1. $HCN\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + CN^-\ (aq)$ $K_a = \dfrac{[H_3O^+][CN^-]}{[HCN]}$

2. $HClO_4$ is a strong acid. $HC_2H_3O_2$ and HCN are both weak acids. Of the two weak acids, HCN has the smaller ionization constant. Therefore HCN is the weakest of the 3acids.

4. As the concentration of a weak acid increases, its degree of dissociation decreases.

5. $\dfrac{0.0010}{6.8 \times 10^{-4}} = 1.47$ This is well below the value of 380 required to insure that the acid be

less than 5% dissociated. The x in the denominator cannot be neglected and the quadratic equation must be solved.

6. $H_3PO_3(aq) + H_2O(l) \rightarrow H_3O^+(aq) + H_2PO_3^-(aq)$ $K_{a1} = \dfrac{[H_3O^+][H_2PO_3^-]}{[H_3PO_3]}$

$H_2PO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HPO_3^{2-}(aq)$ $K_{a2} = \dfrac{[H_3O^+][HPO_3^{2-}]}{[H_2PO_3^-]}$

7. For the doubly deprotonated anion of a diprotic acid, the concentration is approximately equal to K_{a2}. For $H_2C_2O_4$ this is 5.1×10^{-5}, so $[C_2O_4^{2-}] \approx 5.1 \times 10^{-5}$ *M*. This approximation only holds if the yield of H_3O^+ is essentially all from the first ionization so that $[H_3O^+] \approx [HC_2O_4^-]$. If this is the case, then:

$$K_{a2} = \frac{[H_3O^+][C_2O_4^{2-}]}{[HC_2O_4^-]} \approx \frac{[H_3O^+][C_2O_4^{2-}]}{[H_3O^+]} \approx [C_2O_4^{2-}]$$

8. $C_6H_5NH_2\ (aq) + H_2O\ (l) \rightleftharpoons OH^-\ (aq) + C_6H_5NH_3^+\ (aq)$ $K_b = \dfrac{[OH^-][C_6H_5NH_3^+]}{[C_6H_5NH_2]}$

9. According to Table 16.2, methylamine, CH_3NH_2, has the largest value of K_b of the three bases, making it the strongest base among the three.

10. A solution of anilinium chloride will be acidic due to hydrolysis of the anilinium ion.

$C_6H_5NH_3^+$ (aq) + H_2O (l) $\rightleftharpoons$ $C_6H_5NH_2$ (aq) + H_3O^+ (aq)

$$K_a = \frac{[H_3O^+][C_6H_5NH_2]}{[C_6H_5NH_3^+]}$$

K_a is calculated from K_b for aniline and K_w, since $K_aK_b = K_w$ for a conjugate acid-base pair.

Therefore: $K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{4.2 \times 10^{-10}} = 2.4 \times 10^{-5}$ making $C_6H_5NH_3^+$(aq) a slightly

stronger acid than acetic acid.

11. The common-in effect is the shift in an ionic equilibrium that is caused by the addition of a substance that is a source of an ion that is one of the species in equilibrium. For example, nitrous acid is a weak acid that undergoes dissociation in water according to the following equation:

$$HNO_2(aq) + H_2O(l) \rightarrow H_3O^+(aq) + NO_2^-(aq)$$

Addition of $NaNO_2$, a source of the nitrite ion, NO_2^-, to a solution of nitrous acid would cause a shift to the left in the equilibrium shown.

12. The addition of $CH_3NH_3^+Cl^-$ to a 0.10 *M* solution of CH_3NH_2 causes a decrease in the pH by the common ion effect. The dissociation equilibrium for CH_3NH_2 is:

$$CH_3NH_2 \text{ (aq)} + H_2O \text{ (l)} \rightleftharpoons CH_3NH_3^+ \text{ (aq)} + OH^- \text{ (aq)}$$

$CH_3NH_3^+Cl^-$ is a source of the $CH_3NH_3^+$ ion which shifts the above equilibrium to the left, decreasing the OH^- concentration and decreasing the pH.

13. A buffer is a solution containing a weak acid and its conjugate base (or a weak base and its conjugate acid). The buffer is able to resist large changes in pH when acids or bases are added. The weak acid (or conjugate acid of the weak base) is able to neutralize H_3O^+ from any added acid, while the conjugate base of the weak acid (or the weak base) is able to neutralize OH^- from any added base.

14. The capacity of a buffer refers to the maximum amount of acid or base it can neutralize before undergoing a significant change in pH. An example of a buffer with a relatively large capacity would be 1 *M* HF/1 *M* NaF, while 0.1 *M* HF/0.1 *M* NaF would be a buffer with the same pH but a smaller capacity.

15. Before any acid is added, the pH is determined by the dissociation of the weak base. After the addition of acid is started, the pH gradually decreases. At half neutralization, the solution corresponds to a buffer containing equimolar amounts of a weak base and its conjugate acid. The pH at this point is 14.00 − pK_b. At the equivalence point, the pH is determined by the hydrolysis of the conjugate acid of the weak base ($K_a = K_w/K_b$). After the equivalence point, the pH is determined by the amount of excess strong acid which has been added. The equivalence point is the point in the titration when exactly enough acid has been added to react quantitatively with the base. We approximate the equivalence point by observing the endpoint of the titration, the point at which the chosen indicator changes color.

16. Of the indicators in Figure 15.8, phenolphthalein or thymol blue would be most suitable. For this titration, it would be most desirable to use an indicator whose color transition range is centered around 8.0.

18. a. HX is least ionized in solution, because it has the highest pH and therefore the smallest hydronium ion concentration.

    b. HZ has the largest K_a because it is the most ionized under identical conditions.

20. KBr is the salt of a strong acid (HBr) and strong base (NaOH). Neither cation nor anion is subject to hydrolysis. The solution is therefore neutral, its pH = 7 and $[OH^-] = 1 \times 10^{-7}$ *M*. HBr is a strong acid with a pH much less than 7. CH_3NH_2 is a weak base which will react with water to yield $[OH^-] > 1 \times 10^{-7}$ *M*. NH_4Cl is the salt of a weak base and a strong acid and is subject to cation hydrolysis leading to a pH < 7, but not as low as that of a solution of HBr of equal concentration.

    In terms of $[OH^-]$: HBr < NH_4Cl < KBr < CH_3NH_2

22. NH_3 is a weak base. NH_4Br is the salt of a weak base and strong acid and subject to cation hydrolysis, yielding a slightly acidic solution. NaF is the salt of a strong base and weak acid and subject to anion hydrolysis, yielding a slightly basic solution. NaCl is the salt of a strong base and strong acid. Neither ion is subject to hydrolysis, so the solution is neutral.

    In terms of pH: NH_3 > NaF > NaCl > NH_4Br

24. The most obvious feature to look for is the pH at the equivalence point.
    strong acid/strong base: pH = 7
    weak acid/strong base: pH > 7
    strong acid/weak base: pH < 7

27. a. $HBrO(aq) + H_2O(l) \leftrightharpoons H_3O^+(aq) + BrO^-(aq)$
    b. $HClO_2(aq) + H_2O(l) \leftrightharpoons H_3O^+(aq) + ClO_2^-(aq)$
    c. $HNO_2(aq) + H_2O(l) \leftrightharpoons H_3O^+(aq) + NO_2^-(aq)$
    d. $HCN(aq) + H_2O(l) \leftrightharpoons H_3O^+(aq) + CN^-(aq)$

29. $HAcr (aq) + H_2O(l) \rightarrow H_3O^+(aq) + Acr^-(aq)$

pH = 2.63 $[H_3O^+] = [Acr^-] = 10^{-2.63} = 2.3 \times 10^{-3}$ *M*

$[HAcr] = 0.10 - 2.3 \times 10^{-3} = 0.098$ *M* $K_a = \frac{(2.3 \times 10^{-3})^2}{0.098} = 5.4 \times 10^{-5}$

31. $B(OH)_3 (aq) + 2 H_2O (l) \rightleftharpoons B(OH)_4^- (aq)\ H_3O^+ (aq)$ $K = 5.9 \times 10^{-10}$

