)_3\text{NH}^+] = x = 1.91 \times 10^{-3} \text{ M}, \quad [(\text{CH}_3)_3\text{N}] = F-x = 0.058 \text{ M}$$



$$K_b = \frac{x^2}{0.10-x} = \frac{(2.0 \times 10^{-3})^2}{0.10-(2.0 \times 10^{-3})} = 4.1 \times 10^{-5}$$

8-26. 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.

8-27. The pH of a buffer depends on the ratio of the concentrations of HA and A⁻ (pH = pK_a + log [A⁻]/[HA]). When the volume of solution is changed, both concentrations are affected equally and their ratio does not change.

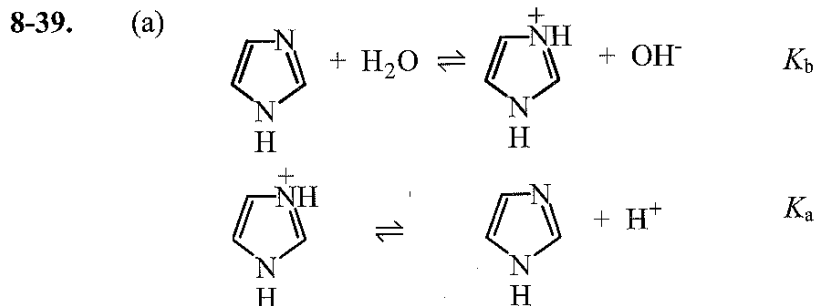
8-31. The Henderson-Hasselbalch is just a rearranged form of the K_a equilibrium expression, which is always true. When we make the approximation that [HA] and [A⁻] are unchanged from what we added, we are neglecting acid dissociation and base hydrolysis, which can change the concentrations in dilute solutions of moderately strong acids or bases.

8-34.
$$\text{pH} = 3.744 + \log \frac{[\text{HCO}_2^-]}{[\text{HCO}_2\text{H}]}$$

pH:	3.000	3.744	4.000
$[\text{HCO}_2^-]/[\text{HCO}_2\text{H}]$:	0.180	1.00	1.80

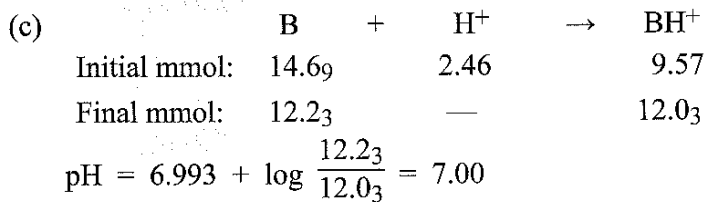
8-37. (a) HEPES is an acid with $\text{p}K_a = 7.56$. When it is dissolved in water, the solution will be acidic and will require NaOH to raise the pH to 7.45.

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



(b) FM of imidazole = 68.08. FM of imidazole hydrochloride = 104.54.

$$\text{pH} = 6.993 + \log \frac{1.00/68.08}{1.00/104.54} = 7.18$$



(d) The imidazole must be half neutralized to obtain $\text{pH} = \text{p}K_a$. Since there are 14.69 mmol of imidazole, this will require $\frac{1}{2}(14.69) = 7.34 \text{ mmol}$ of $\text{HClO}_4 = 6.86 \text{ mL}$.

8-40. (a) $\text{pH} = 2.865 + \log \frac{0.0400}{0.0800} = 2.56$

(b) Using Eqns. (8-20) and (8-21), 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 HNO_3 + 0.080 mol of $\text{Ca}(\text{OH})_2$ react completely, leaving an excess of 0.080 mol of OH^- . This much 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 $\text{pH} = \text{p}K_a = 2.86$.