1. A 0.050 M solution of weak acid, HA, has a pH = 2.23 at 25 °C.

    A) Write the chemical equilibrium of the weak acid in water.

    $$HA\ (aq) \rightleftharpoons H^+\ (aq) + A^-\ (aq)$$

    B) Write an expression for K_a (the weak acid dissociation equilibrium constant).

    $$K_a = \frac{[H^+][A^-]}{[HA]}$$

    C) Determine the value of $[H^+]$ (or $[H_3O^+]$) at equilibrium.
        Because they tell us that pH = 2.23 (at equilibrium), we know that

    $$[H^+] = 10^{-pH} = 10^{-2.23} = 5.9 \times 10^{-3}\ M$$

    D) What is the percent ionization of this acid?
        Percent ionization for an acid will always be:

    $$\% \text{ ionization} = \frac{[H^+]_{eq}}{[HA]_{initial}} \times 100\% = \frac{5.8_8 \times 10^{-3}\ M}{0.050\ M} \times 100\% = 12\%$$

    E) What is the value of K_a for this acid?
        To find K_a, set up an ICE chart, and plug in the equilibrium concentrations.

	HA (aq)	$\rightleftharpoons$	H+ (aq)	+	A⁻ (aq)
I	0.050 M		0 M		0 M
C	− x		+ x		+ x
E	0.050 − x		x		x

    In the ICE chart, replace x with the answer we found in part C.

    $$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{x^2}{0.050 - x} = \frac{\left(5.8_8 \times 10^{-3}\right)^2}{0.050 - 5.8_8 \times 10^{-3}} = 7.9 \times 10^{-4}$$

    F) Without any calculations: If we increase the volume by 10×, do you expect the percent ionization to increase, decrease, or stay the same? What about the pH? Why?

    Hint: What is Q immediately after adding more water?
    Increasing the volume decreases the concentrations and equilibrium will shift to the right.

    $$Q_a = \frac{\frac{1}{10}[H^+]\frac{1}{10}[A^-]}{\frac{1}{10}[HA]} < K_a$$

    . <u>Therefore, percent ionization increases, and pH increases because of dilution.</u>

2. What is the pH of a 0.200 M solution of $C_6H_5NH_2$ if its pK_b = 9.40?
    First, determine K_b from pK_b:

    $$K_b = 10^{-pK_b} = 10^{-9.40} = 3.9_8 \times 10^{-10}$$

    Because K_b is small, this is a weak base, and we can set up the weak base equilibrium ICE chart:

	$C_6H_5NH_2$ (aq)	+	H_2O (l)	$\rightleftharpoons$	$C_6H_5NH_3^+$ (aq)	+	OH⁻ (aq)
I	0.200 M		n/a		0 M		0 M
C	− x		n/a		+ x		+ x
E	0.200 − x		n/a		x		x

    Set up the K_b expression, approximate x to be small, and solve for pOH and pH:

    $$K_b = \frac{[C_6H_5NH_3^+][OH^-]}{[C_6H_5NH_2]}$$

    $$3.9_8 \times 10^{-10} \approx \frac{x^2}{0.200}$$

    $$x = 8.9_2 \times 10^{-10} = [OH^-]$$

    $$pOH = -\log[OH^-] = -\log(8.9_2 \times 10^{-10}) = 5.04_9$$

    $$pH + pOH = 14$$
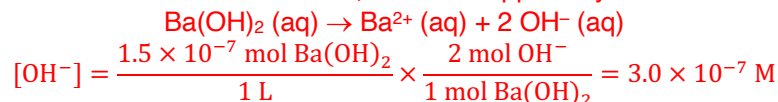 $$pH = 14 - 5.04_9$$
    $$pH = 8.95$$