	$B(OH)_3$ (aq)	+ 2 H_2O (l)	⇌	$B(OH)_4^-$ (aq)	H_3O^+ (aq)
[ ]$_i$	0.021			0	~0
Δ[ ]	−x			+x	+x
[ ]$_{eq}$	0.021 − x			x	x

$$K = 5.9 \times 10^{-10} = \frac{[H_3O^+][B(OH)_4^-]}{[B(OH)_3]} = \frac{x^2}{0.021 - x}$$ Assume x << 5.9×10^{-10}

$$5.9 \times 10^{-10} = \frac{x^2}{0.021}$$

$$x = \sqrt{(0.021)\ 5.9 \times 10^{-10}} = 3.5 \times 10^{-6} \qquad \frac{3.5 \times 10^{-6}}{0.021} \times 100 = 0.017\%$$

The % ionization is 0.017% and the degree of ionization is 0.00017

$[H_3O^+] \approx 3.5 \times 10^{-6}$ *M* pH = $-\log (3.5 \times 10^{-6}) = 5.46$

33. $C_6H_4NH_2CO_2H (aq) + H_2O (l) \rightleftharpoons C_6H_4NH_2CO_2^- (aq) + H_3O^+ (aq)$ $K_a = 2.2 \times 10^{-5}$

	$C_6H_4NH_2CO_2H$ (aq)	+ H_2O (l)	⇌	$C_6H_4NH_2CO_2^-$ (aq)	H_3O^+ (aq)
[ ]$_i$	0.055			0	~0
Δ[ ]	−x			+x	+x
[ ]$_{eq}$	0.055 − x			x	x

$$K_a = 2.2 \times 10^{-5} = \frac{[H_3O^+][C_6H_4NH_2CO_2^-]}{[C_6H_4NH_2CO_2H]} = \frac{x^2}{0.055 - x}$$

Assume x << 0.055

$$2.2 \times 10^{-5} = \frac{x^2}{0.055}$$

$$x = \sqrt{(0.055)\ 2.2 \times 10^{-5}} = 1.1 \times 10^{-3} \qquad \frac{1.1 \times 10^{-3}}{0.055} \times 100 = 2.0\%$$

The % ionization is 2.0% and the degree of ionization is 0.020

$[C_6H_4NH_2CO_2^-] = [H_3O^+] \approx 1.1 \times 10^{-3}\ M$ pH = $-\log(1.1 \times 10^{-3}) = 2.96$

35. $CH_3CO_2H\ (aq) + H_2O\ (l) \rightleftharpoons CH_3CO_2^-\ (aq) + H_3O^+\ (aq)$ $K_a = 1.7 \times 10^{-5}$

$[H_3O^+] = 10^{-2.68} = 2.\underline{0}9 \times 10^{-3}\ M = [CH_3CO_2^-]$

	CH_3CO_2H (aq)	+ H_2O (l)	⇌	$CH_3CO_2^-$ (aq)	H_3O^+ (aq)
$[\ ]_i$	x			0	~0
$\Delta[\ ]$	$-2.\underline{0}9 \times 10^{-3}$			$+2.\underline{0}9 \times 10^{-3}$	$+2.\underline{0}9 \times 10^{-3}$
$[\ ]_{eq}$	$x - 2.\underline{0}9 \times 10^{-3}$			$2.\underline{0}9 \times 10^{-3}$	$2.\underline{0}9 \times 10^{-3}$

$$K_a = 1.7 \times 10^{-5} = \frac{[H_3O^+][CH_3CO_2^-]}{[CH_3CO_2H]} = \frac{(2.\underline{0}9 \times 10^{-3})^2}{(x - 2.\underline{0}9 \times 10^{-3})} = \frac{4.\underline{3}7 \times 10^{-6}}{(x - 2.\underline{0}9 \times 10^{-3})}$$

$1.7 \times 10^{-5}\ x - 3.5 \times 10^{-8} = 4.\underline{3}7 \times 10^{-6}$

$x = [CH_3CO_2H] = 0.26\ M$

37. $HF\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + F^-\ (aq)$ $K_a = 6.8 \times 10^{-4}$

	HF (aq) +	H_2O (l)	⇌	F^- (aq) +	H_3O^+ (aq)
$[\ ]_i$	0.040			0	~0
$\Delta[\ ]$	$-x$			+x	+x
$[\ ]_{eq}$	$0.040 - x$			x	x

$$K_a = \frac{[H_3O^+][F^-]}{[HF]} = \frac{(x)(x)}{(0.040 - x)} = 6.8 \times 10^{-4}$$

Assume x << 0.040.

$$K_a = 6.8 \times 10^{-4} \approx \frac{(x)(x)}{(0.040)}$$

$x^2 = 2.7 \times 10^{-5}$

$x \approx 5.2 \times 10^{-3}$ $\quad \frac{5.2 \times 10^{-3}}{0.040} \times 100 = 13\%$, 13% > 5%, so the approximation is invalid!

Now we need to solve the quadratic equation.

$x^2 + 6.8 \times 10^{-4}\,x - 2.72 \times 10^{-5} = 0$

$$x = \frac{-6.8 \times 10^{-4} \pm \sqrt{(6.8 \times 10^{-4})^2 - 4(1)(-2.72 \times 10^{-5})}}{2(1)} \qquad x = -0.00556 \text{ or } 0.00488$$

$x = [H_3O^+] = 4.9 \times 10^{-3}\ M$

$pH = -\log [H_3O^+] = -\log (4.9 \times 10^{-3}) = 2.31$

39. HDnb (aq) + H_2O (l) ⇌ H_3O^+ (aq) + Dnb^- (aq) $\qquad K_a = 7.94 \times 10^{-2}$

	HDnb (aq) +	H_2O (l)	⇌	Dnb^- (aq) +	H_3O^+ (aq)
$[\ ]_i$	2.00			0	~0
$\Delta [\ ]$	−x			+x	+x
$[\ ]_{eq}$	2.00 − x			x	x

$$K_a = \frac{[H_3O^+][Dnb^-]}{[HDnb]} = \frac{(x)(x)}{(2.00 - x)} = 7.94 \times 10^{-2}$$

$$\frac{C_a}{K_a} = \frac{2.00}{7.94 \times 10^{-2}} = 25.2 \ngeq 380$$ so we'll have to solve a quadratic

$x^2 + 7.94 \times 10^{-2} x - 0.159 = 0$

$$x = \frac{-0.0794 \pm \sqrt{(0.0794)^2 - 4(1)(-0.159)}}{2(1)} \qquad x = -0.440 \text{ or } 0.361$$

$x = [H_3O^+] = 0.361\ M$

$pH = -\log [H_3O^+] = -\log (0.361) = 0442$

41. $H_2Ph\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + HPh^-\ (aq)$ $K_{a1} = 1.2 \times 10^{-3}$

$HPh^-\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + Ph^{2-}\ (aq)$ $K_{a2} = 3.9 \times 10^{-6}$

Since $K_{a1} > 20\ K_{a2}$ we can treat the two ionizations separately.

