Problems Chapter 17 (Aqueous Equilibria)

1. For each of the following cases, decide whether the pH is less than 7, equal to 7, or greater than 7.
    a. Equal volumes of 0.10 M acetic acid (CH_3COOH) and 0.10 M KOH are mixed.
    b. 25 mL of 0.015 M NH_3 is mixed with 12 mL of 0.015 M HCl.
    c. 150 mL of 0.20 M HNO_3 is mixed with 75 mL of 0.40 M NaOH.
    d. 25 mL of 0.45 M H_2SO_4 is mixed with 25 mL of 0.90 M NaOH.

(a) pH > 7 (all CH_3COOH will be converted to its conjugate base CH_3COO^-)
(b) Stoichiometrically, HCl is LR (its moles are only enough to neutralize less than half of available NH_3). With excess unneutralized NH_3 remaining, pH > 7
(c) The moles of HNO_3 and NaOH are equal – so complete neutralization occurs. pH = 7, since it's a strong acid neutralized by a strong base (all resulting ions are very weak acids/bases)
(d) The moles of available OH^- equal those of protons available in H_2SO_4 – enough to convert all H_2SO_4 to HSO_4^- and then HSO_4^- to SO_4^{2-}. In the end SO_4^{2-} will be the major species remaining. Since it's a conjugate of a weak acid HSO_4^-, pH > 7 (not by a lot since HSO_4^- is relatively strong)

2. Calculate the hydronium ion concentration and the pH of the solution that results when 50.0 mL of 0.40 M NH_3 is mixed with 25.0 mL of 0.20 M HCl.

$$0.0500\ L \times \frac{0.40\ mol\ NH_3}{1.000\ L} = 0.020\ mol\ NH_3$$
$$0.0250\ L \times \frac{0.20\ mol\ HCl}{1.000\ L} = 0.0050\ mol\ HCl\ (LR)$$

	NH_3 (aq) +	**HCl (aq) →**	**NH_4Cl (aq) +**	**H_2O (l)**
Initial	0.020 mol	0.0050 mol	0	
Change	–0.0050 mol	–0.0050 mol	+0.0050 mol	
End	0.015 mol	0	0.0050 mol	

Final $[NH_3]$ = 0.20 M
Final $[NH_4^+]$ = 0.067 M

$$\boldsymbol{pH} = pK_a + log\frac{[NH_3]}{[NH_4^+]} = -\log(5.6 \times 10^{-10}) + log\frac{0.20\ M}{0.067\ M} = \mathbf{9.73}$$

$[H_3O^+] = 10^{-9.73} = 1.9 \times 10^{-10}$ M

3. Rank the following compounds in order of increasing solubility in water: Na_2CO_3, $BaCO_3$, Ag_2CO_3.

Na_2CO_3: soluble salt
$BaCO_3$: $K_{sp} = 2.6 \times 10^{-9}$
Ag_2CO_3: $K_{sp} = 8.5 \times 10^{-12}$

$2.6 \times 10^{-9} = [Ba^{2+}][CO_3^{2-}] = x^2 \rightarrow x = 5.1 \times 10^{-5}$ M
$8.5 \times 10^{-12} = [Ag^+]^2[CO_3^{2-}] = (2x)^2(x) \rightarrow 4x^3 = 8.5 \times 10^{-12} \rightarrow x = 1.3 \times 10^{-4}$ M

Na_2CO_3 > Ag_2CO_3 > $BaCO_3$ (least soluble)

4. A buffer solution is prepared by dissolving 1.50 g each of benzoic acid, C_6H_5COOH, and sodium benzoate, NaC_6H_5COO, in 150.0 mL of solution.
   a. What is the pH of this buffer solution?
   b. Which buffer component must be added, and in what quantity, to change the pH to 4.00?
   c. What quantity of 2.0 M NaOH or 2.0 M HCl must be added to the buffer to change the pH to 4.00?

$$1.50\ g\ C_6H_5CO_2H \times \frac{1\ mol}{122.12\ g} = 0.0123\ mol\ C_6H_5CO_2H$$
$$1.50\ g\ NaC_6H_5CO_2 \times \frac{1\ mol}{144.11\ g} = 0.0104\ mol\ NaC_6H_5CO_2$$

$[C_6H_5COOH]$ = 0.0819 M
$[NaC_6H_5COO]$ = 0.0694 M

$$\boldsymbol{pH} = pK_a + log\frac{[C_6H_5CO_2^-]}{[C_6H_5CO_2H]} = -\log(6.3 \times 10^{-5}) + log\frac{0.0694\ M}{0.0819\ M} = \mathbf{4.13}$$

To change the pH to 4.00 (more acidic), we need to add C_6H_5COOH.

$$pH = pK_a + log\frac{[C_6H_5CO_2^-]}{[C_6H_5CO_2H]} \rightarrow 4.00 = -\log(6.3 \times 10^{-5}) + log\frac{0.0694\ M}{(0.0819 + x)M}$$
$$\rightarrow -0.20 = log\frac{0.0694\ M}{(0.0818 + x)M} \rightarrow \frac{0.0694\ M}{(0.0818 + x)M} = 0.63 \rightarrow x$$
$$= 0.028\ M$$

$$\frac{0.028\ mol}{1\ L} \times 0.1500\ L \times \frac{122.12\ g}{1\ mol} = \mathbf{0.52\ g\ C_6H_5CO_2H}$$

To change the pH to 4.00 (more acidic), we need to add HCl. x moles of HCl will convert x moles of $C_6H_5COO^-$ into x moles of C_6H_5COOH.