3. What is the pH of a 1.5×10^{-7} M solution of $Ba(OH)_2$?

   Hint: Before you start this problem, do you expect the pH to be <7, ~7, or >7?
   You may tempted to say pH > 7 because $Ba(OH)_2$ is a strong base, but pH ~7 because it's very dilute.
   Because the solution is very dilute, the dominant process is actually the auto-ionization of water itself!
   However, we start with some initial amount of OH⁻, which is supplied by the dissociation of $Ba(OH)_2$:

   $$Ba(OH)_2 \text{ (aq)} \rightarrow Ba^{2+} \text{ (aq)} + 2\, OH^- \text{ (aq)}$$

   $$[OH^-] = \frac{1.5 \times 10^{-7} \text{ mol } Ba(OH)_2}{1\, L} \times \frac{2 \text{ mol } OH^-}{1 \text{ mol } Ba(OH)_2} = 3.0 \times 10^{-7} \text{ M}$$

   Set up an ICE chart for the auto-ionization equilibrium of water:

	H_2O (l)	$\rightleftharpoons$	H^+ (aq)	+	OH^- (aq)
I	n/a		0 M		3.0×10^{-7} M
C	n/a		+ x		+ x
E	n/a		x		$3.0 \times 10^{-7} + x$

   Set up the K_w expression, solve for x, and solve for pH:

   $$K_w = [H^+][OH^-]$$
   $$1.0 \times 10^{-14} = (3.0 \times 10^{-7} + x)(x)$$
   $$x = 3.0_3 \times 10^{-8} = [H^+]$$

   $$pH = -\log[H^+]$$
   $$= -\log(3.0_3 \times 10^{-8})$$
   $$pH = 7.52$$

4. Rank the following in order of increasing acid strength.

   $$H_2SeO_4 \qquad\qquad H_2SO_4 \qquad\qquad H_2SeO_3 \qquad\qquad H_2SO_3$$
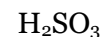
   Hint: Draw a Lewis structure for the conjugate-base of H_2SO_4.

   $$H_2SO_4 > H_2SeO_4 > H_2SO_3 > H_2SeO_3$$

5. You make a 1.00 L solution that is 0.120 M HNO_2 and 0.150 M $NaNO_2$, K_a of $HNO_2 = 4.0 \times 10^{-4}$.

   A) Calculate the pH of this buffer solution.

   The salt dissociates completely via: $NaNO_2$ (aq) $\rightarrow$ Na^+ (aq) + NO_2^- (aq)
   We can set up a weak-acid/conjugate-base equilibrium ICE chart:

	HNO_2 (aq)	$\rightleftharpoons$	H^+ (aq)	+	NO_2^- (aq)
I	0.120 M		0 M		0.150 M
C	− x		+ x		+ x
E	0.120 − x		x		0.150 x

   You may set up an expression for K_a, approximate x as small, solve for x, and then pH.
   Or you can apply the Henderson-Hasselbach equation and approximate x to be small:

   $$pH = pK_a + \log\frac{[NO_2^-]}{[HNO_2]} = -\log(4.0 \times 10^{-4}) + \log\left(\frac{0.150 + x}{0.120 - x}\right) \approx 3.39_8 + \log\left(\frac{0.150}{0.120}\right) = 3.49$$

   B) Calculate the pH after 1.00 mL of 11.6 M HCl is added to the buffer solution.

   Note the HCl will react with the conjugate-base (NO_2^-), so:

	HNO_2 (aq)	$\rightleftharpoons$	H^+ (aq)	+	NO_2^- (aq)
I	0.120 mol		0.0116 mol		0.150 mol
C	+ 0.0116		− 0.0116		− 0.0116
F	0.131₆		0		0.138₄

   $$pH = pK_a + \log\frac{[NO_2^-]}{[HNO_2]} \approx 3.39_8 + \log\left(\frac{0.138_4 \text{ mol}/1.001\, L}{0.131_6 \text{ mol}/1.001\, L}\right) = 3.42$$