	H_2Ph (aq) +	H_2O (l)	$\rightleftharpoons$	HPh^- (aq) +	H_3O^+ (aq)
$[\ ]_i$	0.015			0	~0
$\Delta [\ ]$	−x			+x	+x
$[\ ]_{eq}$	0.015 − x			x	x

$$K_{a1} = \frac{[H_3O^+][HPh^-]}{[H_2Ph]} = \frac{(x)(x)}{(0.015 - x)} = 1.2 \times 10^{-3}$$

$$\frac{C_a}{K_a} = \frac{0.015}{1.2 \times 10^{-3}} = 12.5 \ngeq 380$$ so we'll have to solve a quadratic

$x^2 + 1.2 \times 10^{-3} x - 1.8 \times 10^{-5} = 0$

$$x = \frac{-0.0012 \pm \sqrt{(0.0012)^2 - 4(1)(-1.8 \times 10^{-5})}}{2(1)} \qquad x = -0.0049 \text{ or } 0.0037$$

$x = [H_3O^+] = 0.0037\ M = [HPh^-]$

	HPh^- (aq) +	H_2O (l)	$\rightleftharpoons$	Ph^{2-} (aq) +	H_3O^+ (aq)
$[\ ]_i$	0.0037			0	0.0037
$\Delta[\ ]$	−y			+y	+y
$[\ ]_{eq}$	0.0037 − y			y	0.0037 + y

$$K_{a2} = \frac{[H_3O^+][Ph^{2-}]}{[HPh^-]} = 3.9 \times 10^{-6} = \frac{(0.0037 + y)(y)}{(0.0037 - y)} \approx y$$

$$\frac{3.9 \times 10^{-6}}{0.0037} \times 100 = 0.11\%$$

$[Ph^{2-}] \approx y = 3.9 \times 10^{-6}\ M$

43. CH_3NH_2 (aq) + H_2O (l) $\rightleftharpoons$ OH^- (aq) + $CH_3NH_3^+$ (aq) $\qquad K_b = \frac{[OH^-][CH_3NH_3^+]}{[CH_3NH_2]}$

45. $HOC_2H_4NH_2$ (aq) + H_2O (l) $\rightleftharpoons$ $HOC_2H_4NH_3^+$ (aq) + OH^- (aq)

pH = 11.34 pOH = 14.00 −11.34 = 2.66

$[OH^-] = 10^{-2.66} = 2.2 \times 10^{-3}\ M = [HOC_2H_4NH_3^+]$

$[HOC_2H_4NH_2] = 0.15 - 0.0022 = 0.1\underline{4}78\ M$

$$K_b = \frac{[OH^-][HOC_2H_4NH_3^+]}{[HOC_2H_4NH_2]} = \frac{(0.0022)(0.0022)}{0.1\underline{4}78} = 3.3 \times 10^{-5}$$

47. CH_3NH_2 (aq) + H_2O (l) $\rightleftharpoons$ OH^- (aq) + $CH_3NH_3^+$ (aq) $\qquad K_b = 4.4 \times 10^{-4}$

	CH_3NH_2 (aq) +	H_2O (l)	$\rightleftharpoons$	OH^- (aq) +	$CH_3NH_3^+$ (aq)
$[\ ]_i$	0.060			0	~0
$\Delta[\ ]$	−x			+x	+x
$[\ ]_{eq}$	0.060 − x			x	x

$$\frac{C_a}{K_a} = \frac{0.060}{4.4 \times 10^{-4}} = 136 \ngeq 380$$ so we cannot make the simplifying assumption. We will have to solve a quadratic equation.

$$K_b = 4.4 \times 10^{-4} = \frac{(x)(x)}{(0.060 - x)}$$

$x^2 + 4.4 \times 10^{-4}\, x - 2.64 \times 10^{-5} = 0$

$$x = \frac{-4.4 \times 10^{-4} \pm \sqrt{(4.4 \times 10^{-4})^2 - 4(1)(-2.64 \times 10^{-5})}}{2(1)} \qquad x = -0.0054 \text{ or } 0.0049$$

$x = [OH^-] = [CH_3NH_3^+] = 4.9 \times 10^{-3}\ M$ $[CH_3NH_2] = 0.060 - 0.0049 = 0.05\underline{5}\ M$

$pOH = -\log [OH^-] = -\log (4.9 \times 10^{-3}) = 2.31$ $pH = 14.00 - 2.31 = 11.69$

49. a. NO_3^- is the anion of a strong acid and does not undergo hydrolysis.

b. $OCl^-\ (aq) + H_2O\ (l) \rightleftharpoons HOCl\ (aq) + OH^-\ (aq)$ $K_b = \frac{[OH^-][HOCl]}{[OCl^-]}$

c. $NH_2NH_3^+\ (aq) + H_2O\ (l) \rightleftharpoons NH_2NH_2\ (aq) + H_3O^+\ (aq)$ $K_a = \frac{[H_3O^+][NH_2NH_2]}{[NH_2NH_3^+]}$

d. Br^- is the anion of a strong acid and does not undergo hydrolysis.

51. $Zn(H_2O)_6^{2+}\ (aq) + H_2O\ (l) \rightleftharpoons Zn(H_2O)_5(OH)^+\ (aq) + H_3O^+\ (aq)$

$$K_a = \frac{[H_3O^+][Zn(H_2O)_5(OH)^+]}{[Zn(H_2O)_6^{2+}]}$$

53. a. acidic due to hydrolysis of $Fe(H_2O)_6^{3+}$
b. basic due to hydrolysis of CO_3^{2-}
c. basic due to hydrolysis of CN^-
d. acidic due to hydrolysis of NH_4^+

55. a. K_a for acetic acid is essentially identical to K_b for ammonia, so the solution will be neutral (To 3 significant figures, $K_a = K_b = 1.75 \times 10^{-5}$) .

b. $K_a = 1.7 \times 10^{-5}$ and $K_b = 4.2 \times 10^{-10}$. The cation will be hydrolyzed to a greater extent than the anion, so the solution will be acidic.

57. a. $$K_b = \frac{K_w}{K_a\ (HNO_2)} = \frac{1.0 \times 10^{-14}}{4.5 \times 10^{-4}} = 2.2 \times 10^{-11}$$

b. $$K_a = \frac{K_w}{K_b\ (C_5H_5N)} = \frac{1.0 \times 10^{-14}}{1.4 \times 10^{-9}} = 7.1 \times 10^{-6}$$

59. $CH_3CH_2COO^-\ (aq) + H_2O\ (l) \rightleftharpoons CH_3CH_2COOH\ (aq) + OH^-\ (aq)$

	$CH_3CH_2COO^-$ (aq) +	H_2O (l)	$\rightleftharpoons$	CH_3CH_2COOH (aq) +	OH^- (aq)
$[\ ]_i$	0.025			0	~0
$\Delta [\ ]$	−x			+x	+x
$[\ ]_{eq}$	0.025 − x			x	x

$$K_b = \frac{K_w}{K_a\ (CH_3CH_2CO_2H)} = \frac{1.0 \times 10^{-14}}{1.3 \times 10^{-5}} = 7.7 \times 10^{-10}$$

$$K_b = 7.7 \times 10^{-10} = \frac{[CH_3CH_2COOH][OH^-]}{[CH_3CH_2COO^-]} = \frac{x^2}{(0.025 - x)}$$

Because of the very small size of K_b we will assume that $x << 0.025$.

$$x = \sqrt{(7.7 \times 10^{-10})(0.025)} = 4.4 \times 10^{-6}\ M = [OH^-] = [CH_3CH_2COOH]$$

$$\frac{4.4 \times 10^{-6}}{0.025} \times 100 = 0.018\%$$

$pOH = -\log (4.4 \times 10^{-6}) = 5.36$

$pH = 14.00 - 5.36 = 8.64$

61. $C_5H_5NH^+$ (aq) + H_2O (l) ⇌ C_5H_5N (aq) + H_3O^+ (aq)

	$C_5H_5NH^+$ (aq) +	H_2O (l)	⇌	C_5H_5N (aq) (aq) +	H_3O^+ (aq)
$[\ ]_i$	0.15			0	~0
$\Delta[\ ]$	−x			+x	+x
$[\ ]_{eq}$	0.15 − x			x	x

$$K_a = \frac{K_w}{K_b\ (C_5H_5N)} = \frac{1.0 \times 10^{-14}}{1.4 \times 10^{-9}} = 7.1 \times 10^{-6}$$

$$K_a = 7.1 \times 10^{-6} = \frac{[C_5H_5N][H_3O^+]}{[C_5H_5NH^+]} = \frac{x^2}{(0.15-x)}$$

We will assume that x << 0.15.

$$x = \sqrt{(7.1 \times 10^{-6})(0.15)} = 1.0 \times 10^{-3}\ M = [H_3O^+] = [C_5H_5N]$$

$$\frac{1.0 \times 10^{-3}}{0.15} \times 100 = 0.67\%$$ pH = −log (1.0 x 10^{-3}) = 3.00

