Chapter XV: Acid-Base Equilibria

Part 2, Sections 95 – 98

Unit 95 – Hydrolysis of Salts

95-1 Determine whether aqueous solutions of the following salts are acidic, basic, or neutral:

(a) $Al(NO_3)_3$
(b) RbI
(c) $KHCO_2$
(d) CH_3NH_3Br

Solution

(a) $Al(NO_3)_3$ dissociates into Al^{3+} ions (acidic metal cation) and NO_3^- ions (the conjugate base of a strong acid and therefore essentially neutral). The aqueous solution is therefore acidic.

(b) RbI dissociates into Rb^+ ions (neutral metal cation) and I^- ions (the conjugate base of a strong acid and therefore essentially neutral). The aqueous solution is therefore neutral.

(c) $KHCO_2$ dissociates into K^+ ions (neutral metal cation) and HCO_2^- ions (the conjugate base of a weak acid and therefore basic). The aqueous solution is therefore basic.

(d) CH_3NH_3Br dissociates into $CH_3NH_3^+$ ions (a weak acid) and Br^- ions (the conjugate base of a strong acid and therefore neutral). The aqueous solution is therefore acidic.

95-2 Determine whether aqueous solutions of the following salts are acidic, basic, or neutral:

(a) $FeCl_3$
(b) K_2CO_3
(c) NH_4Br
(d) $KClO_4$

Solution

(a) $FeCl_3$ dissociates into Fe^{3+} ions (acidic metal cation) and Cl^- ions (the conjugate base of a strong acid and therefore essentially neutral). The aqueous solution is therefore acidic.

(b) K_2CO_3 dissociates into K^+ ions (neutral metal cation) and CO_3^{2-} ions (the conjugate base of a weak acid and therefore basic). The aqueous solution is therefore basic.

(c) NH_4Br dissociates into NH_4^+ ions (a weak acid) and Br^- ions (the conjugate base of a strong acid and therefore essentially neutral). The aqueous solution is therefore acidic.

(d) $KClO_4$ dissociates into K^+ ions (neutral metal cation) and ClO_4^- ions (the conjugate base of a strong acid and therefore neutral). The aqueous solution is therefore neutral.

95-3 Determine whether the following 0.10 M aqueous solutions are acidic, basic or neutral. For each solution, indicate what the pH-determining reaction, the major species present, and the pH at 25 ºC. Note that Ka and Kb values for the weak acids and bases are available in the Appendices to this text.

(a) ammonium chloride, NH_4Cl

(b) hydrogen chloride, HCl

(c) lithium nitrite, $LiNO_2$

(d) sodium hydroxide, NaOH

(e) barium hydroxide, $Ba(OH)_2$

Solution:

(a) NH_4Cl dissociates into NH_4^+ ions (a weak acid) and Cl^- ions (the conjugate base of a strong acid and therefore essentially neutral). The aqueous solution is therefore acidic.

- The pH-determining reaction is $NH_4^+ \rightleftharpoons NH_3 + H^+$
- Major species present: H_2O (the solvent), NH_4^+, Cl^-.
- pH determination:

	$NH_4^+ \rightleftharpoons$	NH_3	$+ H^+$
I	0.100	0	~0
C	$-x$	$+x$	$+x$
E	$0.100-x$	x	x

We first need to calculate the Ka for NH_4^+ from the K_b for NH_3 (1.8×10^{-5})

$$K_w = K_a \times K_b$$

$$Ka = 10^{-14} / 1.8 \times 10^{-5} = 5.56 \times 10^{-10}$$

Then,

$$Ka = \frac{[NH_3][H^+]}{[NH_4^+]}$$

$$5.56\,x\,10^{-10} = \frac{[x][x]}{[0.10 - x]}$$

Given the very small value for Ka, we can assume that the "x" is neglible compared to 0.100 M, therefore the equation becomes:

$$5.56\,x\,10^{-10} = \frac{x^2}{0.10}$$

$$5.56 \times 10^{-11} = x^2$$

$$\sqrt{5.56\ x\ 10^{-11}} = \sqrt{x^2}$$

$$x = 7.45 \times 10^{-6}$$

Note that x is < 5% of 0.100, therefore our assumption was correct (we can neglect it in 0.100-x).

$$pH = -\log(7.45 \times 10^{-6})$$

$$pH = 5.13$$

(b) HCl is a strong acid and fully dissociates in aqueous solution. The Cl^- ions are pH neutral and so the solution is acidic.

- The pH-determining reaction is $HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$
- Major species present: H_2O (the solvent), H^+, Cl^-.
- pH determination: Since the HCl dissociates completely, the $[H^+] = 0.10$ M.
  $pH = -\log[H^+] = -\log(0.10) = 1.00$

(c) $LiNO_2$ dissociates into Li^+ ions (Group I metal, pH neutral) and NO_2^- ions (the conjugate base of a weak acid and therefore a weak base). The aqueous solution is therefore basic.

- The pH-determining reaction is $NO_2^- + H_2O \rightleftharpoons HNO_2 + OH^-$
- Major species present: H_2O (the solvent), Li^+, NO_2^-.
- pH determination:

We first need to calculate the Kb for NO_2^- from the K_a for HNO_2 (4.6×10^{-4})

$K_w = K_a \times K_b$
$Kb = 10^{-14} / 4.6 \times 10^{-4} = 2.17 \times 10^{-11}$

Then,

	NO_2^-	$\rightleftharpoons HNO_2$	$+ OH^-$
I	0.100	0	~0
C	$-x$	$+x$	$+x$
E	$0.100-x$	x	x

$$Kb = \frac{[HNO_2][OH^-]}{[NO_2^-]}$$

$$2.17\ x\ 10^{-11} = \frac{[x][x]}{[0.10 - x]}$$

Given the very small value for Kb, we can assume that the "x" is neglible compared to 0.100 M, therefore the equation becomes:

$$2.17\ x\ 10^{-1} = \frac{x^2}{0.10}$$

$$2.17 \text{ x } 10^{-12} = x^2$$

$$\sqrt{2.17\ x\ 10^{-12}} = \sqrt{x^2}$$

$$x = 1.47 \text{ x } 10^{-6}$$

Note that x is < 5% of 0.100, therefore our assumption was correct (we can neglect it in 0.100-x).

$$pOH = -\log(1.47 \text{ x } 10^{-6})$$

$$pOH = 5.83$$

$$pH + pOH = pKw$$

$$pH = 14.00\text{-}5.83$$

$$pH = 8.17$$

(d) sodium hydroxide dissociates completely into Na^+ ions (a group I metal, pH neutral) and OH^- (a strong base), and so the solution will be basic.

- The pH-determining reaction is $NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$
- Major species present: H_2O (the solvent), Na^+, OH^-.
- pH determination: Since the NaOH dissociates completely, the $[OH^-] = 0.10$ M.
  $pOH = -\log[OH^-] = -\log(0.10) = 1.00$
  $pH = pKw - pOH = 14.00 - 1.00 = 13.00$

(e) barium hydroxide dissociates completely into Ba^{2+} ions (a group II metal, pH neuetral0 and OH^- ions (a strong base), and so the solution will be basic.

- The pH determining reaction is $Ba(OH)_2\ (aq) \rightarrow Ba^{2+}(aq) + 2OH^-(aq)$
- Major species present: H_2O (the solvent), Ba^{2+}, OH^-.
- pH determination: Since the $Ba(OH)_2$ dissociates completely, each mole of $Ba(OH)_2$ produces TWO moles of OH^-. Thus the $[OH^-] = 2 \text{ x } 0.10 \text{ M} = 0.20$ M

  $pOH = -\log[OH^-] = -\log(0.20) = 0.70$

  $pH = pKw - pOH = 14.00 - 0.70 = 13.30$

95-4 Determine whether the following 0.10 M aqueous solutions are acidic, basic or neutral. For each solution, indicate what the pH-determining reaction, the major species present, and the pH at 25 ºC. Note that Ka and Kb values for the weak acids and bases are available in the Appendices to this text.

(a) sodium nitrate, $NaNO_3$

(b) sodium benzoate, $NaC_6H_5CO_2$

(c) potassium fluoride, KF

(d) methylammonium chloride, CH_3NH_3Cl

(e) sodium cyanide, NaCN

Solution:

(a) sodium nitrate dissociates completely into Na^+ (a group I neutral metal ion) and NO_3^- (the conjugate base of the strong acid HNO_3, so NO_3^- is an extremely weak base that is essentially pH neutral in aqueous solution). The solution will be neutral.

- The pH determining reaction is $H_2O\ (l) \rightleftharpoons H^+(aq) + OH^-(aq)$
- Major species present: H_2O (the solvent), Na^+, and NO_3^-.
- pH determination: since the only source of protons is through the autoionization of water, we know that the pH can be determined using the Kw of water at 25 oC,

$$Kw = [OH^-][H^+] = 10^{-14}$$

Since the

$$[OH^-] = [H^+],$$
$$([H^+])^2 = 10^{-14}$$
$$\sqrt{[H^+]} = \sqrt{10^{-14}}$$
$$[H^+] = 10^{-7}$$
$$pH = -\log 10^{-7} = 7.0$$

(b) $NaC_6H_5CO_2$ dissociates completely into Na^+ (a group I neutral metal ion) and $C_6H_5CO_2^-$ (the conjugate base of the weak acid benzoic acid, so $C_6H_5CO_2^-$ is a weak base). The solution will be basic.

- The pH-determining reaction is $C_6H_5CO_2^- + H_2O \rightleftharpoons C_6H_5CO_2H + OH^-$
- Major species present: H_2O (the solvent), Na^+, $C_6H_5CO_2^-$.
- pH determination:

We first need to calculate the Kb for $C_6H_5CO_2^-$ from the K_a for $C_6H_5CO_2H$ (6.3×10^{-5})

$K_w = K_a \times K_b$
$Kb = 10^{-14} / 6.3 \times 10^{-5} = 1.59 \times 10^{-10}$

Then,

	$C_6H_5CO_2^- \rightleftharpoons$	$C_6H_5CO_2H$	$+ OH^-$
I	0.100	0	~0
C	-*x*	+*x*	+*x*
E	0.100-*x*	*x*	*x*

$$Kb = \frac{[C_6H_5CO_2-][OH^-]}{[C_6H_5CO_2H]}$$

$$1.59 \times 10^{-10} = \frac{[x][x]}{[0.10 - x]}$$

Given the very small value for Kb, we can assume that the "x" is neglible compared to 0.100 M, therefore the equation becomes:

$$1.59 \times 10^{-10} = \frac{x^2}{0.10}$$

$$1.59 \times 10^{-11} = x^2$$

$$\sqrt{1.59 \times 10^{-11}} = \sqrt{x^2}$$

$$x = 3.99 \times 10^{-6}$$

Note that x is < 5% of 0.100, therefore our assumption was correct (we can neglect it in 0.100-x).

$$pOH = -\log(3.99 \times 10^{-6})$$

$$pOH = 5.40$$

$$pH + pOH = pKw$$

$$pH = 14.00-5.40$$

$$pH = 8.60$$

(c) KF dissociates dissociates completely into K^+ (a group I neutral metal ion) and F^- (the conjugate base of the weak acid HF, so F^- is a weak base). The solution will be basic.

