Answers to Study Questions and Problems

1. The equilibrium constant for the neutralization of any weak acid by any weak base is given by the expression:

$$K_{neut} = \frac{K_a \times K_b}{K_w}$$

which in this case $= (4.0 \times 10^{-10})(1.8 \times 10^{-5})(1 \times 10^{14}) = 0.72$

2. K_a for hydrocyanic acid $= 4.0 \times 10^{-10}$ at 25°C

   K_b for ammonia $= 1.8 \times 10^{-5}$ at 25°C

   The base is stronger than the acid, so the equivalence point will be slightly basic.

3. $HCl(aq) + NH_3(aq) \rightleftharpoons NH_4^+(aq) + Cl^-(aq)$

   The concentration of the salt is 0.025M (the volume has doubled from 50 mL to 100 mL). The ammonium ion will hydrolyze because NH_3 is a weak electrolyte (K_b for ammonia $= 1.8 \times 10^{-5}$).

   $NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$ $K = K_w/K_b = 5.6 \times 10^{-10}$

   $K = \dfrac{[NH_3][H_3O^+]}{[NH_4^+]} = \dfrac{[H_3O^+]^2}{[0.025]}$ so $[H_3O^+] = 3.74 \times 10^{-6}M$

   pH = 5.43

4.

   a. The pH of a 0.20M solution of formic acid HCO_2H:

   $HCO_2H + H_2O \rightleftharpoons H_3O^+ + HCO_2^-$ $K_a = 1.8 \times 10^{-4}$

   $K_a = \dfrac{[H_3O^+][HCO_2^-]}{[HCO_2H]} = \dfrac{[H_3O^+]^2}{[0.20]}$ so $[H_3O^+] = 6.0 \times 10^{-3}M$
   pH = 2.22

   b. Addition of formate ion will suppress the ionization of the formic acid and reduce the hydronium ion concentration. The pH will increase.

   c. $K_a = \dfrac{[H_3O^+][HCO_2^-]}{[HCO_2H]} = \dfrac{[0.10][H_3O^+]}{[0.20]}$ so $[H_3O^+] = 4.0 \times 10^{-4}M$
   pH = 3.44

   d. If the concentration of formate ion is increased to 0.20M, then the $[H_3O^+]$ will equal the K_a for the acid $= 1.8 \times 10^{-4}$.

   e. The pH of this solution = the pK_a for the acid = 3.74.

5. a. The pH of 100 mL of pure water at 25°C = 7.0.

   b. HCl is a strong acid, so the concentration of hydronium ion will be $(0.10 \text{ mL} \times 1L/1000mL \times 12 \text{ mol/L} = 0.0012$ moles in 100 mL = 0.012 M). So the pH = 1.92.

c. A buffer solution composed of equimolar (0.20M) quantities of ammonia and ammonium chloride has a pOH equal to the pK_b for the base.
$pOH = pK_b = 4.74$, so $pH = 9.26$

d. The hydronium ion reacts with the ammonia to produce ammonium ion:

$$H_3O^+(aq) + NH_3(aq) \rightleftharpoons NH_4^+(aq) + H_2O(l) \quad K = 1.8 \times 10^9$$

K is very large, the reaction is virtually complete.
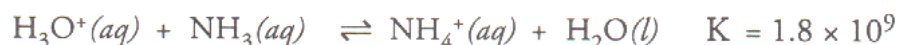
The concentration of HCl added is 0.012 M so the concentration of NH_4^+ initially increases by that amount and the concentration of ammonia decreases by the same amount. Summarize in a table:

		$H_3O^+(aq)$ +	$NH_3(aq)$ $\rightleftharpoons$	$NH_4^+(aq)$ + $H_2O(l)$
I	Initial	0	0.20	0.20
C	Change	+0.012		
N	New concn:	0	0.188	0.212

Assume that the reaction goes to completion, and then adjusts backward slightly to reach equilibrium. For the equilibrium, use either the ionization of the weak electrolyte, or the hydrolysis of the conjugate partner—the result is the same.

Now let the system reach equilibrium; the system moves back to the left:

		$H_3O^+(aq)$ +	$NH_3(aq)$ $\rightleftharpoons$	$NH_4^+(aq)$ + $H_2O(l)$
I	Initial		0.188	0.212
C	Change	+x	+x	−x
E	Equilibrium	x	0.188+x	0.212−x

assume completion →

then adjust ← backward

Solve for x, $x = 6.265 \times 10^{-10}$ so $[H^+] = 6.265 \times 10^{-10}$
$pH = 9.20$ —the pH changes very little!