63. a. HF (aq) + H_2O ⇌ H_3O^+(aq) + F^- (aq)

	HF (aq) +	H_2O (l)	⇌	F^- (aq) +	H_3O^+ (aq)
$[\ ]_i$	0.75			0	~0
$\Delta[\ ]$	−x			+x	+x
$[\ ]_{eq}$	0.75 − x			x	x

$$K_a = \frac{[H_3O^+][F^-]}{[HF]} = \frac{(x)(x)}{(0.75 - x)} = 6.8 \times 10^{-4}$$

We'll make an assumption which might simplify the calculation. Assume x << 0.75.

$$K_a = 6.8 \times 10^{-4} \approx \frac{(x)(x)}{(0.75)}$$

$x^2 = 5.44 \times 10^{-4}$

$x \approx 2.\underline{2}5 \times 10^{-2}$ $\qquad \dfrac{2.\underline{2}5 \times 10^{-2}}{0.75} \times 100 = 3.0\%$, $\qquad$ 3.0% < 5%, so the approximation is valid

The degree of ionization is therefore 0.030 or 3.0%. Solving the quadratic would give us $x \approx 2.\underline{2}2 \times 10^{-2}$. There is practically no difference within the allowed precision.

b.

	HF (aq) +	H_2O (l)	⇌	F^- (aq) +	H_3O^+ (aq)
$[\ ]_i$	0.75			0	0.12
$\Delta [\ ]$	$-x$			$+x$	$+x$
$[\ ]_{eq}$	$0.75 - x$			x	$0.12 + x$

$$K_a = \frac{[H_3O^+][F^-]}{[HF]} = \frac{(0.12 + x)(x)}{(0.75 - x)} = 6.8 \times 10^{-4}$$

We'll again make an assumption. Assume $x << 0.12$.

$$K_a = 6.8 \times 10^{-4} \approx \frac{(0.12)(x)}{(0.75)}$$

$x \approx 4.\underline{2}5 \times 10^{-3}$ $\qquad \dfrac{4.\underline{2}5 \times 10^{-3}}{0.12} \times 100 = 3.5\%$, $\qquad$ 3.5% < 5%, so the approximation is valid

Solving the quadratic would give us $x \approx 4.\underline{0}8 \times 10^{-3}$,

$$\frac{4.\underline{0}8 \times 10^{-3}}{0.75} \times 100 = 0.54\%$$

a degree of ionization of 0.0054 or 0.54%

The point is that the % ionization decreases with the presence of HCl, a source of the common ion H_3O^+.

65. HNO_2 (aq) + H_2O (l) $\rightleftharpoons$ NO_2^- (aq) + H_3O^+ (aq) $K_a = 4.5 \times 10^{-4}$ $pK_a = 3.35$

	HNO_2 (aq) +	H_2O (l)	$\rightleftharpoons$	NO_2^- (aq) +	H_3O^+ (aq)
$[\,]_i$	0.15			0.10	~0
$\Delta [\,]$	−x			+x	+x
$[\,]_{eq}$	0.15 − x			0.10 + x	x

$$K_a = \frac{[H_3O^+][NO_2^-]}{[HNO_2]} = \frac{(x)(0.10 + x)}{(0.15 - x)} = 4.5 \times 10^{-4}$$

We'll assume that the common ion, NO_2^-, suppresses the ionization sufficiently so that x << 0.10.

$$\frac{(x)(0.10)}{(0.15)} \approx 4.5 \times 10^{-4}$$

$x \approx 6.\underline{7}5 \times 10^{-4}$ $\frac{6.\underline{7}5 \times 10^{-4}}{0.10} \times 100 = 0.68\%$ so assumption is valid

$[H_3O^+] = 6.\underline{7}5 \times 10^{-4}\ M$ $pH = -\log(6.\underline{7}5 \times 10^{-4}) = 3.17$

We get the same result using the Henderson-Hasselbalch equation:

$$pH = pK_a + \log \frac{[base]}{[acid]} = 3.35 + \log \frac{(0.10)}{(0.15)} = 3.35 + -0.18 = 3.17$$

67. Again we could use the tabular approach of the previous problem or use the Henderson-Hasselbalch equation:

For $CH_3NH_3^+$

$$K_a = \frac{K_w}{K_b\ (CH_3NH_2)} = \frac{1.0 \times 10^{-14}}{4.4 \times 10^{-4}} = 2.3 \times 10^{-11} \qquad pK_a = 10.64$$

$$pH = pK_a + \log \frac{[base]}{[acid]} = 10.64 + \log \frac{(0.10)}{(0.15)} = 10.64 + -0.18 = 10.46$$

69. For HF $K_a = 6.8 \times 10^{-4}$ so $pK_a = 3.17$

$$[F^-] = 0.15\ M\ \frac{45.0\ ml}{(45.0 + 35.0)\ mL} = 0.08\underline{4}3\ M$$

$$[HF] = 0.10\ M\ \frac{35.0\ ml}{(45.0 + 35.0)\ mL} = 0.04\underline{3}7\ M$$

$$pH = pK_a + \log\frac{[base]}{[acid]} = 3.17 + \log\frac{(0.08\underline{3}7)}{(0.04\underline{3}7)} = 3.17 + 0.28 = 3.45$$

71. For NH_3 $K_b = 1.8 \times 10^{-5}$, so for NH_4^+ $K_a = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$ and $pK_a = 9.26$.

$$pH = pK_a + \log\frac{[base]}{[acid]} = 9.26 + \log\frac{(0.10)}{(0.10)} = 9.26 + 0.00 = 9.26$$

In 125 mL of this buffer we have:

$$\text{mol of } NH_3 = 0.10\ M \times 0.125\ L = 0.01\underline{2}5\ mol$$
$$\text{mol of } NH_4^+ = 0.10\ M \times 0.125\ L = 0.01\underline{2}5\ mol$$

In the added acid we have:

$$\text{mol of } H_3O^+ = 0.20\ M \times 0.012\ L = 0.0024\ mol$$

New number of moles of NH_3 and NH_4^+:

$$\text{mol of } NH_3 = 0.01\underline{2}5\ mol - 0.0024\ mol = 0.0101\ mol$$
$$\text{mol of } NH_4^+ = 0.01\underline{2}5\ mol + 0.0024\ mol = 0.0149\ mol$$

$$[NH_3] = \frac{0.01\underline{0}1\ mol}{0.137\ L} = 0.07\underline{3}7\ M$$

$$[NH_4^+] = \frac{0.01\underline{4}9\ mol}{0.137\ L} = 0.1\underline{0}8\ M$$

$$pH = pK_a + \log\frac{[base]}{[acid]} = 9.26 + \log\frac{(0.07\underline{3}7)}{(0.1\underline{0}8)} = 9.26 + (-0.17) = 9.09$$

Or using the systematic approach:

	NH_3 (aq) +	H_2O (l)	⇌	OH^- (aq) +	NH_4^+ (aq)
$[\ ]_i$	0.07<u>3</u>7				0.1<u>0</u>8
$\Delta[\ ]$	−x			+ x	+ x
$[\ ]_{eq}$	0.07<u>3</u>7 −x			x	0.1<u>0</u>8 + x

$$K_b = 1.8 \times 10^{-5} = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{(x)(0.1\underline{0}8 + x)}{(0.07\underline{3}7 - x)} \approx \frac{0.1\underline{0}8\, x}{0.07\underline{3}7}$$

$x \approx 1.2 \times 10^{-5} = [OH^-]$ pOH = 4.91 pH = 14.00 −4.91 = 9.09

73. For $CH_2ClCOOH$ $K_a = 1.3 \times 10^{-3}$, so $pK_a = 2.89$

$$pH = pK_a + \log\frac{[base]}{[acid]} = 2.89 + \log\frac{(0.10)}{(0.15)} = 2.89 + -0.18 = 2.71$$