- The pH-determining reaction is $F^- + H_2O \rightleftharpoons HF + OH^-$
- Major species present: H_2O (the solvent), K^+, F^-.
- pH determination:

We first need to calculate the Kb for F^- from the K_a for HF (6.4×10^{-4})

$K_w = K_a \times K_b$
$Kb = 10^{-14} / 6.4 \times 10^{-4} = 1.56 \times 10^{-11}$

Then,

	$F^- \rightleftharpoons$	HF	$+ OH^-$
I	0.100	0	~0
C	$-x$	$+x$	$+x$
E	$0.100-x$	x	x

$$Kb = \frac{[F-][OH^-]}{[HF]}$$

$$1.56 \times 10^{-11} = \frac{[x][x]}{[0.10 - x]}$$

Given the very small value for Kb, we can assume that the "x" is neglible compared to 0.100 M, therefore the equation becomes:

$$1.56 \times 10^{-11} = \frac{x^2}{0.10}$$

$$1.56 \times 10^{-12} = x^2$$

$$\sqrt{1.56 \times 10^{-12}} = \sqrt{x^2}$$

$$x = 1.25 \times 10^{-6}$$

Note that x is < 5% of 0.100, therefore our assumption was correct (we can neglect it in 0.100-x).

$$pOH = -\log(1.25 \times 10^{-6})$$

$$pOH = 5.90$$

$$pH + pOH = pKw$$

$$pH = 14.00-5.90$$

$$pH = 8.10$$

(d) CH_3NH_3Cl dissociates completely into $CH_3NH_3^+$ (the conjugate acid of a weak base) and Cl^- (the conjugate base of a very strong acid, so Cl^- is essentially pH neutral). The solution will be acidic.

- The pH-determining reaction is $CH_3NH_3^+ \rightleftharpoons CH_3NH_2 + H^+$
- Major species present: H_2O (the solvent), $CH_3NH_3^+$, Cl^-.

- pH determination:

	$CH_3NH_3^+ \rightleftharpoons$	CH_3NH_2	$+ H^+$
I	0.100	0	~0
C	-*x*	+*x*	+*x*
E	0.100-*x*	*x*	*x*

We first need to calculate the Ka for $CH_3NH_3^+$ from the K_b for CH_3NH_2 (4.4×10^{-4})

$$K_w = K_a \times K_b$$

$$Ka = 10^{-14} / 4.4 \times 10^{-4} = 2.27 \times 10^{-11}$$

Then,

$$Ka = \frac{[CH_3NH_2][H^+]}{[CH_3NH_3^+]}$$

$$2.27\ x\ 10^{-11} = \frac{[x][x]}{[0.10 - x]}$$

Given the very small value for Ka, we can assume that the "x" is neglible compared to 0.100 M, therefore the equation becomes:

$$2.27\ x\ 10^{-11} = \frac{x^2}{0.10}$$

$$2.27 \times 10^{-12} = x^2$$

$$\sqrt{2.27\ x\ 10^{-12}} = \sqrt{x^2}$$

$$x = 1.51 \times 10^{-6}$$

Note that x is < 5% of 0.100, therefore our assumption was correct (we can neglect it in 0.100-x).

$$pH = -\log(1.51 \times 10^{-6})$$

$$pH = 5.82$$

(e) NaCN dissociates dissociates completely into Na^+ (a group I neutral metal ion) and CN^- (the conjugate base of the weak acid HCN, so CN^- is a weak base). The solution will be basic.

- The pH-determining reaction is $CN^- + H_2O \rightleftharpoons HCN + OH^-$
- Major species present: H_2O (the solvent), Na^+, CN^-.
- pH determination:

We first need to calculate the Kb for CN^- from the K_a for HCN (4.9×10^{-10})

$K_w = K_a \times K_b$
$Kb = 10^{-14} / 4.9 \times 10^{-10} = 2.04 \times 10^{-5}$

Then,

	$CN^- \rightleftharpoons$	HCN	$+ OH^-$
I	0.100	0	~0
C	$-x$	$+x$	$+x$
E	$0.100-x$	x	x

$$Kb = \frac{[CN-][OH^-]}{[HCN]}$$

$$2.04 \times 10^{-5} = \frac{[x][x]}{[0.10 - x]}$$

Given the very small value for Kb, we can assume that the "x" is neglible compared to 0.100 M, therefore the equation becomes:

$$2.04 \times 10^{-5} = \frac{x^2}{0.10}$$

$$2.04 \times 10^{-6} = x^2$$

$$\sqrt{2.04 \times 10^{-6}} = \sqrt{x^2}$$

$$x = 1.43 \times 10^{-3}$$

Note that x is < 5% of 0.100, therefore our assumption was correct (we can neglect it in 0.100-x).

$$pOH = -\log(1.43 \times 10^{-3})$$

$$pOH = 2.84$$

$$pH + pOH = pKw$$

$$pH = 14.00-2.84$$

$$pH = 11.16$$

95-5 Novocaine, $C_{13}H_{21}O_2N_2Cl$, is the salt of the base procaine and hydrochloric acid. The ionization constant for procaine is 7×10^{-6}. Is a solution of novocaine acidic or basic? What are $[H_3O^+]$, $[OH^-]$, and pH of a 2.0% solution by mass of novocaine, assuming that the density of the solution is 1.0 g/mL.

Solution

Using the abbreviation Pc for $C_{13}H_{20}O_2N_2$ (procaine), the formula for novocaine is PcHCl, which ionizes to form PcH^+ and Cl^-. The molar mass of novocaine is 272.774 g/mol. For convenience, start with 1.00 L of a 2.0% solution by mass:

$1.00 \times 10^3\ cm^3 \times 1.0\ g\ cm^{-3} = 1.00 \times 10^3\ g$

$$\frac{2.0}{100} \times 1.00 \times 10^3\ g = 20\ g\ novocaine$$

$$= \frac{20\ g}{272.774\ g\ mol^{-1}}$$

$$= 0.073\ mol$$

In exactly 1 L, there is 0.073 *M*. The cation reacts with water:

$$PcH^+(aq) + H_2O(l) \rightleftharpoons Pc(aq) + H_3O^+(aq)$$

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-1}}{7 \times 10^{-6}} = 1.4 \times 10^{-9}$$

It is convenient to set up a table of concentrations:

	$[C_{13}H_{21}O_2N_2H^+]$ or $[PcH^+]$	$[H_3O^+]$	$[C_{13}H_{21}O_2N_2]$ or [Pc]
Initial concentration (*M*)	0.073	0	0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.073 - x$	x	x

$$1.4 \times 10^{-9} = \frac{[Pc][H_3O^+]}{[PcH^+]} = \frac{x^2}{0.073}$$

The change *x* compared with 0.073 *M* is small and, therefore, neglected:

$[H_3O^+] = x = 1.0 \times 10^{-5} = 1 \times 10^{-5}\ M$

The solution is acidic. The hydroxide ion concentration is:

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-5}} = 1 \times 10^{-9}\ M$$

$$pH = -\log(1.0 \times 10^{-5}) = 5.00 = 5.0$$

Unit 96 – Polyprotic Acids

96-1 Which of the following concentrations would be practically equal in a calculation of the equilibrium concentrations in a 0.134-*M* solution of H_2CO_3, a diprotic acid: $[H_3O^+]$, $[OH^-]$, $[H_2CO_3]$, $[HCO_3^-]$, $[CO_3^{2-}]$? No calculations are needed to answer this question.

Solution

$[H_3O^+]$ and $[HCO_3^-]$ are equal in a 0.134-*M* solution of H_2CO_3. K_a of H_2CO_3 is significantly larger than K_a for HCO_3^-. Therefore, very little of HCO_3^- ionizes to give hydronium ions and CO_3^{2-} ions, and the concentrations of H_3O^+ and HCO_3^- are practically equal in an aqueous solution of H_2CO_3.

96-2 Calculate the concentration of each species present in a 0.050 *M* solution of H_2S.