$$\boldsymbol{pH} = pK_a + log\frac{[C_6H_5CO_2^-]}{[C_6H_5CO_2H]} \rightarrow 4.00 = -\log(6.3 \times 10^{-5}) + log\frac{\left(\frac{0.0104 - x}{V}\right)M}{\left(\frac{0.0123 + x}{V}\right)M}$$
$$\rightarrow \frac{(0.0104 - x)mol}{(0.0123 + x)\ mol} = 0.63 \rightarrow x = 0.0016\ mol\ HCl$$

$$0.0016\ mol\ HCl \times \frac{1\ L}{2.0\ mol} = \mathbf{0.82\ mL\ HCl}$$

5. What is the equilibrium constant for the following reaction?

$$AgCl\ (s) + I^-\ (aq) \Leftrightarrow AgI\ (s) + Cl^-\ (aq)$$

Does the equilibrium lie predominantly to the left or to the right? Will AgI form if iodide ion, I^-, is added to a saturated solution of AgCl?

$AgCl\ (s) \Leftrightarrow Ag^+\ (aq) + Cl^-\ (aq)$ $\quad K_{sp} = 1.8 \times 10^{-10}$
$Ag^+\ (aq) + I^-\ (aq) \Leftrightarrow AgI\ (s)$ $\quad K_{sp}^{-1} = (8.5 \times 10^{-17})^{-1}$

Net: $AgCl\ (s) + I^-\ (aq) \rightarrow AgI\ (s) + Cl^-\ (aq)$ $\quad$ **K** $= (1.8 \times 10^{-10})(8.5 \times 10^{-17})^{-1} = \mathbf{2.1 \times 10^6}$
Equilibrium lies to the right. AgI will, therefore, form.

6. A solution contains 0.10 M iodide ion, I^-, and 0.10 M carbonate ion, CO_3^{2-}.
   a. If solid $Pb(NO_3)_2$ is slowly added to the solution, which salt will precipitate first, PbI_2 or $PbCO_3$?
   b. What will be the concentration of the first ion that precipitates (CO_3^{2-} or I^-) when the second, more soluble salt begins to precipitate?

PbI_2: $K_{sp} = 9.8 \times 10^{-9} = [Pb^{2+}][I^-]^2 = 4x^3 \rightarrow x = 1.3 \times 10^{-3}$ M
$PbCO_3$: $K_{sp} = 7.4 \times 10^{-14} = [Pb^{2+}][CO_3^{2-}] = x^2 \rightarrow x = 2.7 \times 10^{-7}$ M

The molar solubility of $PbCO_3$ is much lower than that of PbI_2, so it should precipitate first.

When I^- begins precipitating, equilibrium must have been established between I^- and Pb^{2+}. Since I^- just began precipitating, its concentration is effectively unchanged (0.10 M). We need to find $[Pb^{2+}]$ when I^- just begins precipitating.

$K_{sp} = 9.8 \times 10^{-9} = [Pb^{2+}][I^-]^2 \rightarrow 9.8 \times 10^{-9} = [Pb^{2+}](0.10)^2 \rightarrow [Pb^{2+}] = 9.8 \times 10^{-7}$ M

Use this $[Pb^{2+}]$ to calculate $[CO_3^{2-}]$.

$K_{sp} = 7.4 \times 10^{-14} = [Pb^{2+}][CO_3^{2-}] \rightarrow 7.4 \times 10^{-14} = (9.8 \times 10^{-7}\ M)[CO_3^{2-}] \rightarrow$ $\mathbf{[CO_3^{2-}] = 7.6 \times 10^{-8}}$ **M.**

7. For the titration of 50.0 mL of 0.150 M ethylamine, $C_2H_5NH_2$, with 0.100 M HCl, find the pH at each of the following points, and then use that information to sketch the titration curve and decide on an appropriate indicator (K_b of ethylamine is 4.3×10^{-4}).
   a. At the beginning, before HCl is added.
   b. At the halfway point in the titration.

c. When 75% of the required acid has been added.
d. At the equivalence point.
e. When 10.0 mL more HCl has been added than is required.
f. Sketch the titration curve.
g. Suggest an appropriate indicator for this titration.

Ethylamine $K_b = 4.3 \times 10^{-4}$

(a) Initial pH: $[OH^-] = \sqrt{K_b[ethylamine]} = \sqrt{(4.3 \times 10^{-4})(0.150\ M)} = 8.0 \times 10^{-3}$
pOH = –log[OH^-] = 2.10
pH = 14.00 – pOH = **11.90**

(b) HEP pOH = pK_b = –log(4.3×10^{-4}) = 3.37
pH = 14.00 -3.37 = **10.63**

(c) $0.0500\ L \times \frac{0.150\ mol}{1\ L} = 7.50\ \times 10^{-3}\ mol\ ethylamine$
(7.50×10^{-3} mol)(0.75) = 5.63×10^{-3} mol acid added

	$CH_3CH_2NH_2$ +	HCl	→ H_2O	+ $CH_3CH_2NH_3^+$
Initial	0.00750 mol	0.00563 mol		0
Change	–0.00563 mol	–0.00563 mol		+0.00563 mol
End	0.00187 mol	0		0.00563 mol

$$pOH = pK_b + log\frac{CH_3CH_2NH_3^+}{CH_3CH_2NH_2} = -\log(4.3 \times 10^{-4}) + log\frac{0.00563\ mol}{0.00187\ mol} = 3.84$$
pH = 14.00 – pOH = **10.16**