75. For C_5H_5N, $K_b = 1.4 \times 10^{-9}$, so for $C_5H_5NH^+$ $K_a = \dfrac{1.0 \times 10^{-14}}{1.4 \times 10^{-9}} = 7.1 \times 10^{-6}$

and $pK_a = 5.15$.

$$pH = pK_a + \log\frac{[base]}{[acid]} = 5.15 + \log\frac{(0.15)}{(0.10)} = 5.15 + 0.18 = 5.33$$

77. For CH_3COOH $K_a = 1.7 \times 10^{-5}$, so $pK_a = 4.77$

$$pH = pK_a + \log\frac{[base]}{[acid]}$$

$$5.00 = 4.77 + \log\frac{[CH_3COO^-]}{(0.10)}$$

$$5.00 = 4.77 + \log[CH_3COO^-] - \log(0.10)$$

$$-0.77 = \log[CH_3COO^-]$$

$[CH_3COO^-] = 10^{-0.77} = 0.17$ *M*

$$0.17\ M \times 2.0\ L = 0.34\ mol\ NaC_2H_3O_2$$

79. $0.015\ \text{L} \times 0.10\ M\ OH^- = 0.0015\ \text{mol}\ OH^-$

$0.025\ \text{L} \times 0.10\ M\ H_3O^+ = 0.0025\ \text{mol}\ H_3O^+$

This leaves an excess of 0.0010 mol H_3O^+ in 40 mL

$$[H_3O^+] = \frac{0.0010\ \text{mol}}{0.040\ \text{L}} = 2.5 \times 10^{-2}\ M\ H_3O^+$$

pH = $-\log(2.5 \times 10^{-2}) = 1.60$

81. $$1.24\ \text{g}\ C_6H_5COOH \times \frac{1\ \text{mol}}{122.12\ \text{g}} = 0.0102\ \text{mol}$$

To reach the equivalence point, we must add 0.0102 mole OH^-. The corresponding volume of the NaOH solution is given by:

$$\frac{0.0102\ \text{mol}\ OH^-}{0.180\ \frac{\text{mol}}{\text{L}}} = 5.67 \times 10^{-2}\ \text{L} = 56.7\ \text{mL}$$

total volume at equivalence point = 50.0 + 56.7 mL = 106.7 mL = 0.1067 L

At equivalence point, all of the C_6H_5COOH initially present has been converted to $C_6H_5COO^-$. The concentration of $C_6H_5COO^-$ is:

$$[C_6H_5COO^-] = \frac{0.0102\ \text{mol}}{0.1067\ \text{L}} = 9.56 \times 10^{-2}\ M$$

The $C_6H_5COO^-$ will undergo anion hydrolysis.

For C_6H_5COOH, $K_a = 6.3 \times 10^{-5}$ so K_b for $C_6H_5COO^-$ = $\frac{1.0 \times 10^{-14}}{6.3 \times 10^{-5}} = 1.6 \times 10^{-10}$

	$C_6H_5COO^-$ (aq) +	H_2O (l)	⇌	OH^- (aq) +	C_6H_5COOH (aq)
$[\ ]_i$	0.0956			~0	0
$\Delta[\ ]$	$-x$			$+x$	$+x$
$[\ ]_{eq}$	$0.0956 - x$			x	x

$$K_b = 1.6 \times 10^{-10} = \frac{[C_6H_5COOH][OH^-]}{[C_6H_5COO^-]} = \frac{x^2}{(0.0956 - x)} \approx \frac{x^2}{0.0956}$$

$x \approx 3.9 \times 10^{-6} = [OH^-]$ pOH = $-\log (3.9 \times 10^{-6}) = 5.41$

pH = 14.00 − 5.41 = 8.59

83. $$0.032\ L \times \frac{0.087\ mol\ C_2H_5NH_2}{1\ L} = 2.8 \times 10^{-3}\ mol\ C_2H_5NH_2$$

To reach the equivalence point, we must add 0.0028 mole H_3O^+. The corresponding volume of the HCl solution is given by:

$$\frac{0.0028\ mol\ H_3O^+}{0.15\ \frac{mol}{L}} = 1.9 \times 10^{-2}\ L = 19\ mL$$

total volume at equivalence point = 32 + 19 mL = 51 mL = 0.051 L

At equivalence point, all of the $C_2H_5NH_2$ initially present has been converted to $C_2H_5NH_3^+$. The concentration of $C_2H_5NH_3^+$ is:

$$[C_2H_5NH_3^+] = \frac{0.0028\ mol}{0.051\ L} = 5.5 \times 10^{-2}\ M$$

The $C_2H_5NH_3^+$ will undergo cation hydrolysis.

For $C_2H_5NH_2$, $K_b = 4.7 \times 10^{-4}$ so K_a for $C_2H_5NH_3^+$ = $\frac{1.0 \times 10^{-14}}{4.7 \times 10^{-4}} = 2.1 \times 10^{-11}$

	$C_2H_5NH_3^+$ (aq) +	H_2O (l)	⇌	H_3O^+ (aq) +	$C_2H_5NH_2$ (aq)
$[\ ]_i$	0.055			~0	0
$\Delta[\ ]$	−x			+ x	+ x
$[\ ]_{eq}$	0.055 −x			x	x

$$K_a = 2.1 \times 10^{-11} = \frac{[C_2H_5NH_2][H_3O^+]}{[C_2H_5NH_2]} = \frac{x^2}{(0.055 - x)} \approx \frac{x^2}{0.055}$$

$x \approx 1.1 \times 10^{-6}\ M = [H_3O^+]$ pH = $-\log (1.1 \times 10^{-6}) = 5.96$

85. 0.5000 L x 0.10 M NH_3 = 0.050 mol NH_3

0.2000 L x 0.15 M H_3O^+ = 0.030 mol H_3O^+

So 0.030 mol of NH_3 is converted to NH_4^+ and 0.020 mol NH_3 remain. The total volume is 0.7000 L

$$[NH_3] = \frac{0.020 \text{ mol}}{0.7000 \text{ L}} = 2.9 \times 10^{-2}\ M\ NH_3$$

$$[NH_4^+] = \frac{0.030 \text{ mol}}{0.7000 \text{ L}} = 4.3 \times 10^{-2}\ M\ NH_4^+$$

This is a buffer solution :

$$pH = pK_a + \log\frac{[\text{base}]}{[\text{acid}]} = 9.26 + \log\frac{(0.029)}{(0.043)} = 9.26 + (-0.17) = 9.09$$

87. $$\frac{2.2 \text{ g HSal} \times \dfrac{1 \text{ mol HSal}}{138.12 \text{ g}}}{1 \text{ L}} = 0.016\ M \text{ HSal}$$

Since pH = 2.43, $[H_3O^+] = 10^{-2.43} = 3.7 \times 10^{-3}\ M = [Sal^-]$

	HSal (aq) +	H_2O (l)	$\rightleftharpoons$	H_3O^+ (aq) +	Sal^- (aq)
$[\ ]_i$	0.016			~0	0
$[\ ]_{eq}$	0.016 − 0.0037			0.0037	0.0037

$$K_a = \frac{[Sal^-][H_3O^+]}{[HSal]} = \frac{(0.0037)^2}{(0.016 - 0.0037)} = 1.1 \times 10^{-3}$$

89. Since pH = 1.73, $[H_3O^+] = 10^{-1.73} = 1.9 \times 10^{-2}\ M = [SO_4^{2-}]$

	HSO_4^- (aq) +	H_2O (l)	$\rightleftharpoons$	H_3O^+ (aq) +	SO_4^{2-} (aq)
$[\ ]_i$	0.050			~0	0
$[\ ]_{eq}$	0.050 − 0.019			0.019	0.019

$$K_{a2} = \frac{[SO_4^{2-}][H_3O^+]}{[HSO_4^-]} = \frac{(0.019)^2}{(0.050 - 0.019)} = 1.2 \times 10^{-2}$$

91. For HCN, $K_a = 4.9 \times 10^{-10}$ so K_b for CN^- = $\frac{1.0 \times 10^{-14}}{4.9 \times 10^{-10}} = 2.0 \times 10^{-5}$

For HCO_3^-, $K_a = 4.8 \times 10^{-11}$ so K_b for CO_3^{2-} = $\frac{1.0 \times 10^{-14}}{4.8 \times 10^{-11}} = 2.1 \times 10^{-4}$

CO_3^{2-} is the stronger base since it has the larger value of K_b.