Compared to adding 0.10 mL of 12M HCl to water with a decrease in pH from 7.00 to 1.92, this decrease from 9.26 to 9.20 is negligible.

Alternatively, using the ionization of ammonia:

		$NH_3(aq)$ + H_2O $\rightleftharpoons$		$NH_4^+(aq)$ +	$OH^-(aq)$
I	Initial	0.188		0.212	0
C	Change	−x		+x	+x
E	Equilibrium	0.188−x		0.212+x	x

Solve for x, $x = 1.596 \times 10^{-5}$ so $[OH^-] = 1.596 \times 10^{-5}$
$[H^+] = 6.265 \times 10^{-10}$ and $pH = 9.20$ —the result is the same.

6. Desired pH = 7.25:
possible choices (look for a pK_a near 7.25):

H_2S	$K_a = 1 \times 10^{-7}$	$pK_a = 7.00$
$H_2PO_4^-$	$K_a = 6.2 \times 10^{-8}$	$pK_a = 7.21$
HSO_3^-	$K_a = 6.2 \times 10^{-8}$	$pK_a = 7.21$
$HClO$	$K_a = 3.5 \times 10^{-8}$	$pK_a = 7.46$

For $H_2PO_4^-$ or HSO_3^- use the Henderson-Hasselbalch equation to determine the ratio of acid and its conjugate base required:

Maintain a sufficient number of significant figures. Recall that only the mantissa of a logarithm is counted in determining significant figures.

[The *mantissa* of a logarithm is the part of the number after the decimal point. The part before the decimal point is called the *characteristic* of the logarithm.]

$$pH = pK_a + log(\frac{[\text{conjugate base}]}{[\text{acid}]})$$

$$log(\frac{[\text{conjugate base}]}{[\text{acid}]}) = 7.25 - 7.21 = 0.04(24)$$

$$\frac{[\text{conjugate base}]}{[\text{acid}]} = 1.10$$

The desired pH is slightly more basic than the pK_a, so slightly more base than acid is required.

7.   Desired pH = 9.25:
     possible choices (look for a pK_a near 9.25):

$[Co(H_2O)_6]^{2+}$ $K_a = 1.3 \times 10^{-9}$ $pK_a = 8.89$
$B(OH)_3$ $K_a = 7.3 \times 10^{-10}$ $pK_a = 9.14$
NH_4^+ $K_a = 5.6 \times 10^{-10}$ $pK_a = 9.25$
HCN $K_a = 4.0 \times 10^{-10}$ $pK_a = 9.40$

The ammonia/ammonium ion buffer appears to be perfect in an equimolar ratio (equal number of moles of ammonia and ammonium ion). For an equimolar buffer, $pH = pK_a$ or pK_b

8.   The salt sodium benzoate is formed in the reaction. However, although the number of moles of sodium benzoate formed equals the number of moles of acid (or base) used, its concentration is decreased by dilution:
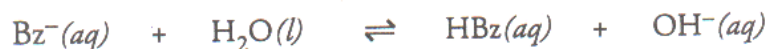
Volume of benzoic acid = 25 mL
Volume of sodium hydroxide = 50 mL (i.e. 25 mL × 0.100 M/0.050 M)
Total volume = 75 mL
Concentration of sodium benzoate = 0.100M × 25mL/75mL = 0.033 M

At the equivalence point:

$$Bz^-(aq) + H_2O(l) \rightleftharpoons HBz(aq) + OH^-(aq)$$

$$K = K_w/K_a = 1.59 \times 10^{-10} = [OH^-]^2/0.033$$

$$[OH^-] = 2.29 \times 10^{-6} \text{ and } pOH = 5.64; \quad pH = 8.36$$

9.   The two salts KH_2PO_4 and K_2HPO_4 are conjugate partners; they form a buffer solution. You can use the Henderson-Hasselbalch equation to determine the ratio:

$$pH = pK_a + log(\frac{[\text{conjugate base}]}{[\text{acid}]})$$

$$7.10 = 7.21 + log(\frac{[\text{conjugate base}]}{[\text{acid}]})$$

$$\frac{[\text{conjugate base}]}{[\text{acid}]} = 0.776$$

The mole ratio of K_2HPO_4 (base) to KH_2PO_4 (acid) is 0.776 to 1.