(d) At the equivalence point all $CH_3CH_2NH_2$ has been converted to $CH_3CH_2NH_3^+$ (0.00750 mol). It took 0.00750 mol HCl to get there. The volume of HCl added is

$$0.00750\ mol\ HCl \times \frac{1\ L}{0.100\ mol} = 75.0\ mL$$

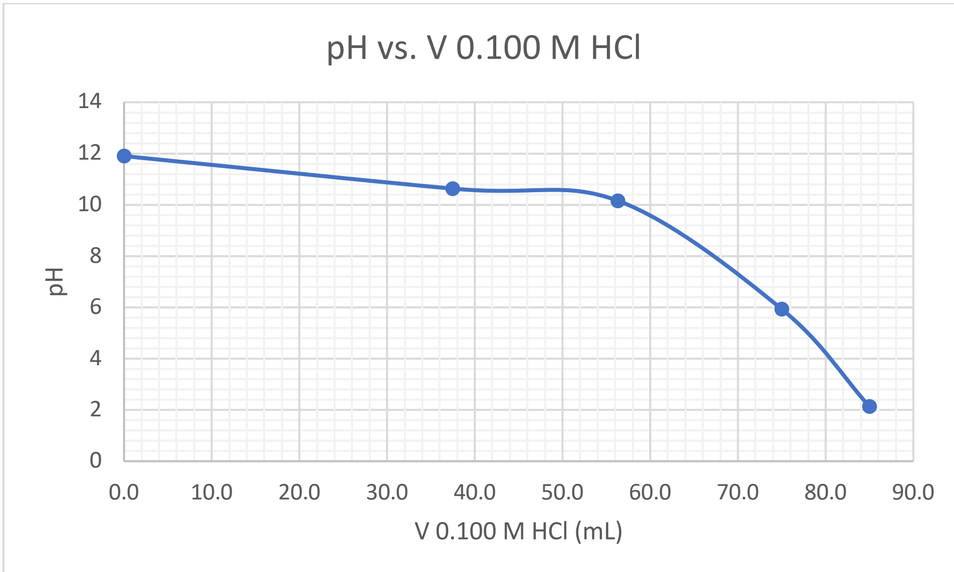
The total volume is 75.0 mL + 50.0 mL = 125.0 mL. [$CH_3CH_2NH_3^+$] = 0.0600 M

$$K_a = \frac{K_w}{4.3 \times 10^{-4}} = 2.3 \times 10^{-11}$$

$$[H^+] = \sqrt{2.3 \times 10^{-11}(0.0600\ M)} = 1.2\ \times 10^{-6}\ M$$
pH = –log[H^+] = **5.93**

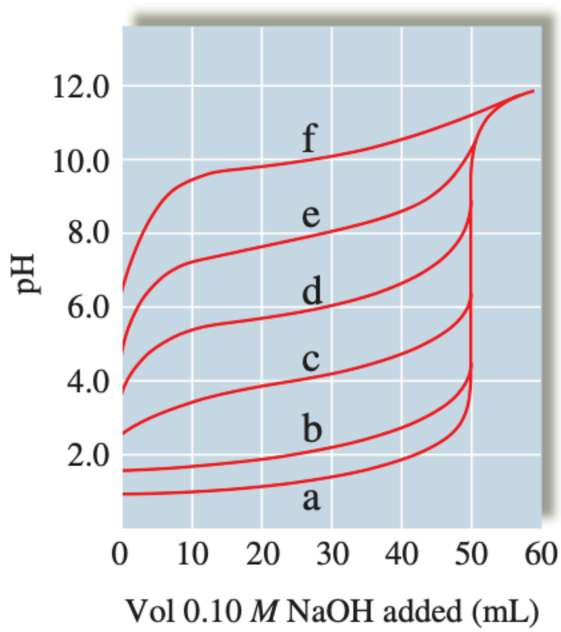
(e) 10.0 mL HCl will contain 1.00 x 10^{-3} mol H^+. The total volume is 135.0 mL. So $[H^+]$ = 7.41 x 10^{-3} M and **pH = 2.13**

(f)



(g) The color must change around pH 6 – bromcresol purple should work.

8. The following plot shows the pH curves for the titrations of various acids by 0.10 M NaOH (all of the acids were 50.0-mL samples of 0.10 M concentration).



   a. Which pH curve corresponds to the weakest acid?

b. Which pH curve corresponds to the strongest acid? Which point on the pH curve would you examine to see if this acid is a strong acid or a weak acid (assuming you did not know the initial concentration of the acid)?
c. Which pH curve corresponds to an acid with $K_a \approx 1 \times 10^{-6}$?

(a) The acid with curve (f). If the acids are equimolar (which is the case here), the weaker the acid, the higher the initial pH (since a smaller proportion of the weaker acid molecules donate their protons to H_2O to make H_3O^+).
(b) The acid with curve (a). Equivalence point is a good place to look (if pH = 7, the acid is strong – if pH > 7, the acid is weak).
(c) pH = pK_a at half equivalence point (here, 25.0 mL). (d) matches this.

9. Tris(hydroxymethyl)aminomethane, commonly called TRIS or Trizma, is often used as a buffer in biochemical studies. Its buffering range is pH 7 to 9, and K_b is 1.19×10^{-6} for the aqueous reaction.

$$\underset{\text{TRIS}}{(HOCH_2)_3CNH_2} + H_2O \Leftrightarrow \underset{\text{TRISH}^+}{(HOCH_2)_3CNH_3^+} + OH^-$$

a. What is the optimal pH for TRIS buffers?
b. Calculate the ratio [TRIS]/[TRISH$^+$] at pH = 7.00 and at pH = 9.00.
c. A buffer is prepared by diluting 50.0 g TRIS base and 65.0 g TRIS hydrochloride (written as TRISHCl) to a total volume of 2.0 L. What is the pH of this buffer? What is the pH after 0.50 mL of 12 M HCl is added to a 200.0-mL portion of the buffer?

a.