Solution

$$H_2S(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HS^-(aq) \qquad (K_{a1} = 8.9 \times 10^{-8})$$
$$HS^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + S^{2-}(aq) \qquad (K_{a2} = 1.0 \times 10^{-1})$$

As indicated by the K_a values, H_2S is a much stronger acid than HS^-, so H_2S is a dominant producer of H_3O^+ in solution:

	[H_2S]	[H_3O^+]	[HS^-]
Initial concentration (*M*)	0.05	~0	~0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.05 - x$	x	x

Assume that $(0.05 - x) = 0.05$. Thus:

$$K_{a1} = \frac{[H_3O^+][HS^-]}{[H_2S]} = 8.9 \times 10^{-8}$$
$$= \frac{(x)(x)}{0.05} = \frac{x^2}{0.05}$$

$x^2 = 0.05 \times 8.9 \times 10^{-8}$

$x = 6.7 \times 10^{-5}$

$[H_2S] = 0.050 - x = 0.050 - 6.7 \times 10^{-5} = 0.050\ M$

$[H_3O^+] = [HS^-] = x = 6.7 \times 10^{-5}\ M$

$$K_{a2} = \frac{[H_3O^+][S^{2-}]}{[HS^-]} = 1.0 \times 10^{-19}$$
$$= \frac{(6.7 \times 10^{-5})[S^{2-}]}{6.7 \times 10^{-5}} = 1.0 \times 10^{-19}\ M$$
$$[S^{2-}] = \frac{(1.0 \times 10^{-19})(6.7 \times 10^{-5})}{6.7 \times 10^{-5}} = 1 \times 10^{-1}\ \ M$$

The $[OH^-]$ can be calculated from K_w as follows:

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{6.7 \times 10^{-5}} = 1.5 \times 10^{-10}\ M$$

In summary, the concentrations of all species present in a 0.050-*M* solution of H_2S are:

$[H_2S] = 0.050\ M$

$[HS^-] = 6.7 \times 10^{-5}\ M$

$[H_3O^+] = 6.7 \times 10^{-5}\ M$

$[S^{2-}] = 1 \times 10^{-19}\ M$

$[OH^-] = 1.5 \times 10^{-10}\ M$

96-3 Calculate the concentration of each species present in a 0.010-*M* solution of phthalic acid, $C_6H_4(CO_2H)_2$.

$$C_6H_4(CO_2H)_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_6H_4(CO_2H)(CO_2)^-(aq) \qquad K_a = 1.1 \times 10^{-3}$$
$$C_6H_4(CO_2H)(CO_2)\ (aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_6H_4(CO_2)_2{}^{2-}(aq) \qquad K_a = 3.9 \times 10^{-6}$$

Solution

$[C_6H_4(CO_2H)_2]$ 7.2 × 10^{-3}*M*, $[C_6H_4(CO_2H)(CO_2)^-]$ = $[H_3O^+]$ 2.8 × 10^{-3}*M*, $[C_6H_4(CO_2)_2{}^{2-}]$ 3.9 × 10^{-6}*M*, $[OH^-]$ 3.6 × 10^{-12}*M*]

96-4 Salicylic acid, $HOC_6H_4CO_2H$, and its derivatives have been used as pain relievers for a long time. Salicylic acid occurs in small amounts in the leaves, bark, and roots of some vegetation (most notably historically in the bark of the willow tree). Extracts of these plants have been used as medications for centuries. The acid was first isolated in the laboratory in 1838.

(a) Both functional groups of salicylic acid ionize in water, with K_a = 1.0 × 10^{-3} for the—CO_2H group and 4.2 × 10^{-13} for the–OH group. What is the pH of a saturated solution of the acid (solubility = 1.8 g/L).

(b) Aspirin was discovered as a result of efforts to produce a derivative of salicylic acid that would not be irritating to the stomach lining. Aspirin is acetylsalicylic acid, $CH_3CO_2C_6H_4CO_2H$. The–CO_2H functional group is still present, but its acidity is reduced, K_a = 3.0 × 10^{-4}. What is the pH of a solution of aspirin with the same concentration as a saturated solution of salicylic acid (See Part a).

Solution

(a) First, find the concentration of the saturated solution. The molar mass of salicylic acid is 138.123 g/mol. This gives:

$$\frac{1.8\ \text{g L}^{-1}}{138.123\ \text{g mol}^{-1}} = 0.0130\ M$$

The reactions and equilibrium constants are:

$$HOC_6H_4CO_2H(aq) + H_2O(l) \rightleftharpoons HOC_6H_4CO_2{}^-(aq) + H_3O^+(aq) \qquad K_a = 1.0 \times 10^{-3}$$

$$HOC_6H_4CO_2H(aq) + H_2O(l) \rightleftharpoons HO_2CC_6H_4O^-(aq) + H_3O^+(aq) \qquad K_a = 4.2 \times 10^{-13}$$

Because the equilibrium constant for the first reaction is so much larger than for the second reaction, it will dominate. The equilibrium expression for this reaction is:

$$K_a = \frac{[HOC_6H_4CO_2{}^-][H_3O^+]}{[HOC_6H_4CO_2H]} = 1.0 \times 10^{-3}$$

The initial and equilibrium concentrations for this system can be written as follows:

	$[CH_3CO_2C_6H_4CO_2H]$	$[CH_3CO_2C_6H_4CO_2{}^-]$	$[H_3O^+]$
Initial concentration (*M*)	0.0130	0	0
Change (*M*)	−*x*	+*x*	+*x*
Equilibrium (*M*)	0.0130 − *x*	*x*	*x*

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumption that (0.0130 –*x*) ≈ 0.0130, gives:

$$\frac{[HOC_6H_4CO_2{}^-][H_3O^+]}{[HOC_6H_4CO_2H]} = \frac{(x)(x)}{(0.0130 - x)} \approx \frac{(x)(x)}{0.0130} = 1.0 \times 10^{-3}$$

Solving for *x* gives 3.61 × 10^{-3}*M*. Because this value is 28% of 0.0130 *M*, our assumption is incorrect. Therefore, use the quadratic formula. Using the provided data gives the quadratic equation:

$x^2 + 1.0 \times 10^{-3}x - 1.30 \times 10^{-5} = 0$

Using the quadratic formula gives (*a* = 1, *b* = 1.0 × 10^{-3}, and *c* = –1.30 × 10^{-5})

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-(1.0 \times 10^{-3}) \pm \sqrt{(1.0 \times 10^{-3})^2 - 4(1)(-1.30 \times 10^{-5})}}{2(1)}$$

$$= \frac{-(1.0 \times 10^{-3}) \pm (7.28 \times 10^{-3})}{2} = 3.14 \times 10^{-3}\ M \quad \text{(positive root)}$$

Thus, $[H^+] = 3.14 \times 10^{-3}\ M$

pH = $-\log(3.14 \times 10^{-3}) = 2.503 = 2.50$;

(b) The reaction and equilibrium constant are:

$$CH_3CO_2C_6H_4CO_2H(aq) + H_2O(l) \rightleftharpoons CH_3CO_2C_6H_4CO_2^-(aq) + H_3O^+(aq)$$

$$K_a = 3.0 \times 10^{-4}$$

The equilibrium expression for this reaction is:

$$K_a = \frac{[CH_3CO_2C_6H_4CO_2^-][H_3O^+]}{[CH_3CO_2C_6H_4CO_2H]} = 3.0 \times 10^{-4}$$

For a 0.0130-*M* initial concentration, the initial and equilibrium concentrations for this system can be written as follows:

	$[CH_3CO_2C_6H_4CO_2H]$	$[CH_3CO_2C_6H_4CO_2^-]$	$[H_3O^+]$
Initial concentration (*M*)	0.0130	0	0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.0130 - x$	x	x

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumption that $(0.0130 - x) \approx 0.0130$, gives:

$$\frac{[CH_3CO_2C_6H_4CO_2^-][H_3O^+]}{[CH_3CO_2C_6H_4CO_2H]} = \frac{(x)(x)}{(0.0130 - x)} \approx \frac{(x)(x)}{0.0130} = 3.0 \times 10^{-4}$$

Solving for *x* gives $1.97 \times 10^{-3}\ M$. Because this value is 15% of 0.0130, our assumption is incorrect. Therefore, use the quadratic formula. Using the above data gives the quadratic equation:

$x^2 + 3.0 \times 10^{-4}x - 3.90 \times 10^{-6} = 0$

Using the quadratic formula gives ($a = 1$, $b = 3.0 \times 10^{-4}$, and $c = -3.90 \times 10^{-6}$)

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-(3.0 \times 10^{-4}) \pm \sqrt{(3.0 \times 10^{-4})^2 - 4(1)(-3.90 \times 10^{-6})}}{2(1)}$$

$$= \frac{-(3.0 \times 10^{-4}) \pm (3.96 \times 10^{-3})}{2} = 1.83 \times 10^{-3}\ M \quad \text{(positive root)}$$

Thus, $[H^+] = 1.83 \times 10^{-3}\ M$

pH = $-\log(1.83 \times 10^{-3}) = 2.737 = 2.74$

96-5 The ion HTe^- is an amphiprotic species; it can act as either an acid or a base.

(a) What is K_a for the acid reaction of HTe^- with H_2O?

(b) What is K_b for the reaction in which HTe^- functions as a base in water?

(c) Demonstrate whether or not the second ionization of H_2Te can be neglected in the calculation of $[HTe^-]$ in a 0.10 *M* solution of H_2Te.

Solution

(a) as an acid,

$$HTe^-(aq) + H_2O(l) \rightleftharpoons Te^{2-}(aq) + H_3O^+(aq)$$

$K_{a2} = \frac{[Te^{2-}][H_3O^+]}{[HTe^-]} = 1.6 \times 10^{-1}$;

(b) as a base,

$$HTe^-(aq) + H_2O(l) \rightleftharpoons H_2Te(aq) + OH^-(aq)$$

$K_b = \frac{[H_2Te][OH^-]}{[HTe^-]} = \frac{K_w}{K_{a_1}} = \frac{1.0 \times 10^{-14}}{2.3 \times 10^{-3}} = 4.3 \times 10^{-12}$;

(c) The reactions and ionization constants are:

$$H_2Te(aq) + H_2O(l) \rightleftharpoons HTe^-(aq) + H_3O^+(aq) \qquad K_{a1} = 2.3 \times 10^{-3}$$
$$HTe^-(aq) + H_2O(l) \rightleftharpoons Te^{2-}(aq) + H_3O^+(aq) \qquad K_{a2} = 1.6 \times 10^{-11}$$

As a general rule, if the first ionization constant is larger than the second by a factor of at least 20, then the second ionization can be neglected. Since K_{a1} is 230-times larger than K_{a2}, the assumption should hold true for HTe^-. To test the assumptions, find [HTe^-] from the first reaction. The equilibrium expression for this reaction is $K_{a1} = \frac{[HTe^-][H_3O^+]}{[H_2Te]} = 2.3 \times 10^{-3}$.

The initial and equilibrium concentrations for this system can be written as follows:

	[H_2Te]	[HTe^-]	[H_3O^+]
Initial concentration (*M*)	0.10	0	0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.10 - x$	x	x

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumption that $(0.10 - x) \approx 0.10$, gives $\frac{[HTe^-][H_3O^+]}{[H_2Te]} = \frac{(x)(x)}{(0.10 - x)} \approx \frac{(x)(x)}{0.10} = 2.3 \times 10^{-3}$.