93.

	$Al(H_2O)_6^{3+}$ (aq) +	H_2O (l)	$\rightleftharpoons$	H_3O^+ (aq) +	$Al(H_2O)_5(OH)^{2+}$ (aq)
$[\ ]_i$	0.15			~0	0
$\Delta[\ ]$	$-x$			$+x$	$+x$
$[\ ]_{eq}$	$0.15 - x$			x	x

$$K_a = 1.4 \times 10^{-5} = \frac{[Al(H_2O)_5(OH)^{2+}][H_3O^+]}{[Al(H_2O)_6^{3+}]} = \frac{x^2}{(0.15 - x)} \approx \frac{x^2}{0.15}$$

$x \approx 1.4 \times 10^{-3}$ M = $[H_3O^+]$ pH = $-\log(1.4 \times 10^{-3}) = 2.85$

95.

$$\frac{11.0 \text{ g HTar} \times \frac{1 \text{ mol HTar}}{150.09 \text{ g}}}{1 \text{ L}} = 0.0733\ M \text{ HTar}$$

$$\frac{20.0 \text{ g Tar}^- \times \frac{1 \text{ mol Tar}^-}{188.18 \text{ g}}}{1 \text{ L}} = 0.106\ M \text{ Tar}^-$$

For HTar $K_{a1} = 1.0 \times 10^{-3}$ so $pK_{a1} = 3.00$

$$pH = pK_a + \log\frac{[\text{base}]}{[\text{acid}]} = 3.00 + \log\frac{(0.106)}{(0.0733)} = 3.00 + 0.16 = 3.16$$

97. For H_2CO_3 $K_{a1} = 4.3 \times 10^{-7}$ so $pK_{a1} = 6.37$

$$pH = pK_a + \log \frac{[base]}{[acid]}$$

$$7.40 = 6.37 + \log \frac{[HCO_3^-]}{[H_2CO_3]}$$

$$1.03 = \log \frac{[HCO_3^-]}{[H_2CO_3]}$$

$$\frac{[HCO_3^-]}{[H_2CO_3]} = 10^{1.03} = 10.7$$

99. 0.456 L x 0.10 M H_3O^+ = 0.0456 mol H_3O^+

0.285 L x 0.15 M OH^- = 0.0428 mol OH^-

This leaves an excess of 0.0028 mol H_3O^+ in 741 mL or 0.741 L

$$[H_3O^+] = \frac{0.0028 \text{ mol}}{0.741 \text{ L}} = 3.8 \times 10^{-3}\ M\ H_3O^+$$

pH = −log (3.8 x 10^{-3}) = 2.42

101. $$0.025 \text{ L} \times \frac{0.065 \text{ mol } C_7H_7NH_2}{1 \text{ L}} = 1.6 \times 10^{-3} \text{ mol } C_7H_7NH_2$$

To reach the equivalence point, we must add 0.0016 mole H_3O^+. The corresponding volume of the HCl solution is given by:

$$\frac{0.0016 \text{ mol } H_3O^+}{0.050 \frac{\text{mol}}{\text{L}}} = 3.2 \times 10^{-2} \text{ L} = 32 \text{ mL}$$

total volume at equivalence point = 32 + 25 mL = 57 mL = 0.057 L

At equivalence point, all of the $C_7H_7NH_2$ initially present has been converted to $C_7H_7NH_3^+$. The concentration of $C_7H_7NH_3^+$ is:

$$[C_7H_7NH_3^+] = \frac{0.0016 \text{ mol}}{0.057 \text{ L}} = 2.8 \times 10^{-2}\ M$$

The $C_7H_7NH_3^+$ will undergo cation hydrolysis.

For $C_7H_7NH_2$, $K_b = 4.7 \times 10^{-10}$ so K_a for $C_2H_5NH_3^+$ = $\frac{1.0 \times 10^{-14}}{4.7 \times 10^{-10}} = 2.1 \times 10^{-5}$

	$C_7H_7NH_3^+$ (aq) +	H_2O (l)	⇌	H_3O^+ (aq) +	$C_7H_7NH_2$ (aq)
[ ]$_i$	0.028			~0	0
Δ[ ]	−x			+ x	+ x
[ ]$_{eq}$	0.028 −x			x	x

$$K_a = 2.1 \times 10^{-5} = \frac{[C_7H_7NH_2][H_3O^+]}{[C_7H_7NH_2]} = \frac{x^2}{(0.028 - x)} \approx \frac{x^2}{0.028}$$

$x \approx 7.7 \times 10^{-4}$ $\quad \frac{7.7 \times 10^{-4}}{0.028} \times 100 = 2.8\%$

$x \approx 7.7 \times 10^{-4}\ M = [H_3O^+]$ pH = −log $(7.7 \times 10^{-4}) = 3.11$

103. a. Ignoring the second ionization, $[H_3O^+] = 0.100\ M$.

b. Following the first ionization, $[H_3O^+] = [HSO_4^-] = 0.100\ M$, and we use this as a starting point for an equilibrium calculation.

	HSO_4^- (aq) +	H_2O (l)	⇌	H_3O^+ (aq) +	SO_4^{2-} (aq)
[ ]$_i$	0.100			0.100	0
Δ[ ]	−x			+ x	+ x
[ ]$_{eq}$	0.100 −x			0.100 + x	x

$$K_{a2} = \frac{[SO_4^{2-}][H_3O^+]}{[HSO_4^-]} = \frac{(x)(0.100 + x)}{(0.100 - x)} = 1.1 \times 10^{-2}$$

Even with the relatively large $[H_3O^+]$ from the first ionization, the second ionization is still likely to proceed to an appreciable extent.

$x^2 + 0.100\ x = 1.1 \times 10^{-3} - 1.1 \times 10^{-2}\ x$

$x^2 + 0.111\ x - 1.1 \times 10^{-3} = 0$

$x = -0.12$ or 0.0092

$[H_3O^+] = 0.100 + 0.0092 = 0.109\ M$

105. a.

	$CH_3NH_3^+$ (aq) +	H_2O (l)	$\rightleftharpoons$	H_3O^+ (aq) +	CH_3NH_2 (aq)
$[\ ]_i$	0.10			~0	0
$[\ ]_{eq}$	$0.10 - 1.5 \times 10^{-6}$			1.5×10^{-6}	1.5×10^{-6}

$$K_a = \frac{[CH_3NH_2][H_3O^+]}{[CH_3NH_3^+]} = \frac{(1.5 \times 10^{-6})^2}{(0.10 - 1.5 \times 10^{-6})} = 2.3 \times 10^{-11}$$

$pK_a = -\log (2.3 \times 10^{-11}) = 10.64$

b. $$K_b = \frac{1.0 \times 10^{-14}}{2.3 \times 10^{-11}} = 4.3 \times 10^{-4}$$

c. $$pH = pK_a + \log \frac{[base]}{[acid]} = 10.64 + \log \frac{(0.250)}{(0.450)} = 10.64 + (-0.26) = 10.38$$

107. a. This is generally true because most weak acids have values of K_a such that the degree of dissociation is very small and the concentration of the undissociated acid is close to the initial concentration of the acid.

b. This is generally true for the reason given in a.

c. This is false. $[OH^-] = [H_3O^+]$ for neutral solutions. Unless K_a is very small ($\approx 1.0 \times 10^{-14}$, $[OH^-] << [H_3O^+]$.

d. This is false. It would be true only if HA were a strong acid.

e. This is false. It would be true only if HA were a strong acid.

f. This is generally true. We can assume that the only source of H_3O^+ is the ionization of HA, giving equal concentrations of H_3O^+ and A^-.