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.19 \times 10^{-6}} = 8.4 \times 10^{-9}$$

$$pH = pK_a = -\log(8.4 \times 10^{-9}) \sim \mathbf{8}$$

b.

$$7.00 = 8.08 + log\frac{[TRIS]}{[TRISH^+]} \to \frac{[TRIS]}{[TRISH^+]} = \mathbf{0.084}$$
$$9.00 = 8.08 + log\frac{[TRIS]}{[TRISH^+]} \to \frac{[TRIS]}{[TRISH^+]} = \mathbf{8.4}$$

c.

$$50.0\ g\ TRIS \times \frac{1\ mol}{121.4\ g} = 0.413\ mol\ TRIS$$
$$65.0\ g\ TRISH^+ \times \frac{1\ mol}{157.6\ g} = 0.412\ mol\ TRISH^+$$

$$pH = 8.08 + log\frac{0.413\ mol\ TRIS}{0.412\ mol\ TRISH^+} = \mathbf{8.08}$$

$$0.00050\ L \times \frac{12\ mol\ HCl}{1\ L} \times \frac{1\ mol\ H^+}{1\ mol\ HCl} = 0.0060\ mol\ H^+$$

$$0.2000\ L \times \frac{0.413\ mol\ TRIS}{2.0\ L} = 0.0413\ mol\ TRIS$$

$$0.2000\ L \times \frac{0.412\ mol\ TRISH^+}{2.0\ L} = 0.0412\ mol\ TRISH^+.$$

0.0060 mol H^+ will convert 0.0060 mol TRIS to 0.0060 mol $TRISH^+$. So there will be (0.0413 mol – 0.0060 mol) = 0.0353 mol TRIS and (0.0412 mol + 0.0060 mol) = 0.0472 mol $TRISH^+$.

$$\boldsymbol{pH} = 8.08 + log\frac{0.0353\ mol\ TRIS}{0.0472\ mol\ TRISH^+} = \mathbf{7.95}$$

10. Calculate the solubility of $Mg(OH)_2$ in 0.50 M NH_4Cl.

$Mg(OH)_2$ (s) ⇔ Mg^{2+} (aq) + 2 OH^- (aq) $K_{sp} = 5.6 \times 10^{-12}$

OH^- (aq) + NH_4^+ (aq) ⇔ H_2O (l) + NH_3 (aq) $K = K_b^{-1} = (1.8 \times 10^{-5})^{-1} = 5.5 \times 10^4$

2 OH^- (aq) + 2 NH_4^+ (aq) ⇔ 2 H_2O (l) + 2 NH_3 (aq) $K^2 = (5.5 \times 10^4)^2 = 3.1 \times 10^9$

Net rxn:

$Mg(OH)_2$ (s) + 2 NH_4^+ (aq) ⇔ Mg^{2+} (aq) + 2 H_2O (l) + 2 NH_3 (aq)

$K = K_{sp}K^2 = 1.7 \times 10^{-2}$

	$Mg(OH)_2$ (s) +	2 NH_4^+ (aq) ⇔	Mg^{2+} (aq) +	2 H_2O (l) +	2 NH_3 (aq)
I		0.50 M	0		0
C		–2x	+x		+2x
E		0.50 – 2x	x		2x

$$K = 1.7 \times 10^{-2} = \frac{[Mg^{2+}][NH_3]^2}{[NH_4^+]^2} = \frac{x(2x)^2}{(0.50 - 2x)^2} \rightarrow \boldsymbol{x = 0.079\ M}$$

11. One method for determining the purity of aspirin (molecular formula $C_9H_8O_4$) is to hydrolyze it with NaOH solution and then to titrate the remaining NaOH. The reaction of aspirin with NaOH is as follows:

$$\underset{\text{Aspirin}}{C_9H_8O_4(s)} + 2OH^-(aq) \xrightarrow[\text{10 min}]{\text{Boil}} \underset{\text{Salicylate ion}}{C_7H_5O_3^-(aq)} + \underset{\text{Acetate ion}}{C_2H_3O_2^-(aq)} + H_2O(l)$$

A sample of aspirin with a mass of 1.427 g was boiled in 50.00 mL of 0.500 M NaOH. After the solution was cooled, it took 31.92 mL of 0.289 M HCl to titrate the excess NaOH. Calculate the purity of the aspirin. What indicator should be used for this titration? Why?

$$0.03192\ L \times \frac{0.289\ mol\ HCl}{1\ L} \times \frac{1\ mol\ NaOH}{1\ mol\ HCl} = 9.22 \times 10^{-3}\ mol\ NaOH\ remain.$$

$$0.05000\ L \times \frac{0.500\ mol}{1\ L} = 0.0250\ mol\ NaOH\ originally\ present$$

0.0250 mol – 0.00922 mol = 0.0158 mol NaOH reacted

$$0.0158\ mol\ OH^- \times \frac{1\ mol\ C_9H_8O_4}{2\ mol\ OH^-} \times \frac{180.159\ g}{1\ mol\ C_9H_8O_4} = 1.42\ g$$

The aspirin is 99.6% pure.

In a strong base – strong acid titration, the pH at equivalence point is 7. Bromothymol blue is a good choice of indicator because it changes color around pH = 7.