Solving for x gives 0.0152 *M*. Because this value is 15% of 0.10 *M*, our assumption is incorrect. Therefore, use the quadratic formula. Using the data gives the quadratic equation:

$x^2 + 2.3 \times 10^{-3}x - 2.3 \times 10^{-4} = 0$

Using the quadratic formula gives ($a = 1$, $b = 2.3 \times 10^{-3}$, and $c = -2.3 \times 10^{-4}$)

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-(2.3 \times 10^{-3}) \pm \sqrt{(2.3 \times 10^{-3})^2 - 4(1)(-2.3 \times 10^{-4})}}{2(1)}$$

$$= \frac{-(2.3 \times 10^{-3}) \pm (0.0304)}{2} = 0.0141\ M \quad \text{(positive root)}$$

Thus [HTe^-] = 0.014 *M*. For the second ionization, $K_{a2} = \frac{[Te^{2-}][H_3O^+]}{[HTe^-]} = 1.6 \times 10^{-11}$.

The initial and equilibrium concentrations for this system can be written as follows:

	[HTe^-]	[Te^{2-}]	[H_3O^+]
Initial concentration (*M*)	0.0141	0	0.0141
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.0141 - x$	x	$0.0141 + x$

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumptions that $(0.0140 - x) \approx$ and $(0.0141 + x) \approx 0.0141$, gives:

$$\frac{[\mathrm{Te}^{2-}][H_3O^+]}{[\mathrm{HTe}^-]} = \frac{(x)(0.0141\ +\ x)}{(0.0141\ -\ x)} \approx \frac{(x)(0.0141)}{0.0141} = 1.6 \times 10^{-1}$$

Solving for x gives 1.6×10^{-11} M. Therefore, compared with 0.014 M, this value is negligible (1.1×10^{-7} %).

Unit 97 – Buffers

97-1 Explain why a buffer can be prepared from a mixture of NH_4Cl and NaOH but not from NH_3 and NaOH.

Solution

OH^- is a base, and NH_4^+ is a weak acid. They react with one another to form NH_3, thereby setting up the equilibrium $NH_4^+(aq) + OH^-(aq) \rightleftharpoons NH_3(aq) + H_2O(l)$. Because both the base (NH_3) and the conjugate acid (NH_4^+) are present, a buffer is formed. However, in the second case, NH_3 and OH^- are both bases, so no buffer is possible.

97-2 Explain why the pH does not change significantly when a small amount of an acid or a base is added to a solution that contains equal amounts of the acid H_3PO_4 and a salt of its conjugate base NaH_2PO_4.

Solution

Excess H_3O^+ is removed primarily by the reaction:

$$H_3O^+(aq) + H_2PO_4^-(aq) \rightarrow H_2O(l) + H_3PO_4(aq)$$

Excess base is removed by the reaction:

$$OH^-(aq) + H_3PO_4(aq) \rightarrow H_2PO_4^-(aq) + H_2O(l)$$

97-3 Explain why the pH does not change significantly when a small amount of an acid or a base is added to a solution that contains equal amounts of the base NH_3 and a salt of its conjugate acid NH_4Cl.

Solution

A mixture of NH_3 and NH_4Cl is a buffer because it contains a weak base and its conjugate acid (the salt). If hydroxide ions are added, the ammonium ions in the buffer react with the hydroxide ions to form ammonia and water and reduce the hydroxide ion concentration toward its original value: $NH_4^+(aq) + OH^-(aq) \rightleftharpoons NH_3(aq) + H_2O(l)$.

If hydronium ions are added, the ammonia molecules in the buffer react with them to form ammonium ions, reducing the hydronium ion concentration toward its original value: $NH_3(aq) + H_3O^+(aq) \rightleftharpoons NH_4^+(aq) + H_2O(l)$.

97-4 What is $[H_3O^+]$ in a solution of 0.25 *M* CH_3CO_2H and 0.030 *M* $NaCH_3CO_2$?

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq) \qquad Ka = 1.8 \times 10^{-5}$$

Solution
The equilibrium expression is:

$$K_a = \frac{[CH_3CO_2^-][H_3O^+]}{[CH_3CO_2H]} = 1.8 \times 10^{-5}$$

The initial and equilibrium concentrations for this system can be written as follows:

	$[CH_3CO_2H]$	$[H_3O^+]$	$[CH_3CO_2^-]$
Initial concentration (*M*)	0.25	0	0.030
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.25 - x$	x	$0.030 + x$

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumptions that ($0.25 - x \approx 0.25$ and $0.030 + x \approx 0.030$.

$$\frac{[CH_3CO_2^-][H_3O^+]}{[CH_3CO_2H]} = \frac{(x)(0.030 + x)}{(0.25 - x)} \approx \frac{(x)(0.030)}{0.25} = 1.8 \times 10^{-5}$$

Solving for *x* gives $1.50 \times 10^{-4} M$. Because this value is less than 5% of both 0.25 and 0.030, our assumptions are correct. Therefore, $[H_3O^+] = 1.5 \times 10^{-4}\ M$.

This problem more easily be solved using the Henderson-Hasselbalch equation:

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

We can determine the pKa value from $pK_a = -\log(K_a) = -\log(1.8 \times 10^{-5}) = 4.74$

The [acid] ≈ 0.25M (since CH_3CO_2H is a weak acid, it does not significantly dissociate).
The [base] = 0.030 M (since $CH_3CO_2^-$ is a weak base, it does not significantly accept protons).
Thus,

$$pH = 4.74 + \log\frac{0.030\ M}{0.25\ M} = 4.74 + \log(0.12) = 4.74 + (-0.92) = 3.82$$

This number for the pH makes sense since [acid] > [base], and so the pH should be more acidic (lower) than the pKa value.

Since pH = -log $[H_3O^+]$,

3.82 = -log $[H_3O^+]$ and thus $[H_3O^+] = 10^{-3.82} = 1.5 \times 10^{-4}$ M.

97-5 What is $[H_3O^+]$ in a solution of 0.075 *M* HNO_2 and 0.030 *M* $NaNO_2$?

$$HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq) \qquad Ka = 4.6 \times 10^{-5}$$

Solution

This is another example of a problem that is easily solved using the Henderson-Hasselbach equation. We are provided with significant concentrations of both a weak acid, HNO_2, and its conjugate base, NO_2^-. (We know that HNO_2 is a weak acid since we are given its Ka value).

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

We can determine the pKa value from $pK_a = -\log(K_a) = -\log(4.6 \times 10^{-5}) = 4.34$

The [acid] ≈ 0.75M (since HNO_2 is a weak acid, it does not significantly dissociate); the [base] = 0.030 M (since NO_2^- is a weak base, it does not significantly accept protons).
Thus,

$$\text{pH} = 4.34 + \log\frac{0.030\text{ M}}{0.75\text{ M}} = 4.34 + \log(0.040) = 4.34 + (-1.40) = 2.94$$

This number for the pH makes sense since [acid] > [base], and so the pH should be more acidic (lower) than the pKa value.

Since pH = -log $[H_3O^+]$,

2.94 = -log $[H_3O^+]$ and thus $[H_3O^+] = 10^{-2.94} = 1.1 \times 10^{-3}$ M.

(Note that, depending on how many significant figures you carried through your calculations, you may obtain numbers such as 1.2×10^{-3} M which is fine).

97-6 What is $[OH^-]$ in a solution of 0.125 *M* CH_3NH_2 and 0.130 *M* CH_3NH_3Cl?

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

Solution:

The equilibrium expression is:

$$K_b = \frac{[CH_3NH_3^+][OH^-]}{[CH_3NH_2]} = 4.4 \times 10^{-4}$$

The initial and equilibrium concentrations for this system can be written as follows:

	$[CH_3NH_2]$	$[CH_3NH_3^+]$	$[OH^-]$
Initial concentration (*M*)	0.125	0.130	0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.125 - x$	$0.130 + x$	x

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumptions that $(0.125 - x) \approx 0.125$ and $(0.130 - x) \approx 0.130$, gives:

$$4.4 \times 10^{-4} = \frac{[CH_3NH_3^+][OH^-]}{[CH_3NH_2]}$$

$$4.4 \times 10^{-4} = \frac{[0.130 + x][x]}{[0.125 - x]}$$

$$4.4 \times 10^{-4} \approx \frac{[0.130][x]}{[0.125]}$$

$$x \approx \frac{(4.4 \times 10^{-4})(0.125)}{(0.130)}$$

$$x \approx 4.2 \times 10^{-4}\,M, \text{ thus } [OH^-] = 4.2 \times 10^{-4}\,M$$

Solving for x gives $4.23 \times 10^{-4}\,M$. Because this value is less than 5% of both 0.125 and 0.130, our assumptions are correct.

97-7 What is $[OH^-]$ in a solution of 1.25 *M* NH_3 and 0.78 *M* NH_4NO_3?

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \qquad Kb = 1.8 \times 10^{-5}$$

Solution
The equilibrium expression is

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5}$$

The initial and equilibrium concentrations for this system can be written as follows:

	$[NH_3]$	$[NH_4^+]$	$[OH^-]$
Initial concentration (*M*)	1.25	0.78	0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.125 - x$	$0.78 + x$	x

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumptions that $(1.25 - x) \approx 1.25$ and $(0.78 + x) \approx 0.78$, gives:

$$\frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{(0.78 - x)(x)}{(1.25 - x)} \approx \frac{(0.78)(x)}{(1.25)} = 1.8 \times 10^{-5}$$

Solving for x gives $2.88 \times 10^{-5} M$. Because this value is less than 5% of both 1.25 and 0.78, our assumptions are correct. Therefore, $[OH^-] = 2.9 \times 10^{-5}\ M$.

This problem can also be solved using the Henderson-Hasselbalch equation:

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

Caution is required: the H-H equation is written with respect to the pKa of the weak ACID. You cannot simply substitute with the pKb value; it is also important to assign the base and its conjugate acid properly. The solution contains 1.25 *M* NH_3 and 0.78 *M* NH_4NO_3. Since NO_3^- is simply a "spectator ion", there are appreciable quantities of both the acid (NH_4^+) and the conjugate base (NH_3) present. Let us rewrite the reaction in terms of the behaviour of the acid in aqueous solution:

$$NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq)$$

Note that the base is NH_3 and the conjugate acid is NH_4^+. Thus, [base] = $[NH_3] \approx 1.25$ M; [acid] = $[NH_4^+] \approx 0.78\ M$.

The H-H equation requires the pKa value for the acid NH_4^+] is related to the pKb of the conjugate base: pKa = pKw – pKb. The pKb = –logKb = –log (1.8×10^{-5}) = – (4.74) = 4.74. Thus the pKa = 14.00 – 4.74 = 9.26.