109. The moles of acid will be equal to the moles of NaOH added at the equivalence point.

a. 0.03383 L x 0.115 *M* OH^- = 0.00389 mol OH^-

$$\text{molar mass of acid} = \frac{0.288\ \text{g}}{0.00389\ \text{mol}} = 74.0\ \frac{\text{g}}{\text{mol}}$$

b. 16.92 mL is the half equivalence point at which pH = pK_a. This would have greatly simplified the determination of pK_a and therefore K_a.

0.01754 L x 0.115 *M* OH^- = 0.00202 mol OH^-.

So we have 0.00202 mol A^- and 0.00187 mol HA

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

Here we can use the mole ratio because the volume will just cancel out

$$4.92 = pK_a + \log\frac{0.00202}{0.00187} = pK_a + 0.034$$

$pK_a = 4.92 - 0.034 = 4.89$ $\quad K_a = 10^{-4.89} = 1.3 \times 10^{-5}$

111. a. The titration curve appears at the end of the problem. At 0% titration, we have a solution of weak base:

	NH_3 (aq) +	H_2O (l)	$\rightleftharpoons$	OH^- (aq) +	NH_4^+ (aq)
$[\ ]_i$	0.10			~0	0
$\Delta[\ ]$	−x			+ x	+ x
$[\ ]_{eq}$	0.10 −x			x	x

$$K_b = 1.8 \times 10^{-5} = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{(x)^2}{(0.10 - x)} \approx \frac{x^2}{0.10}$$

$x \approx 1.3 \times 10^{-3}\ M = [OH^-]$ $pOH = -\log(1.3 \times 10^{-3}) = 2.89$

$pH = 14.00 - 2.89 = 11.11$

At 30% titration we have added 15.0 mL of HCl

$0.0500\ L \times 0.10\ M\ NH_3 = 0.0050\ mol\ NH_3$

$0.0150\ L \times 0.10\ M\ H_3O^+ = 0.0015\ mol\ H_3O^+$

So 0.0015 mol of NH_3 is converted to NH_4^+ and 0.0035 mol NH_3 remain. The total volume is 0.0650 L

$$[NH_3] = \frac{0.0035\ mol}{0.0650\ L} = 5.4 \times 10^{-2}\ M\ NH_3$$

$$[NH_4^+] = \frac{0.0015\ mol}{0.0650\ L} = 2.3 \times 10^{-2}\ M\ NH_4^+$$

This is a buffer solution :

$$pH = pK_a + \log\frac{[base]}{[acid]} = 9.26 + \log\frac{(0.054)}{(0.023)} = 9.26 + (0.37) = 9.63$$

At 50% titration, we have a buffer in which we have equal concentrations of the base and conjugate acid.

$$pH = pK_a + \log\frac{[base]}{[acid]} = 9.26 + \log(1) = 9.26 + 0 = 9.26$$

At 100% titration, we are at the equivalence point

$$[NH_4^+] = \frac{0.0050\ mol}{0.1000\ L} = 5.0 \times 10^{-2}\ M\ NH_4^+$$ which undergoes hydrolysis

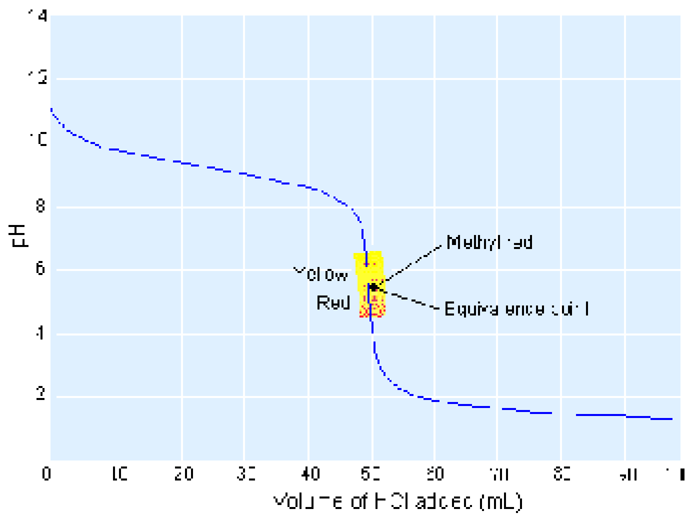
For NH_3, $K_b = 1.8 \times 10^{-5}$ so K_a for $NH_4^+ = \dfrac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$

	NH_4^+ (aq) +	H_2O (l)	$\rightleftharpoons$	H_3O^+ (aq) +	NH_3 (aq)
$[\ ]_i$	0.050			~0	0
$\Delta[\ ]$	− x			+ x	+ x
$[\ ]_{eq}$	0.050 − x			x	x

$$K_a = 5.6 \times 10^{-10} = \frac{[NH_3][H_3O^+]}{[NH_4^+]} = \frac{x^2}{(0.050 - x)} \approx \frac{x^2}{0.050}$$

$x \approx 5.3 \times 10^{-6}$ $M = [H_3O^+]$ pH = − log (5.3×10^{-6}) = 5.28

b. As indicated by the pH, the solution will be acidic at the equivalence point. This is the general case for the titration of a weak base with a strong acid.



113. a. We should select the pair whose acid has a pK_a closest to 2.88

$H_2C_2O_4$	$K_a = 5.6 \times 10^{-2}$	$pK_a = 1.25$
H_3PO_4	$K_a = 6.9 \times 10^{-3}$	$pK_a = 2.16$
HCOOH	$K_a = 1.7 \times 10^{-4}$	$pK_a = 3.77$

The best candidate is $H_3PO_4/H_2PO_4^-$.

b. $$pH = 2.88 = pK_a + \log\frac{[base]}{[acid]} = 2.16 + \log\frac{[base]}{[acid]}$$

$$\log\frac{[base]}{[acid]} = 0.72$$

$$\frac{[\text{base}]}{[\text{acid}]} = 10^{0.72} = 5.25$$

Since the concentrations of H_3PO_4 (A) and $H_2PO_4^-$ (B) are both 0.10, the volume ratio can be substituted for the concentration ratio.

So, $V_A + V_B = 50$ mL and $\frac{V_{base}}{V_{acid}} = 5.25$

$V_A + 5.25\ V_A = 50$ mL

$V_A = 6$ mL
$V_B = 42$ mL

115. a. $V_A\ M_A = V_B\ M_B$, since we have a monoprotic acid and a monoprotic base.

$$M_b = M_a \times \frac{V_a}{V_b} = 0.150\ M \times \frac{35.8 \text{ mL}}{25.0 \text{ mL}} = 0.215\ M$$

b. At the equivalence point we have a solution of NH_3OH^+ whose concentration is:

$$[NH_3OH^+] = \frac{25.0 \text{ mL} \times 0.215\ M}{(25.0 + 35.8) \text{ mL}} = 0.0884\ M$$

For NH_2OH, $K_b = 1.1 \times 10^{-8}$ so K_a for NH_3OH^+ = $\frac{1.0 \times 10^{-14}}{1.1 \times 10^{-8}} = 9.1 \times 10^{-7}$

	NH_3OH^+ (aq) +	H_2O (l)	$\rightleftharpoons$	H_3O^+ (aq) +	NH_2OH (aq)
$[\ ]_i$	0.0884			~0	0
$\Delta[\ ]$	$-x$			$+x$	$+x$
$[\ ]_{eq}$	$0.08840 - x$			x	x

$$K_a = 9.1 \times 10^{-7} = \frac{[NH_2OH][H_3O^+]}{[NH_3OH^+]} = \frac{x^2}{(0.0884 - x)} \approx \frac{x^2}{0.0884}$$

$x \approx 2.8 \times 10^{-4}\ M = [H_3O^+]$ pH = $-\log(2.8 \times 10^{-4}) = 3.55$

c. See Figure 15.8. Since the pH at the equivalence point will be about 3.55, we need an indicator that has a transition range around 3-4. Of those given, bromphenol blue is the only suitable indicator. The other two will turn well past the equivalence point.