12. You are asked to prepare a KH_2PO_4 – Na_2HPO_4 solution that has the same pH as human blood, 7.40.
    a. What should be the ratio of concentrations $[HPO_4^{2-}]/[H_2PO_4^-]$ in this solution?
    b. Suppose you have to prepare 1.00 L of the solution described in part (a) and that this solution must be isotonic with blood (have the same osmotic pressure as blood). What masses of KH_2PO_4 and of $Na_2HPO_4 \cdot 12\ H_2O$ would you use? (A solution of NaCl with 9.2 g NaCl/L solution is isotonic with blood. Assume that NaCl is completely ionized in aqueous solution)

(a) $7.40 = -\log(6.2 \times 10^{-8}) + log\frac{HPO_4^{2-}}{H_2PO_4^-} \rightarrow \frac{\boldsymbol{HPO_4^{2-}}}{\boldsymbol{H_2PO_4^-}} = \mathbf{1.56}$

(b) $9.2\ g\ NaCl \times \frac{1\ mol\ NaCl}{58.44\ g} \times \frac{2\ mol\ ions}{1\ mol\ NaCl} = 0.31\ mol\ ions/L$

Let x = $[HPO_4^{2-}]$ and y = $[H_2PO_4^-]$

$[HPO_4^{2-}] = 0.5[Na^+] \rightarrow [Na^+] = 2x$

$[H_2PO_4^-] = [K^+] \rightarrow [K^+] = y$

x = 1.56 y

$[Na^+] + [HPO_4^{2-}] + [K^+] + [H_2PO_4^-] = 0.314\ M \rightarrow 2x + x + y + y = 0.314\ M \rightarrow 3x + 2y = 0.314\ M \rightarrow 3(1.56y) + 2y = 0.31\ M \rightarrow y = 0.047\ M$

So 1.00 L of the solution should contain 0.047 mol $K^+/H_2PO_4^-$

$$0.047\ mol\ KH_2PO_4 \times \frac{136.086\ g}{1\ mol} = \mathbf{6.4\ g\ KH_2PO_4}$$

x = 0.073 M, so 1.00 L of the solution should contain 0.073 mol HPO_4^{2-}.

$$0.073\ mol\ Na_2HPO_4 \cdot 12H_2O \times \frac{358.102\ g}{1\ mol} = \mathbf{26\ g\ Na_2HPO_4 \cdot 12H_2O}$$

13. Because an acid-base indicator is a weak acid, it can be titrated with a strong base. Suppose you titrate 25.00 mL of a 0.0100 M solution of the indicator p-nitrophenol $HOC_6H_4NO_2$, with 0.0200 M NaOH. The pK_a of p-nitrophenol is 7.15, and it changes from colorless to yellow in the pH range from 5.6 to 7.6.
    a. Sketch the titration curve for this titration.
    b. Show the pH range over which p-nitrophenol changes color.
    c. Explain why p-nitrophenol cannot serve as its own indicator in this titration.

Initial pH

$$[H_3O^+] = \sqrt{(10^{-7.15})(0.0100\ M)} = 2.7 \times 10^{-5}\ M$$

pH = –log(2.7 x 10^{-5} M) = **4.57**

Equivalence point

$$0.02500\ L \times \frac{0.0100\ mol}{1\ L} = 2.50 \times 10^{-4}\ mol\ p-nitrophenol\ (HA)$$

$$2.50 \times 10^{-4}\ mol\ NaOH \times \frac{1\ L}{0.0200\ mol\ NaOH} = 0.0125\ L\ NaOH\ (aq) = 12.5\ mL$$

V = 25.00 mL HA + 12.5 mL NaOH = **37.5 mL**

$$\frac{2.50 \times 10^{-4}\ mol\ A^-}{0.0375\ L} = 6.67 \times 10^{-3}\ M\ A^-$$

$$K_b = \frac{1.0 \times 10^{-14}}{10^{-7.15}} = 1.4 \times 10^{-7}$$

$$[OH^-] = \sqrt{(1.4 \times 10^{-7})(6.67 \times 10^{-3}\ M)} = 3.1 \times 10^{-5}\ M$$

pOH = –log(3.1 x 10^{-5} M) = 4.51
pH = 14.00 – 4.51 = **9.49**

Half-equivalence point

pH = pK_a = **7.15**
V = 0.5(12.5 mL) = **6.25 mL**

Buffer region point 1: when **5.00 mL** of NaOH is added

$$0.00500\ L \times \frac{0.0200\ mol}{1\ L} = 1.00 \times 10^{-4}\ mol\ NaOH$$

Mol A^- = 1.00 x 10^{-4} mol
Mol HA = 2.50 x 10^{-4} mol – 1.00 x 10^{-4} mol = 1.50 x 10^{-4} mol

$$\boldsymbol{pH} = pK_a + log\frac{mol\ A^-}{mol\ HA} = 7.15 + log\frac{1.00 \times 10^{-4}\ mol}{1.50 \times 10^{-4}\ mol} = \boldsymbol{6.97}$$

Buffer region point 1: when **10.00 mL** of NaOH is added

$$0.01000\ L \times \frac{0.0200\ mol}{1\ L} = 2.00 \times 10^{-4}\ mol\ NaOH$$

Mol A^- = 2.00 x 10^{-4} mol
Mol HA = 2.50 x 10^{-4} mol – 2.00 x 10^{-4} mol = 5.0 x 10^{-5} mol

$$\boldsymbol{pH} = pK_a + log\frac{mol\ A^-}{mol\ HA} = 7.15 + log\frac{2.00 \times 10^{-4}\ mol}{5.0 \times 10^{-5}\ mol} = \boldsymbol{7.75}$$

Point past EP 1: when 15.00 mL of NaOH is added (2.50 mL past EP)

$$0.00250\ L \times \frac{0.0200\ mol}{1\ L} = 5.00 \times 10^{-5}\ mol\ NaOH$$

$$\frac{5.00 \times 10^{-5}\ mol\ OH^-}{0.04000\ L} = 1.25 \times 10^{-3}\ M\ OH^-$$