The Henderson-Hasselbalch equation becomes:

$$\text{pH} = \text{pKa} + \log\frac{[\,NH_3]}{[NH_4^+]}$$

$$\text{pH} = 9.26 + \log\frac{(1.25)]}{(0.78)} = 9.26 + \log(1.60) = 9.26 + (0.20)$$

$$pH = 9.46$$

We are asked for $[OH^-]$ (not pH), so the last step is to convert pH into $[OH^-]$. Recall that

$$pKw = pH + pOH.$$

Thus,

$$pOH = pKw - pH$$
$$pOH = 14.00 - 9.46 = 4.54$$
$$[OH^-] = 10^{-4.54} = 2.9 \times 10^{-5}\ M$$

97-8 What is the effect on the concentration of acetic acid, hydronium ion, and acetate ion when the following are added to an acidic buffer solution of equal concentrations of acetic acid and sodium acetate:

(a) HCl
(b) KCH_3CO_2
(c) NaCl
(d) KOH
(e) CH_3CO_2H

Solution
The equilibrium reaction and equilibrium constant are as follows:

$$CH_3CO_2H(aq) \rightleftharpoons H^+(aq) + CH_3CO_2^-(aq) \qquad Ka = 1.8 \times 10^{-5}$$

(a) HCl is a strong acid, and so will dissociate to form H^+ and Cl^- in aqueous solution. Thus the addition of HCl will increase the $[H^+]$. This will shift the equilibrium reaction indicated above to the left: i.e., the H^+ will react with the acetate ($CH_3CO_2^-$), thus producing more acetic acid (CH_3CO_2H). Thus, $[CH_3CO_2^-]$ decreases and $[CH_3CO_2H]$ increases.

(b) Potassium salts are extremely soluble in water, so the added KCH_3CO_2 will dissociate to form K^+ and $CH_3CO_2^-$ ions, thus increasing the $[CH_3CO_2^-]$. This will shift the equilibrium above to the left: the extra $CH_3CO_2^-$ will react with H^+, thus $[H^+]$ decreases slightly, while $[CH_3CO_2H]$ increases.

(c) The added NaCl will have no effect on the concentration of the ions. The NaCl will dissolve in the aqueous solution to form Na^+ and Cl^- ions, but these are not involved in the equilibrium above.

(d) The KOH is a strong base, and the ions will dissociate in aqueous solution to form K^+ and OH^- ions. The hydroxide ions will react with H^+ according to the neutralization reaction

$$OH^-(aq) + H^+(aq) \rightarrow H_2O(l)$$

Thus the $[H^+]$ will decrease. This will pull the equilibrium reaction above to the right: some CH_3CO_2H will dissociate to attempt to replenish the H^+, also producing more $CH_3CO_2^-$ in the process. Thus, $[CH_3CO_2H]$ decreases slightly and $[CH_3CO_2^-]$ increases.

(e) The addition of more CH_3CO_2H will shift the equilibrium above to the right. As some of the CH_3CO_2H dissociates, more H^+ and $CH_3CO_2^-$ will be produced. Thus both $[CH_3CO_2^-]$ and $[H^+]$ will increase.

97-9 What is the effect on the concentration of ammonia, hydroxide ion, and ammonium ion when the following are added to a basic buffer solution of equal concentrations of ammonia and ammonium nitrate:

(a) KI
(b) NH_3
(c) HI
(d) NaOH
(e) NH_4Cl

Solution
The equilibrium reaction and equilibrium constant are as follows:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \qquad Kb = 1.8 \times 10^{-5}$$

(a) The added KI will dissociate into K^+ and I^- ions in aqueous solution, but since neither ion is involved in the equilibrium, there will be no effect on the concentrations of the ammonia, hydroxide ions, or ammonium ions.
(b) The added NH_3 will increase its concentration, which will shift the equilibrium above to the right, producing more OH^- and NH_4^+. Thus, $[OH^-]$ and $[NH_4^+]$ both increase.
(c) The HI is a strong acid, and would dissociate completely in aqueous solution to form H^+ and I-. However, the H^+ will not persist since it will immediately react with OH- in a neutralization reaction according to

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

Since the OH^- is, thus, being used in this neutralization reaction, the $[OH^-]$ decreases, pulling the equilibrium reaction above to the right. Thus some NH_3 will react with water in order to attempt to partially replenish the OH^-, forming more NH_4^+ in the process. Thus $[NH_3]$ decreases and $[NH_4^+]$ increases.
(d) NaOH is a strong base and will completely dissociate in aquaeous solution to form Na+ and OH^- ions. Thus the $[OH^-]$ will increase, pushing the equilibrium above to the left. The OH- will react with some NH_4^+, forming NH_3 in the process. Thus the of $[NH_4^+]$ decreases and $[NH_3]$ increases.
(e) Ammonium salts are very soluble in water and will ionize to form NH_4^+ and Cl^- ions. Thus the $[NH_4^+]$ will increase, pushing the equilibrium above to the left. The NH_4^+ will react with some OH^-, forming some NH_3 will form in the process. Thus, $[OH^-]$ decreases and $[NH_3]$ increases.

97-10 What will be the pH of a buffer solution prepared from 0.20 mol NH_3, 0.40 mol NH_4NO_3, and just enough water to give 1.00 L of solution?

Solution
Nitrates are highly soluble in water, and ammonium nitrate (NH_4NO_3) will dissociate into the complex ions NH_4^+ and NO_3^- immediately in aqueous solution. The nitrate is a spectator ion and does not affect the pH; the ammonium (NH_4^+) is the conjugate acid of the weak base ammonia (NH_3). The reaction and equilibrium constant are:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \qquad Kb = 1.8 \times 10^{-5}$$

The equilibrium expression is:

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5}$$

The initial concentrations of NH_3 and NH_4^+ are 0.20 *M* and 0.40 *M*, respectively. The equilibrium concentrations for this system can be written as follows:

	$[NH_3]$	$[NH_4^+]$	$[OH^-]$
Initial concentration (*M*)	0.20	0.40	0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.20 - x$	$0.40 + x$	x

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumptions that $(0.20 - x) \approx 0.20$ and $(0.40 + x) \approx 0.40$, gives:

$$K_b = 1.8 \times 10^{-5} = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$1.8 \times 10^{-5} = \frac{(0.40 + x)(x)}{(0.20 - x)}$$

$$1.8 \times 10^{-5} \approx \frac{(0.40)(x)}{(0.20)}$$

$$x = \frac{(1.8 \times 10^{-5})(0.20)}{(0.40)}$$

$x = 9.00 \times 10^{-6}$ M

Solving for *x* gives 9.00×10^{-6} *M*. Because this value is less than 5% of both 0.20 and 0.40, our assumptions are correct. Therefore, $[OH^-] = 9.00 \times 10^{-6}$ *M*. Thus:

$$pOH = -\log(9.00 \times 10^{-6}) = 5.046$$

$$pH = 14.000 - pOH = 14.000 - 5.046 = 8.954 = 8.95$$

97-11 Calculate the pH of a buffer solution prepared from 0.155 mol of phosphoric acid, 0.250 mole of KH_2PO_4, and enough water to make 0.500 L of solution.

Solution

The reaction and equilibrium constant are:

$$H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + H_2PO_4^-(aq) \qquad Ka = 7.5 \times 10^{-3}$$

The equilibrium expression is

$$K_a = \frac{[H_3O^+][H_2PO_4^-]}{[H_3PO_4]} = 7.5 \times 10^{-3}$$

The initial concentration of $H_2PO_4^-$ = 0.250 mol / 0.500 L = 0.500 M; that of H_3PO_4= 0.155 mol / 0.500 L = 0310 M. The equilibrium concentrations for this system can be written as follows:

	$[H_3PO_4]$	$[H_3O^+]$	$[H_2PO_4^-]$
Initial concentration (*M*)	0.310	0	0.500
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.310 - x$	x	$0.500 + x$

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumptions that $(0.310 - x) \approx 0.310$ and $(0.500 + x) \approx 0.500$, gives:

$$K_a = \frac{[H_3O^+][H_2PO_4^-]}{[H_3PO_4]} = 7.5 \times 10^{-3}$$

$$7.5 \times 10^{-3} = \frac{(x)(0.500 + x)}{(0.310 - x)} \approx \frac{(x)(0.500)}{(0.310)}$$

$$x = \frac{(7.5 \times 10^{-3})(0.310)}{(0.0.500)} \approx 7.5 \text{ x } 10^{-3}$$

Solving for x gives 4.65×10^{-3} *M*. Because this value is less than 5% of both 0.310 and 0.500, our assumptions are correct. Therefore, $[H_3O^+] = 4.65 \times 10^{-3}$ *M*. Thus:

$$pH = -\log(4.65 \times 10^{-3}) = 2.333 = 2.33$$

97-12 How much solid $NaCH_3CO_2 \cdot 3H_2O$ must be added to 0.300 L of a 0.50-*M* acetic acid solution to give a buffer with a pH of 5.00? (Hint: Assume a negligible change in volume as the solid is added.)

Solution

This problem is most conveniently solved using the Henderson-Hasselbalch equation:

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

where the base is acetate ion and the acid is acetic acid.

The pK_a for acetic acid is

$$pK_a = -\log K_a = -\log 1.8 \text{ x } 10^{-5} = 4.74$$

Substitution of this value and the provided pH into the Henderson-Hasselbalch equation and rearranging to isolate the conjugate acid/base ratio yields

$$[C_2H_3O_2^-] / [HC_2H_3O_2] = 10^{(5.00 - 4.74)} = 10^{0.26} = 1.82$$

The small K_a for acetic acid means very little will undergo acid ionization, and so its concentration will be ~0.50 M. The molarity of acetate ion required is therefore

$$[C_2H_3O_2^-] = [HC_2H_3O_2] \times 1.82 = 0.50 \times 1.82 = 0.91 \text{ M}$$

The mass of sodium acetate trihydrate required is then

$$0.91 \text{ mol/L} \times 136.1 \text{ g/mol} \times 0.300 \text{ L} = 37 \text{ g}$$

97-13 What mass of NH_4Cl must be added to 0.750 L of a 0.100-*M* solution of NH_3 to give a buffer solution with a pH of 9.26? (Hint: Assume a negligible change in volume as the solid is added.)

Solution
This problem is most conveniently solved using the Henderson-Hasselbalch equation:

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

where the base is ammonia and the acid is ammonium ion.