117. a. $NH_3 + H_3O^+ \rightarrow NH_4^+ + H_2O$

b. $NH_4^+ + OH^- \rightarrow NH_3 + H_2O$

c. Note that the concentrations of NH_3 and NH_4^+ will be equal (there are two moles of NH_4^+ per one mole $(NH_4)_2SO_4$, so 0.50 M $(NH_4)_2SO_4$ is actually 1.0 M in NH_4^+.

$$0.1000\ L \times \frac{1.0\ mol\ NH_3}{1\ L} = 0.100\ mole\ NH_3$$

$$0.1000\ L \times \frac{1.0\ mol\ NH_4^+}{1\ L} = 0.100\ mole\ NH_4^+$$

$$0.0100\ L \times \frac{1.00\ mol\ H_3O^+}{1\ L} = 0.0100\ mole\ H_3O^+$$

The H_3O^+ will react with NH_3 changing the moles of NH_3 to 0.090 mol and NH_4^+ to 0.110. The total volume of the solution is now 0.110 L

$$[NH_3] = \frac{0.090\ mol}{0.110\ L} = 0.818\ M\ NH_3$$

$$[NH_4^+] = \frac{0.110\ mol}{0.110\ L} = 1.00\ M\ NH_4^+$$

$$pH = = pK_a + \log\frac{[base]}{[acid]} = 9.26 + \log\frac{0.818}{1.00} = 9.26 + (-0.087) = 9.17$$

d. This is a buffer, and the addition of acid causes only a slight change in the ratio of $[NH_3]$ to $[NH_4^+]$, causing only a very slight change in the pH.

119. a. For $H_2PO_4^-$ $K_a = 6.2 \times 10^{-8}$ and $pK_a = 7.21$

$$pH = = pK_a + \log \frac{[base]}{[acid]}$$

$$7.44 = 7.21 + \log \frac{[HPO_4^{2-}]}{[H_2PO_4^-]}$$

$$\log \frac{[HPO_4^{2-}]}{[H_2PO_4^-]} = 0.23$$

$$\frac{[HPO_4^{2-}]}{[H_2PO_4^-]} = 10^{0.23} = 1.7$$

$$\frac{[H_2PO_4^-]}{[HPO_4^{2-}]} = \frac{1}{1.7} = 0.59$$

b. Assume $[HPO_4^{2-}]$ = 1.7 *M* and therefore $[H_2PO_4^-]$ = 1.0 *M*. If 25% of the HPO_4^{2-} is converted to $H_2PO_4^-$, $[HPO_4^{2-}]$ becomes 0.75 x 1.7 *M* = 1.$\underline{2}$75 *M* and $[H_2PO_4^-]$ becomes 1.0 *M* + 0.25 x 1.7*M* = 1.$\underline{4}$25 *M*

$$pH = 7.21 + \log \frac{[HPO_4^{2-}]}{[H_2PO_4^-]} = 7.21 + \log \frac{1.\underline{2}75}{1.\underline{4}25} = 7.21 + (-0.048) = 7.16$$

c. Again assume $[HPO_4^{2-}]$ = 1.7 *M* and therefore $[H_2PO_4^-]$ = 1.0 *M*. If 15% of the $H_2PO_4^-$ is converted to HPO_4^{2-}, $[HPO_4^{2-}]$ becomes 1.7 + 0.15 x 1.0 *M* = 1.$\underline{8}$5 *M* and $[H_2PO_4^-]$ becomes 0.85 x 1.0 *M* = 0.8$\underline{5}$ *M*

$$pH = 7.21 + \log \frac{[HPO_4^{2-}]}{[H_2PO_4^-]} = 7.21 + \log \frac{1.\underline{8}5}{0.8\underline{5}} = 7.21 + (0.34) = 7.55$$

121. a. $H_2A\ (aq) + H_2O\ (l) \rightleftharpoons HA^-\ (aq) + H_3O^+\ (aq)$ $$K_1 = \frac{[H_3O^+][HA^-]}{[H_2A]}$$

$HA^-\ (aq) + H_2O\ (l) \rightleftharpoons A^{2-}\ (aq) + H_3O^+\ (aq)$ $$K_2 = \frac{[H_3O^+][A^{2-}]}{[HA^-]}$$

The equation whose K is K_1 x K_2 is given by the sum of these two equations:

H_2A (aq) + 2 H_2O (l) $\rightleftharpoons$ A^{2-} (aq) + 2 H_3O^+ (aq)

$$K_1 \times K_2 = \frac{[H_3O^+]^2[A^{2-}]}{[H_2A]}$$

b. $[H_2A] >> [H_3O^+] \approx [HA^-] >> [A^{2-}]$

$[H_2A]$ will be close to 0.50 *M* since $K_1 << 1$.

$[H_3O^+] \approx \{HA^-]$ since virtually all of the hydronium ion comes from the first ionization.

$[A^{2-}] \approx K_2$.

c.

	H_2A (aq) +	H_2O (l)	$\rightleftharpoons$	HA^- (aq) +	H_3O^+ (aq)
$[\ ]_i$	0.0250			0	~0
$\Delta[\ ]$	−x			+x	+x
$[\ ]_{eq}$	0.0250 − x			x	x

$$K_{a1} = \frac{[H_3O^+][HA^-]}{[H_2A]} = \frac{(x)(x)}{(0.0250 - x)} = 1.0 \times 10^{-3}$$

$x^2 + 1.0 \times 10^{-3} x - 2.5 \times 10^{-5} = 0$

x = 0.0045 or −0.0055 (reject negative root)

$[H_3O^+] = [HA^-] = 0.0045$ *M*

$[H_2A] = 0.0250 - 0.0045 = 0.0205$ *M*

Now use this as the starting point of the K_{a2} calculation:

	HA^- (aq) +	H_2O (l)	$\rightleftharpoons$	A^{2-} (aq) +	H_3O^+ (aq)
$[\ ]_i$	0.0045			0	0.0045
$\Delta[\ ]$	−y			+y	+y
$[\ ]_{eq}$	0.0045 − y			y	0.0045 + y

$$K_{a2} = \frac{[H_3O^+][A^{2-}]}{[HA^-]} = 4.6 \times 10^{-5} = \frac{(0.0045 + y)(y)}{(0.0045 - y)} \approx y$$

y = 4.6 x 10^{-5} M = $[A^{2-}]$

$[H_3O^+]$ = 0.0045 M + 4.6 x 10^{-5} M ≈ 0.0045 M pH = −log (0.0045) = 2.35

$[HA^-]$ = 0.0045 M − 4.6 x 10^{-5} M ≈ 0.0045 M

123. This solution will be a buffer with pH = 4.45 K_a = 1.7 x 10^{-5} pK_a = 4.77

$$4.45 = 4.77 + \log \frac{[CH_3CO_2^-]}{[CH_3CO_2H]}$$

$$\log \frac{[CH_3CO_2^-]}{[CH_3CO_2H]} = -0.32$$

$$\frac{[CH_3CO_2^-]}{[CH_3CO_2H]} = 10^{-0.32} = 0.479$$

In this solution therefore the ratio of moles of acetate to acetic acid will be 0.479 to 1

$$\frac{n_{CH_3CO_2^-}}{n_{CH_3CO_2H}} = 0.479 = \frac{x}{0.15 - x}$$ x = 0.04$\underline{8}$6 mole

$$[CH_3CO_2^-] = \frac{0.04\underline{8}6 \text{ mol}}{0.375 \text{ L}} = 0.13\ M$$

b. To get 0.04$\underline{8}$6 mol $CH_3CO_2^-$ we needed to add 0.04$\underline{8}$6 mol OH^-.

$$V_{NaOH} = \frac{0.04\underline{8}6 \text{ mol}}{0.25 \frac{\text{mol}}{\text{L}}} = 0.1\underline{9}4 \text{ L} = 1.9 \times 10^2 \text{ mL}$$

c. The original volume of the acetic acid solution is 375 mL − 1$\underline{9}$4 mL = 1$\underline{8}$1 mL = 0.1$\underline{8}$1 L

$$[CH_3CO_2H] = \frac{0.15 \text{ mol}}{0.1\underline{8}1 \text{ L}} = 0.83\ M$$