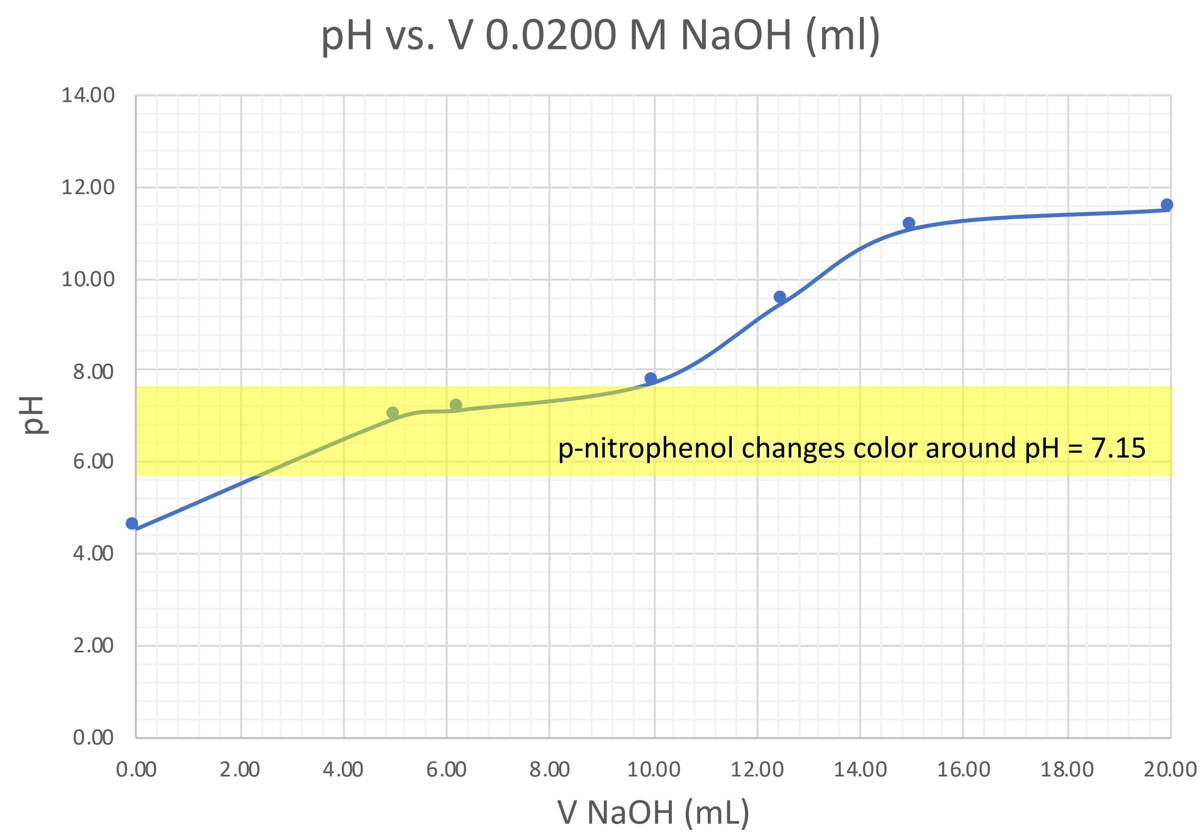
pOH = –log(1.25 x 10^{-3} M) = 2.90
pH = 14.00 – 2.90 = **11.10**

Point past EP 2: when 20.00 mL of NaOH is added (7.50 mL past EP)

$$0.00750\ L \times \frac{0.0200\ mol}{1\ L} = 5.00 \times 10^{-5}\ mol\ NaOH$$

$$\frac{5.00 \times 10^{-5}\ mol\ OH^-}{0.04500\ L} = 3.33 \times 10^{-3}\ M\ OH^-$$

pOH = –log(3.33 x 10^{-3} M) = 2.48
pH = 14.00 – 2.48 = **11.52**



p-nitrophenol changes color around the pH equal its pK_a (7.15). However, the pH at the equivalence point is 9.49. As a result, p-nitrophenol cannot serve as its own indicator as it will change color before its equivalence point is reached.

14. A series of titrations of lactic acid, $CH_3CH(OH)COOH$ (pK_a = 3.86) is planned. About 1.00 mmol of the acid will be titrated with NaOH (aq) to a final volume of about 100 mL at the equivalence point.
    a. Which acid-base indicator would you select for the titration?
    b. To assist in locating the equivalence point in the titration, a buffer solution is to be prepared having the same pH as that at the equivalence point. A few drops of the indicator in this buffer will produce the color to be matched in the titrations. Which of the following combinations would be suitable for the buffer solutions?
        i. CH_3COOH/CH_3COO^-
        ii. $H_2PO_4^-/HPO_4^{2-}$
        iii. NH_4^+/NH_3
    c. What ratio of conjugate base to acid is required in the buffer?

a. At the equivalence point, the concentration of lactate (CB of lactic acid) is

$$\frac{0.00100\ mol}{0.1\ L} = 0.01\ M$$

pK_b = 14.000 – 3.86 = 10.14

$$[OH^-] = \sqrt{(10^{-10.14})(0.01\ M)} = 8 \times 10^{-7}\ M$$

pOH = log[OH^-] = 6.1
pH = 14.00 – 6.1 = 7.93

b. We need an indicator that will change color around pH 7.9. ***m*-nitrophenol or phenol red will work.**

CH_3COOH: pK_a = –log(1.8 x 10^{-5}) = 4.74
$H_2PO_4^-$: pK_a = –log(6.2 x 10^{-8}) = 7.21
NH_4^+: pK_a = –log(5.6 x 10^{-10}) = 9.25

H_2PO_4/HPO_4^- match the required pH the closest

c.