The pK_a for ammonium ion is

$$pK_a = pK_w - pK_b = 14.00 - (-\log K_b) = 14.00 - 4.74 = 9.26$$

Substitution of this value and the provided pH into the Henderson-Hasselbalch equation and rearranging to isolate the conjugate acid/base ratio yields

$$[NH_3] / [NH_4^+] = 10^{(9.26 - 9.26)} = 10^{0.00} = 1.0$$

The small K_b for ammonia means very little will undergo base ionization, and so its concentration will be ~0.100 M. The molarity of ammonium ion required is therefore

$[NH_4^+] = [NH_3] / 1.0 = 0.100 / 1.00 = 0.10$ M

The mass of ammonium chloride required is then

0.10 mol/L × 53.49 g/mol × 0.750 L = 4.0 g

97-14 A buffer solution is prepared from equal volumes of 0.200 *M* acetic acid and 0.600 *M* sodium acetate. Use 1.80×10^{-5} as K_a for acetic acid.

(a) What is the pH of the solution?
(b) Is the solution acidic or basic?
(c) What is the pH of a solution that results when 3.00 mL of 0.034 *M* HCl is added to 0.200 L of the original buffer?

Solution
(a) The reaction and equilibrium constant are:

$$CH_3CO_2H(aq) \rightleftharpoons H^+(aq) + CH_3CO_2^-(aq) \qquad Ka = 1.8 \times 10^{-5}$$

The pH of the solution can be readily determined using the H-H equation. The acid is acetic acid, and its concentration was 0.200 M before dilution; the base is acetate and its

concentration was 0.600 M before dilution. We do not know the actual volumes of the two solutions added, but since equal volumes were added, the concentrations would be divided by 2. Since acetic acid and acetate are a weak acid and its conjugate base, we know that the final concentrations are about the same as the initial concentrations.

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

$$\text{pH} = -\log\left(1.8 \times 10^{-5}\right) + \log\frac{0.600\ \text{M}/2}{0.200\ \text{M}/2}$$

$$\text{pH} = 3.74 + \log 3.000$$

$$\text{pH} = 3.74 + (0.477) = 4.22$$

(b) The solution is acidic (since the pH is less than neutral).

(c) When 3.00 mL of 0.034 *M* HCl is added to 0.200 L of the original buffer, the moles of H+ added are as follows:

$$\text{Moles H}^+ = 3.00\ \text{mL} \times \frac{1\ L}{1000\ mL} \times \frac{0.034\ mol}{L}$$

$$\text{moles H}^+ = 1.02 \times 10^{-4}\ \text{mol}$$

This added H^+ will react with the base (acetate) to shift the equilibrium to the left

$$CH_3CO_2H(aq) \rightleftharpoons H^+(aq) + CH_3CO_2^-(aq)$$

resulting in the formation of more acetic acid. This changes the ratio of [acetate]:[acetic acid], and thus changes the pH. We can determine the exact ratio through stoichiometry: the extra 1.02×10^{-4} mol of H^+ will react with the same amount of acetate, forming 1.02×10^{-4} mol of acetic acid. We just need to first calculate how much acetate and acetic acid are initially present in 0.200 L of buffer:

For the acetic acid, the initial moles present equal 0.1000 *M* × 0.200 L = 0.0200 mol, and for acetate ion, 0.300 *M* × 0.200 L = 0.0600 mol. Thus:

	$CH_3CO_2H\ (aq) \rightleftharpoons$	$H^+(aq)$	$CH_3CO_2^-\ (aq)$
I	0.0200 mol	0.000102 mol	0.0600 mol
C	+0.000102 mol	-0.000102 mol	-0.000102 mol
E	0.020102	~0	0.059898 mol

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

$$\text{pH} = 3.74 + \log\frac{0.059898\ \text{mol}/0.200\ \text{L}}{0.020102\ \text{mol}/0.200\text{L}}$$

$$\text{pH} = 3.74 + \log 2.9797$$

$$\text{pH} = 3.74 + (0.474) = 4.22$$

You can see that the addition of a relatively small amount of extra acid has a negligible effect on the pH of the buffer solution: if we use the appropriate number of significant figures, the pH of the buffer is the same as it was before the HCl was added. This is to be expected of a buffer solution: it will resist a change in pH when extra acid or base is added.

97-15 A 5.36 g sample of NH_4Cl was added to 25.0 mL of 1.00 *M* NaOH and the resulting solution diluted to 0.100 L.

(a) What is the pH of this buffer solution?

(b) Is the solution acidic or basic?

(c) What is the pH of a solution that results when 3.00 mL of 0.034 *M* HCl is added to the solution?

Solution

(a) Ammonium chloride (NH_4Cl) will dissolve in aqueous solution to form ammonium (NH_4^+) and chloride (Cl^-) ions. Chloride ions are pH neutral (they do not affect the pH), but ammonium is a weak acid. It cannot form a buffer on its own, but since some strong base NaOH is also added to the solution, the OH^- ions will react with the NH_4^+ to form some ammonia (NH_3) in the solution. Then, since both NH_4^+ and its conjugate base are present, the solution is a buffer.

Thus, the approach to the problem is to first determine the stoichiometry of the reaction between the NH_4^+ and the OH^-, in order to determine the ratio between the NH_4^+ and it conjugate base, in order to determine the pH of the solution.

$$NH_4^+(aq) + OH^-(aq) \rightarrow NH_3(aq) + H_2O(l)$$

The MW of NH_4Cl is 53.4912 g/mol. Thus, the moles of NH_4^+ originally added can be determined as follows:

$$\text{mol } NH_4^+ = 5.36 \text{ g } NH_4Cl \times \frac{1 \text{ mol } NH_4Cl}{53.4912 \text{ g } NH_4Cl} \times \frac{1 \text{ mol } NH_4^+}{1 \text{ mol } NH_4Cl} = 0.1002 \text{ mol}$$

The moles of OH- added can be determined as follows:

$$\text{mol } OH^- = 1.00 \text{ M x } 0.0250 \text{ L} = 0.0250 \text{ mol.}$$

We can use an ICE table to determine the amounts of NH_4^+ and its conjugate base left after reaction:

	$NH_4^+(aq)$	$+ OH^-(aq) \rightarrow$	$NH_3(aq)$	$+ H_2O(l)$
I	0.1002 mol	0.0250 mol	0	
C	-0.0250 mol	-0.0250 mol	+0.0250 mol	
E	0.0752 mol	~0	0.0250 mol	

The equilibrium between ammonia and ammonium can be represented as below:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \qquad K_b = 1.8 \times 10^{-5}$$

It is easiest to solve for pH using the H-H equation, so we need to consider the equilibrium with the ammonium as the acid. We can determine the Ka from the Kb using either Ka x Kb = Kw, or else pKa + pKb = pKw. Since we ultimately need the pKa for the H-H equation, it is easier to use the latter approach.

pKb = -log(Kb) = -log (1.8×10^{-5}) = 4.74
pKa = pKw – pKb = 14.00 – 4.74 = 9.26

Thus,

$$NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq) \qquad pKa = 9.26$$

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

$$pH = 9.26 + \log\frac{0.0250/0.100L}{0.0752\ mol/0.100L}$$

$$pH = 9.26 + \log 0.332 = 9.26 + (-0.48) = 8.78$$

Note that we were told in the problem that the final volume of the buffer was 0.100 L. The volumes actually cancel out when we are using the H-H equation, the pH is determined by the ratio of [base]:[acid].

Unit 98 – Acid-Base Titrations

98-1 A 245.0 mL sample of 0.15 M $Ba(OH)_2$ is added to 438.0 mL of 0.200 M HNO_3. What is the pH of the resulting solution?

Solution:

Approach: note that $Ba(OH)_2$ is a strong base, which dissociates in solution to form two moles of OH^- for every mole of $Ba(OH)_2$ that was dissolved in the water. The HNO_3 is a strong acid, which also fully dissociates to H^+ and NO_3^-. The Ba^{2+} and NO_3^- are spectator ions; however the OH^- and H^+ will react in a neutralization reaction as follows:

$$OH^-(aq) + H^+(aq) \rightarrow H_2O(l)$$

Thus the key to solving this problem is to determine the number of moles of OH^- and H^+ that were originally added, in order to determine what the concentrations are after the neutralization reaction. An ICE table is useful for this purpose.

Thus:

$$\text{mol OH- = 245.0 mL Ba(OH)}_2 \times \frac{0.15\ mol\ Ba(OH)_2}{1000\ mL} \times \frac{2\ mol\ OH^-}{1\ mol\ Ba(OH)_2} = 0.0735 \text{ mol OH}^-$$

$$\text{mol H}^+ = 438.0 \text{ mL HNO}_3 \times \frac{0.200\ mol\ HN\ _3}{1000\ mL} \times \frac{1\ mol\ H^{\mp}}{1\ mol\ HNO_3} = 0.0876 \text{ mol H}^+$$

	$OH^-(aq)$ +	$H^+(aq)$	$\rightarrow H_2O(l)$
I	0.0735 mol	.0876 mol	
C	-0.0735 mol	-0.0735 mol	
E	~0	0.0141 mol	

Thus we know that we will be left with 0.0141 mol H+ in 683 mL (245+438) or 0.683 L of solution. The pH can be determined as follows:

$$\text{pH} = -\log[H^+] = -\log\frac{0.0141\ mol\ H^+}{0.683\ L} = -\log(0.02064) = -(-1.685) = 1.685$$

98-2 A 50.0 mL sample of 0.100 M NaOH is titrated with 45.0 mL of 0.100 M HCl. What is the pH of the resulting solution?

Solution:
This is another situation where we have the addition of a strong acid (H^+) to a strong base (OH^-), where we need to consider the stoichiometry of the neutralization reaction before determining the pH.

$$\text{mol OH}^- = 0.050 \text{ L x } 0.100 \text{ mol OH}^- / \text{L} = 0.0050 \text{ mol OH}^-$$

$$\text{mol H}^+ = 0.045 \text{ L x } 0.100 \text{ mol H}^+ / \text{L} = 0.0045 \text{ mol H}^+$$

	$OH^-(aq)$ +	$H^+(aq)$	$\rightarrow H_2O(l)$
I	0.0050 mol	0.0045 mol	
C	-0.0045 mol	-0.0045 mol	
E	0.00050 mol	~ 0 mol	

$$\text{pOH} = -\log[OH^-] = -\log\frac{0.00050\ mol\ OH^-}{(0.050+0.045)L} = -\log 0.00526 = -(-2.279) = 2.28$$

Since we know that pOH + pH = pKw, we can easily determine the pH as

$$\text{pH} = \text{pKw} - \text{pOH} = 14.00 - 2.28 = 11.72$$

98-3 A 45.0 mL sample of 0.150 M HCl is added to 38.0 mL of 0.200 M NaOH. What is the $[H^+]$ of the resulting solution? What is the pH? What is the pOH?