$$pH = pK_a + log\frac{[HPO_4^{2-}]}{[H_2PO_4^-]} \rightarrow 7.9 = 7.21 + log\frac{[HPO_4^{2-}]}{[H_2PO_4^-]} \rightarrow \frac{[HPO_4^{2-}]}{[H_2PO_4^-]} = 10^{0.7} = \mathbf{5.3}$$

15. Two buffers are prepared by adding an equal number of moles of formic acid (HCOOH) and sodium formate (HCOONa) to enough water to make 1.00 L of solution. Buffer A is prepared using 1.00 mol each of formic acid and sodium formate. Buffer B is prepared by using 0.010 mol of each.
    a. Calculate the pH of each buffer.
    b. Which buffer will have the greater buffer capacity?
    c. Calculate the change in pH for each buffer upon the addition of 1.0 mL of 1.00 M HCl.
    d. Calculate the change in pH for each buffer upon the addition of 10. mL of 1.00 M HCl.

a. Since for both cases [$HCOO^-$] = [HCOOH], **pH** = pK_a = –log(1.8 x 10^{-4}) = **3.74**

b. The more concentrated buffer (1.00 M) has the greater buffering capacity (contains more moles of buffer, which can react with more H^+/OH^-).

c. $0.0010\ L \times \frac{1.00\ mol\ HCl}{1\ L} = 0.0010\ mol\ HCl$

0.0010 mol H^+ will convert 0.0010 mol $HCOO^-$ into HCOOH. So now there will be 0.999 mol $HCOO^-$ in the first buffer and 1.001 mol HCOOH.
In the second buffer, there will be 0.009 mol $HCOO^-$ and 0.011 mol HCOOH.

$$\boldsymbol{pH} = pK_a + log\frac{[HCOO^-]}{[HCOOH]} = 3.74 + log\frac{0.999\ mol}{1.001\ mol} = \mathbf{3.74}$$
$$\boldsymbol{pH} = pK_a + log\frac{[HCOO^-]}{[HCOOH]} = 3.74 + log\frac{0.009\ mol}{0.011\ mol} = \mathbf{3.66}$$

d.

$$0.010\ L \times \frac{1.00\ mol\ HCl}{1\ L} = 0.010\ mol\ HCl$$

0.010 mol H^+ will convert 0.010 mol $HCOO^-$ into HCOOH. So now there will be 0.99 mol $HCOO^-$ in the first buffer and 1.01 mol HCOOH.

In the second buffer, there will be 0 mol $HCOO^-$ and 0.020 mol HCOOH. It's not a buffer anymore, just a solution of HCOOH containing 0.020 mol HCOOH in 1.01 L (0.020 M HCOOH)

First buffer:

$$\boldsymbol{pH} = pK_a + log\frac{[HCOO^-]}{[HCOOH]} = 3.74 + log\frac{0.99\ mol}{1.01\ mol} = \boldsymbol{3.74}$$

(virtually no change in pH)

Second buffer:

$$[H^+] = \sqrt{(0.020\ M)(1.8 \times 10^{-4})} = 1.9 \times 10^{-3} M$$

pH = –log[H^+] = **2.72**

(pH drops by 1.02 units)

16. A biochemist needs 750 mL of an acetic acid – sodium acetate buffer with pH 4.50. Solid sodium acetate (CH_3COONa) and glacial acetic acid (CH_3COOH) are available. Glacial acetic acid is 99% CH_3COOH by mass and has a density of 1.05 g/mL. If the buffer is to be 0.15 M in CH_3COOH, how many grams of CH_3COONa and how many milliliters of glacia acetic acid must be used?

$$4.50 = -\log(1.8 \times 10^{-5}) + log\frac{[CH_3COO^-]}{0.15\ M} \rightarrow [CH_3COO^-] = 0.085\ M$$

$$0.75\ L \times \frac{0.15\ mol\ CH_3COOH}{1\ L} \times \frac{60.052\ g\ CH_3COOH}{1\ mol\ CH_3COOH} \times \frac{100\ g\ GAA}{99\ g\ CH_3COOH} \times \frac{1\ mL}{1.05\ g\ GAA}$$
$$= \boldsymbol{6.5\ mL\ GAA}$$

$$0.75\ L \times \frac{0.085\ mol\ CH_3COO^-}{1\ L} \times \frac{1\ mol\ CH_3COONa}{1\ mol\ CH_3COO^-} \times \frac{82.0343\ g}{1\ mol\ CH_3COONa}$$
$$= \boldsymbol{5.2\ g\ CH_3COONa}$$

17. The solubility of $CaCO_3$ is pH dependent.
   a. Calculate the molar solubility of $CaCO_3$ ($K_{sp} = 4.5 \times 10^{-9}$) neglecting the acid-base character of the carbonate ion.
   b. Use the K_b expression for the CO_3^{2-} ion to determine the equilibrium constant for the reaction

   $$CaCO_3\ (s) + H_2O\ (l) \Leftrightarrow Ca^{2+}\ (aq) + HCO_3^-\ (aq) + OH^-\ (aq)$$

   c. If we assume that the only sources of Ca^{2+}, HCO_3^- and OH^- ions are from the dissolution of $CaCO_3$, what is the molar solubility of $CaCO_3$ using the equilibrium expression from part (b)?

d. What is the molar solubility of $CaCO_3$ at the pH of the ocean (8.3)?
e. If the pH is buffered at 7.5, what is the molar solubility of $CaCO_3$?

a. $4.5 \times 10^{-9} = [Ca^{2+}][CO_3^{2-}] \rightarrow 4.5 \times 10^{-9} = x^2 \rightarrow$ **$x = 6.7 \times 10^{-5}$ M**
b. $CaCO_3\ (s) \Leftrightarrow Ca^{2+}\ (aq) + CO_3^{2-}\ (aq)$ $K_{sp} = 4.5 \times 10^{-9}$
$CO_3^{2-}\ (aq) + H_2O\ (l) \Leftrightarrow HCO_3^-\ (aq) + OH^-\ (aq)$ $K_b = 2.1 \times 10^{-4}$
$K_{net} = K_{sp}K_b = (4.5 \times 10^{-9})(2.1 \times 10^{-4}) =$ **9.4×10^{-13}**
c. $K_{net} = [Ca^{2+}][HCO_3^-][OH^-] = x^3 \rightarrow$ **$x = 9.8 \times 10^{-5}$ M**
d. pOH = 14.00 – 8.3 = 5.7
$[OH^-] = 10^{-5.7} = 2.0 \times 10^{-6}$ M
$9.4 \times 10^{-13} = x^2[2.0 \times 10^{-6}] \rightarrow$ **$x = 6.7 \times 10^{-4}$ M**
e. pOH = 14.00 – 7.5 = 6.5
$[OH^-] = 10^{-6.5} = 3.2 \times 10^{-7}$ M
$9.4 \times 10^{-13} = x^2[3.2 \times 10^{-7}] \rightarrow$ **$x = 1.7 \times 10^{-3}$ M**

18. The value of K_{sp} for $Cd(OH)_2$ is 2.5×10^{-14}.
    a. What is the molar solubility of $Cd(OH)_2$?
    b. The solubility of $Cd(OH)_2$ can be increased through formation of the complex ion $[CdBr_4]^{2-}$ ($K_f = 5 \times 10^3$). If solid $Cd(OH)_2$ is added to a NaBr solution, what is the initial concentration of NaBr needed to increase the molar solubility of $Cd(OH)_2$ to 1.0×10^{-3} M?

a. $2.5 \times 10^{-14} = [Cd^{2+}][OH^-]^2 \rightarrow 2.5 \times 10^{-14} = x(2x)^2 \rightarrow$ **$x = 1.8 \times 10^{-5}$ M**
b. $Cd(OH)_2\ (s) + 4\ Br^-\ (aq) \rightarrow CdBr_4^{2-}\ (aq) + 2\ OH^-\ (aq)$
$K_{net} = K_fK_{sp} = (5 \times 10^3)(2.5 \times 10^{-14}) = 1 \times 10^{-10}$

	$Cd(OH)_2$ (s) +	4 Br^- (aq) $\Leftrightarrow$	$CdBr_4^{2-}$ (aq) +	2 OH^- (aq)
I		x	0	0
C		–4y	+y	+2y
E		x – 4y	1.0×10^{-3}	2.0×10^{-3}

$y = 1.0 \times 10^{-3}$

$$1 \times 10^{-10} = \frac{[CdBr_4^{2-}][OH^-]^2}{[Br^-]^4} = \frac{(1.0 \times 10^{-3})(2.0 \times 10^{-3})^2}{(x - 4.0 \times 10^{-3})^4} \rightarrow \boldsymbol{x = 2\ M}$$

19. Gout – a condition that results in join swelling and pain – is caused by the formation of sodium urate ($NaC_5H_3N_4O_3$) crystals within tendons, cartilage, and ligaments. Sodium urate precipitates out of blood plasma when uric acid levels become abnormally high. This sometimes happens as a result of eating too many rich foods and consuming too much alcohol, which is why gout is sometimes referred to as the "disease of kings". If

the sodium concentration in blood plasma is 0.140 M, and K_{sp} for sodium urate is 5.76 x 10^{-8}, what minimum concentration of urate would result in precipitation?

K_{sp} = 5.76 x 10^{-8} = $[Na^+][C_5H_3N_4O_3^-]$

	$NaC_5H_3N_4O_3$ ⇔	Na^+ (aq) +	$C_5H_3N_4O_3^-$ (aq)
I		0.140 M	0
C		~0	+ x
E		0.140 M	x

5.76 x 10^{-8} = (0.140 M)x → **x = 4.11 x 10^{-7} M**

20.

a. Using the K_{sp} value for $Cu(OH)_2$ (1.6 x 10^{-19}) and the overall formation constant for $[Cu(NH_3)_4]^{2+}$ (1.0 x 10^{13}), calculate the value for the equilibrium constant for the following reaction:

$$Cu(OH)_2\ (s) + 4\ NH_3\ (aq) \Leftrightarrow [Cu(NH_3)_4]^{2+}\ (aq) + 2\ OH^-\ (aq)$$

b. Use the value of the equilibrium constant you calculated in part (a) to calculate the solubility (in M) of $Cu(OH)_2$ in 5.0 M NH_3. In 5.0 M NH_3, the concentration of OH^- is 0.0095 M.

$Cu(OH)_2$ (s) ⇔ Cu^{2+} (aq) + 2 OH^- (aq) K_{sp} = 1.6 x 10^{-19}
Cu^{2+} (aq) + 4 NH_3 (aq) ⇔ $Cu(NH_3)_4^{2+}$ (aq) K_f = 1.0 x 10^{13}
K_{net} = $K_{sp}K_f$ = **1.6 x 10^{-6}**

	$Cu(OH)_2$ (s) +	4 NH_3 (aq) ⇔	$Cu(NH_3)_4^{2+}$ (aq) +	2 OH^- (aq)
I		5.0 M	0	0.0095 M
C		–4x	+x	+2x
E		5.0 – 4x	x	0.0095 + 2x

$$1.6 \times 10^{-6} = \frac{x(0.0095 + 2x\ M)^2}{(5.0 - 4x\ M)^4} \rightarrow \boldsymbol{x = 0.056\ M}$$

Problems Chapter 17 (Aqueous Equilibria)