Solution:

This is another example of a strong acid being added to a strong base, so that a neutralization reaction will occur.

$$\text{mol } OH^- = 0.0380 \text{ L} \times 0.200 \text{ mol } OH^- / \text{L} = 0.00760 \text{ mol } OH^-$$

$$\text{mol } H^+ = 0.0450 \text{ L} \times 0.150 \text{ mol } H^+ / \text{L} = 0.00675 \text{ mol } H^+$$

	$OH^-(aq)$ +	$H^+(aq)$	$\rightarrow H_2O(l)$
I	0.00760 mol	0.00675 mol	
C	-0.00675 mol	-0. 0.00675 mol	
E	0.00085 mol	~ 0 mol	

$$\text{pOH} = -\log[OH^-] = -\log \frac{0.00085\ mol\ OH^-}{(0.0380+0.0450)L} = -\log 0.0102 = -(-1.990) = 1.990$$

Since we know that pOH + pH = pKw, we can easily determine the pH as

$$\text{pH} = \text{pKw} - \text{pOH} = 14.00 - 1.990 = 12.010$$

The $[H^+]$ can be determined from the pH as follows:

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

$$12.010 = -\log[H^+]$$

$$[H^+] = 10^{-12.010} = 9.80 \times 10^{-13} \text{ M}$$

98-4 A 45.0 mL sample of 0.15 M NaOH is added to 38.0 mL of 0.20 M acetic acid. What is the $[H^+]$ of the resulting solution? What is the pH? What is the pOH?

Solution:

This is another example of a neutralization reaction, but this situation could be a little different since a strong base is added to a weak acid. We start off the same way (looking at the stoichiometry of the neutralization reaction), but the method might be a little different afterwards, depending on the answer that we get.

$$CH_3CO_2H(aq) + OH^-(aq) \rightarrow CH_3CO_2^-(aq) + H_2O(l)$$

$$\text{mol } OH^- = 0.0450 \text{ L} \times 0.150 \text{ mol } OH^- / \text{L} = 0.00675 \text{ mol } OH^-$$

$$\text{mol } CH_3CO_2H = 0.0380 \text{ L} \times 0.200 \text{ mol } CH_3CO_2H / \text{L} = 0.00760 \text{ mol } CH_3CO_2H$$

	$CH_3CO_2H(aq)$	$+ OH^-(aq) \rightarrow$	$CH_3CO_2^-(aq)$	$+ H_2O(l)$
I	0.00760 mol	0.00675 mol		
C	-0.00675 mol	-0.00675 mol	+0.00675 mol	
E	0.00085 mol	~0	0.00675 mol	

We can see that the resulting solution has appreciable quantities of both a weak acid (CH_3CO_2H) and its conjugate base ($CH_3CO_2^-$), so we have created a buffer system. The pH can be determined using the Henderson-Hasselbach equation. Note that the equation technically requires the concentration of the acid and base, but since they are both in the same solution the volumes will cancel and we can just use moles. (You COULD include the volume – (45 mL + 38 mL = 83 mL or 0.083 L, but it is unnecessary to work it out since it will cancel).

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

$$\text{pH} = 4.76 + \log\frac{0.00675\ \text{mol/volume}}{0.00085\ \text{mol/volume}} = 4.76 + \log 7.941 = 4.76 + 0.8999 = 5.66$$

Since we know that pOH + pH = pKw, we can easily determine the pH as

$$\text{pOH} = \text{pKw} - \text{pH} = 14.00 - 5.66 = 8.34$$

The $[H^+]$ can be determined from the pH as follows:

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

$$5.66 = -\log[H^+]$$

$$[H^+] = 10^{-5.66} = 2.190 \times 10^{-6}\ \text{M}$$

98-5 Calculate the pH at the following points in a titration of 40.0 mL of 0.100 *M* barbituric acid (K_a = 9.8 x 10^{-5}) with 0.100 *M* KOH.

(a) no KOH added

(b) 20 mL of KOH solution added

(c) 39 mL of KOH solution added

(d) 40 mL of KOH solution added

(e) 41 mL of KOH solution added

Solution

(a) Let HA represent barbituric acid and A^- represent the conjugate base. The reaction and equilibrium constant are:

$$HA(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + H_3O^+(aq) \qquad K_a = 9.8 \times 10^{-5}$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = 9.8 \times 10^{-5}$$

The initial and equilibrium concentrations for this system can be written as follows:

	[HA]	[H_3O^+]	[A^-]
Initial concentration (*M*)	0.100	0	0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.100 - x$	x	x

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumption that $(0.100 - x) \approx 0.100$, gives:

$$\frac{[H_3O^+][A^-]}{[HA]} = \frac{(x)(x)}{(0.100 - x)} \approx \frac{(x)(x)}{0.100} = 9.8 \times 10^{-5}$$

Solving for x gives $3.13 \times 10^{-3} M$. Because this value is less than 5% of 0.100, our assumption is correct. Therefore, $[H_3O^+] = 3.13 \times 10^{-3}\ M$:
pH = –log (3.13×10^{-3}) = 2.504 = 2.50;

(b) The moles of OH^- added are given by:

$$\text{mol } OH^- = M \times V = (0.100\ M) \times (0.020\ \text{L}) = 0.00200\ \text{mol}$$

The initial moles of barbituric acid are given by:

$$\text{mol HA} = M \times V = (0.100\ M) \times (0.040\ \text{L}) = 0.00400\ \text{mol}$$

Assume that the added hydroxide ion reacts completely with an equal number of moles of HA, forming an equal number of moles of A^- in the process. Thus, the moles of the ions are given by:

$$\text{mol HA} = 0.00400 - 0.00200 = 0.00200\ \text{mol}$$
$$\text{mol } A^- = 0.00200\ \text{mol}$$

The total volume is:

$$40.0\ \text{mL} + 20.0\ \text{mL} = 60.0\ \text{mL} = 0.0600\ \text{L}$$

The initial concentrations of the ions are given by:

$$[HA] = \frac{0.00200\ \text{mol}}{0.0600\ \text{L}} = 0.0333\ M$$

$$[A^-] = \frac{0.00200\ \text{mol}}{0.0600\ \text{L}} = 0.0333\ M$$

The initial and equilibrium concentrations for this system can be written as follows:

	[HA]	[H_3O^+]	[A^-]
Initial concentration (*M*)	0.0333	0	0.0333
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.0333 - x$	x	$0.0333 + x$

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumptions that $(0.0333 - x) \approx 0.0333$ and $(0.0333 + x) \approx 0.0333$, gives:

$$\frac{[H_3O^+][A^-]}{[\text{HA}]} = \frac{(x)(0.0333 + x)}{(0.0333 - x)} \approx \frac{(x)(0.0333)}{0.0333} = 9.8 \times 10^{-5}$$

Solving for x gives $9.8 \times 10^{-5} M$. Because this value is less than 5% of 0.0333, our assumptions are correct. Therefore, $[H_3O^+] = 9.8 \times 10^{-5} M$:

$$\text{pH} = -\log(9.8 \times 10^{-5}) = 4.009 = 4.01;$$

(c) The moles of OH^- added are given by:

$\text{mol } OH^- = M \times V = (0.100\ M) \times (0.039\ \text{L}) = 0.00390 \text{ mol}$

The initial moles of barbituric acid are given by:

$\text{mol HA} = M \times V = (0.100\ M) \times (0.040\ \text{L}) = 0.00400 \text{ mol}$

Assume that the added hydroxide ion reacts completely with an equal number of moles of HA, forming an equal number of moles of A^- in the process. Thus, the moles of the ions are given by:

$\text{mol HA} = 0.00400 - 0.00390 = 0.00010 \text{ mol}$

$\text{mol } A^- = 0.00930 \text{ mol}$

The total volume is:

$40.0 \text{ mL} + 39.0 \text{ mL} = 79.0 \text{ mL} = 0.0790 \text{ L}$

The initial concentrations of the ions are given by:

$$[\text{HA}] = \frac{0.00010 \text{ mol}}{0.0790 \text{ L}} = 0.00127\ M$$

$$[A^-] = \frac{0.00390 \text{ mol}}{0.0790 \text{ L}} = 0.0494\ M$$

The initial and equilibrium concentrations for this system can be written as follows:

	[HA]	$[H_3O^+]$	$[A^-]$
Initial concentration (*M*)	0.00127	0	0.0494
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.00127 - x$	x	$0.0494 + x$

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumption that $(0.00127 - x) \approx 0.00127$ and $(0.0494 + x) \approx 0.0494$, gives:

$$\frac{[H_3O^+][A^-]}{[\text{HA}]} = \frac{(x)(0.0494 + x)}{(0.00127 - x)} \approx \frac{(x)(0.0494)}{0.00127} = 9.8 \times 10^{-5}$$

Solving for x gives $2.52 \times 10^{-6} M$. Because this value is less than 5% of 0.00127 and 0.0494, our assumptions are correct. Therefore, $[H_3O^+] = 2.52 \times 10^{-6} M$:

$$\text{pH} = -\log(2.52 \times 10^{-6}) = 5.599 = 5.60;$$

(d) The moles of OH^- added are given by:

$\text{mol } OH^- = M \times V = (0.100\ M) \times (0.040\ \text{L}) = 0.00400 \text{ mol}$

The initial moles of barbituric acid are given by:

$$\text{mol HA} = M \times V = (0.100\ M) \times (0.040\ \text{L}) = 0.00400 \text{ mol}$$

This is the equivalence point, where the moles of base added equal the moles of acid present initially. At the equivalence point:

$$\text{mol } A^- = 0.00400 \text{ mol}$$

The total volume is:

$$40.0 \text{ mL} + 40.0 \text{ mL} = 80.0 \text{ mL} = 0.0800 \text{ L}$$

The initial concentration of the conjugate base is:

$$[A^-] = \frac{0.00400 \text{ mol}}{0.0800 \text{ L}} = 0.0500\ M$$

The reaction and equilibrium constant are:

$$A^-(aq) + H_2O(l) \leftrightarrows HA(aq) + OH^-(aq)$$

$$K_b = \frac{[HA][OH^-]}{[A^-]} = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{9.8 \times 10^{-4}} = 1.08 \times 10^{-10}$$

The initial and equilibrium concentrations for this system can be written as follows:

	$[A^-]$	[HA]	$[OH^-]$
Initial concentration (*M*)	0.0500	0	0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.0500 - x$	x	x

Substituting the equilibrium concentrations into the equilibrium expression, and making the assumption that $(0.0500 - x) \approx 0.0500$, gives:

$$\frac{[HA][OH^-]}{[A^-]} = \frac{(x)(x)}{(0.0500 - x)} \approx \frac{(x)(x)}{0.0500} = 1.02 \times 10^{-10}$$

Solving for x gives $2.26 \times 10^{-6}\ M$. Because this value is less than 5% of 0.0500, our assumption is correct. Therefore, $[OH^-] = 2.26 \times 10^{-6}\ M$:

$$\text{pOH} = -\log(2.26 \times 10^{-6}) = 5.646$$

$$\text{pH} = 14.000 - \text{pOH} = 14.000 - 5.646 = 8.354 = 8.35;$$

(e) The moles of OH^- added are given by:

$$\text{mol } OH^- = M \times V = (0.100\ M) \times (0.041 \text{ L}) = 0.00410 \text{ mol}$$

The initial moles of barbituric acid are given by:

$$\text{mol HA} = M \times V = (0.100\ M) \times (0.040 \text{ L}) = 0.00400 \text{ mol}$$

This is past the equivalence point, where the moles of base added exceed the moles of acid present initially. The excess moles of hydroxide ion are given by:

$$\text{mol } OH^- = 0.00410 - 0.00400 = 0.00010 \text{ mol}$$

The total volume is:

$$40.0 \text{ mL} + 41.0 \text{ mL} = 81.0 \text{ mL} = 0.0810 \text{ L}$$

The concentration of OH^- is:

$$[OH^-] = \frac{0.00010 \text{ mol}}{0.0810 \text{ L}} = 0.0012\ M$$

$$\text{pOH} = -\log(0.0012) = 2.921$$

$$\text{pH} = 14.000 - \text{pOH} = 14.000 - 2.921 = 11.079 = 11.08$$

98-6 Consider the titration of 100.0 mL of 0.150 M formic acid (HCOOH, Ka = 1.8 x 10^{-4}) with 0.100 M NaOH. What is the pH at the following points?

(a) The start

(b) At the midpoint

(c) After 25.0 mL of the NaOH has been added

(d) After 90.0 mL of the NaOH has been added.

(e) At the equivalence point.

Solution:

(a) At the start of the titration, we have a solution that only contains a weak acid. We can determine the pH using the Ka expression:

The reaction is:

$$HCO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_2^-(aq)$$

The equilibrium expression is:

$$K_a = \frac{[HCO_2^-][H_3O^+]}{[HCO_2H]} = 1.8 \times 10^{-4}$$

The initial and equilibrium concentrations for this system can be written as follows:

	$HCO_2H \rightleftharpoons$	H_3O^+	HCO_2^-
I	0.150 M	~0	0
C	-*x*	+*x*	+*x*
E	0.150 - *x*	*x*	*x*

$$K_a = \frac{[HCO_2^-][H_3O^+]}{[HCO_2H]}$$

$$1.8 \times 10^{-4} = \frac{(x)(x)}{(0.150 - x)}$$

Since the Ka value is so small, we can assume that x would be negligible compared to 0.150 so that we can assume that we can neglect it. The equation thus becomes:

$$1.8 \times 10^{-4} = \frac{(x)(x)}{(0.150)}$$

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

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

$$x = 5.2 \times 10^{-3}\ M$$

Thus *x* is very small compared to the [ ] of the acid, so our assumption that we could neglect *x* was valid.

Since x = $[H^+]$ = 5.20 x 10^{-3}. The pH = -log$[H^+]$ = -log (5.20 x 10^{-3}) = - (-2.28) = 2.28

(b) At the midpoint, the acid would be "half-titrated", so that the [acid] = [conjugate base]. When this occurs, the pH = pKa.

pKa = -log (Ka) = -log (1.8 x 10^{-4}) = 3.74.

(c) The addition of 25.0 mL of 0.100 M NaOH to 100.0 mL of 0.150 M formic acid will cause a neutralization reaction.

$HCO_2H(aq) + OH^-(aq) \rightarrow HCO_2^-(aq) + H_2O(l)$

Depending on the stoichiometry of reaction, both formic acid and the conjugate base will be present in appreciable quantities, and so a buffer could be formed (depending on the ratio).

mol OH^- = 0.0250 L x 0.100 mol OH^- / L = 0.00250 mol OH^-

mol HCO_2H = 0.1000 L x 0.150 mol HCO_2H / L = 0.0150 mol HCO_2H

	$HCO_2H(aq)$	$+ OH^-(aq) \rightarrow$	$HCO_2^-(aq)$	$+ H_2O(l)$
I	0.0150 mol	0.00250 mol		
C	-0.00250 mol	-0.00250 mol	+0.00250 mol	
E	0.0125 mol	~0	0.00250 mol	

We can use the H-H equation to determine the pH. Since the volumes cancel out, we need only concern ourselves with the ratio of moles:

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

$$\text{pH} = 3.74 + \log\frac{[0.00250 \text{ mol/volume}]}{[0.0125 \text{ mol/volume}]}$$

pH = 3.74 + log 0.200 = 3.74 + (-0.699) = 3.04

Note that this pH is less than the pH at the midpoint (part b), which makes sense since we are not yet at the midpoint.

(d) The calculation of the pH after 90.0 mL of base has been added is very similar to the one that we just did.

mol OH^- = 0.0900 L x 0.100 mol OH^- / L = 0.00900 mol OH^-

mol HCO_2H = 0.1000 L x 0.150 mol HCO_2H / L = 0.0150 mol HCO_2H

	$HCO_2H(aq)$	$+ OH^-(aq) \rightarrow$	$HCO_2^-(aq)$	$+ H_2O(l)$
I	0.0150 mol	0.00900 mol		
C	-0.00900 mol	-0.00900 mol	+0.00900 mol	
E	.00600 mol	~0	0.00900 mol	

We can use the H-H equation to determine the pH. Since the volumes cancel out, we need only concern ourselves with the ratio of moles:

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

$$\text{pH} = 3.74 + \log\frac{[0.00900\ \text{mol/volume}]}{[0.00600\ \text{mol/volume}]}$$

$$\text{pH} = 3.74 + \log 1.5 = 3.74 + (0.176)) = 3.92$$

Here we have a pH > pKa, which makes sense since passed the midpoint (where the pH = pKa).

(e) At the equivalence point, enough base has been added to completely titrate the weak acid to its conjugate base.

$$HCO_2H(aq) + OH^-(aq) \rightarrow HCO_2^-(aq) + H_2O(l)$$

Since the number of moles of acid are 0.0150 mol

$$\text{mol } HCO_2H = 0.1000\ \text{L} \times 0.150\ \text{mol } HCO_2H / \text{L} = 0.0150\ \text{mol } HCO_2H$$

according to the stoichiometry of the neutralization reaction, it will required 0.0150 mol of hydroxide to attain the equivalence point. The volume of 0.100 M NaOH required to provide 0.0150 mol of base can be determined as follows:

$$\text{volume of } OH^- = 0.0150\ \text{mol } OH^- \times \frac{1\ L}{0.100\ mol} = 0.150\ L$$

Thus at the equivalence point, the pH-determining species will be the formate (HCO_2^-), which will be at a concentration of 0.0150 mol in 0.250 L (0.100 L + 0.150 L), or 0.0600 M.

The formate is, itself, a weak base and so will react with water as indicated:

$$HCO_2^-(aq) + H_2O(l) \rightleftharpoons HCO_2H(aq) + OH^-(aq)$$

We can determine the pH of the solution using the Kb expression. Note that we can determine the Kb since Ka x Kb = Kw.

	HCO_2^-	$\rightleftharpoons HCO_2H$	$OH^-(aq)$
I	0.0600 M	~0	0
C	$-x$	$+x$	$+x$
E	0.0600 M - x	x	x

$$K_b = \frac{[HCO_2H][OH^-]}{[HCO_2^-]}$$

$$\frac{1\ x\ 10^{-1}}{1.8\ x\ 10^{-4}} = \frac{(x)(x)}{(0.0600 - x)}$$

Since the Kb value is so small, we can assume that x would be negligible compared to 0.0600 so that we can assume that we can neglect it. The equation thus becomes:

$$5.56\ \times 10^{-11} = \frac{(x)(x)}{(0.0600)}$$

$$3.33 \text{ x } 10^{-12} = x^2$$

$$\sqrt{3.33\ \times 10^{-12}}\ = \sqrt{x^2}$$

$$x = 1.82 \text{ x } 10^{-6}$$

Thus *x* is <5% of the [ ] of the base, so our assumption that we could neglect *x* was valid.

Since x = $[OH^-]$ = 1.82 x 10^{-6}; The pOH = -log$[OH^-]$ = -log (1.82 x 10^{-6}) = - (-5.74) = 5.74

$$pH = pK_w - pOH = 14.00 - 5.74 = 8.26$$

This number looks about right, since we expect that the equivalence point of the titration of a weak acid with a strong base will be slightly basic.

98-7 Explain how to choose the appropriate acid-base indicator for the titration of a weak base with a strong acid.

Solution

At the equivalence point in the titration of a weak base with a strong acid, the resulting solution is slightly acidic due to the presence of the conjugate acid. Thus, pick an indicator that changes color in the acidic range and brackets the pH at the equivalence point. Methyl orange is a good example

98-8 Explain why an acid-base indicator changes color over a range of pH values rather than at a specific pH.

Solution

The color in an indicator depends on the ratio of nonionized to ionized forms. The predominant color in acid requires at least a 1:10 ratio of forms, whereas the predominant color in base requires a 10:1 ratio of forms. The transition from one condition to the other comes about by addition of acid or base requiring, in general, a change of two pH units between colors.