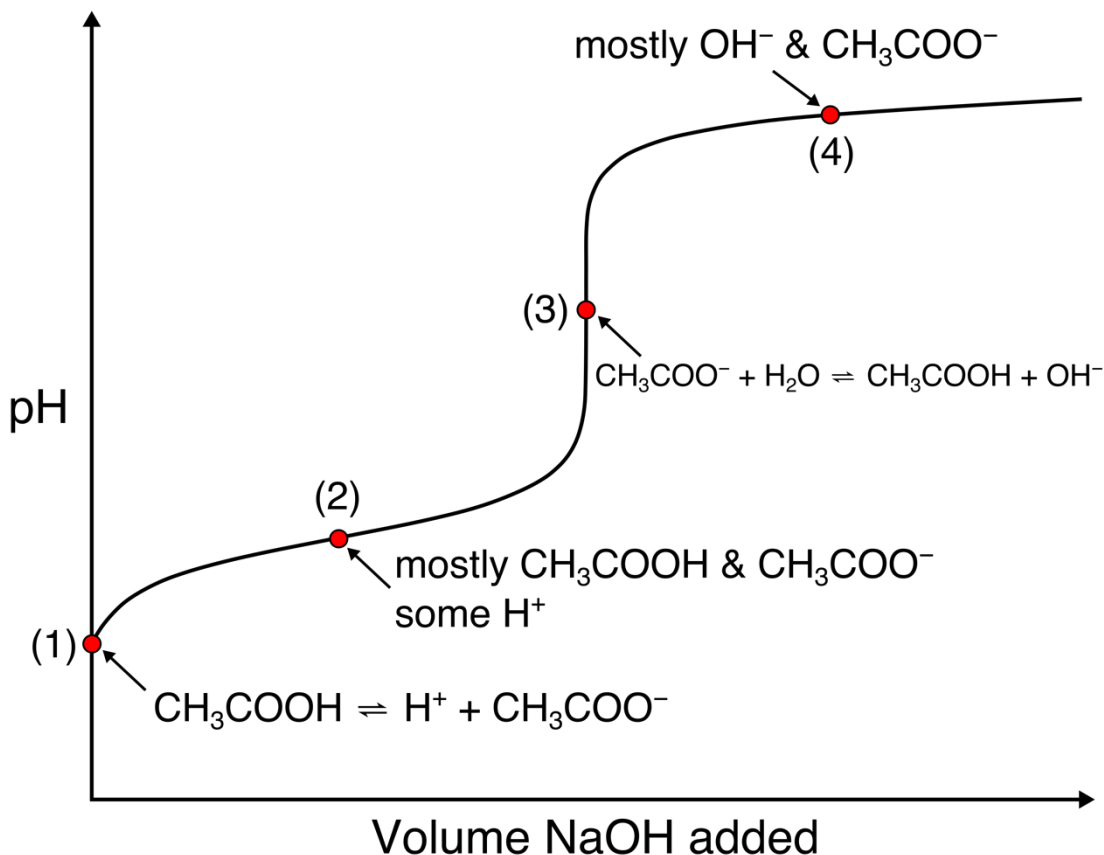   C) Calculate the pH after 1.00 mL of 11.6 M NaOH is added to the buffer solution.

   Note the NaOH will react with the acid (HNO_2), so:

	HNO_2 (aq)	+	OH^- (aq)	$\rightleftharpoons$	NO_2^- (aq)	+	H_2O (l)
I	0.120 mol		0.0116 mol		0.150 mol		n/a
C	− 0.0116		− 0.0116		+ 0.0116		n/a
F	0.108₄		0		0.161₆		n/a

   $$pH = pK_a + \log\frac{[NO_2^-]}{[HNO_2]} \approx 3.39_8 + \log\left(\frac{0.161_6 \text{ mol}/1.001\, L}{0.108_4 \text{ mol}/1.001\, L}\right) = 3.57$$

6. You are titrating 2.0 mL of 1.0 M acetic acid (CH_3COOH, $K_a = 1.76 \times 10^{-5}$) with 1.0 M NaOH.

A) Below is a sketch of the titration curve. At each labelled point, what is the dominant species in solution?

mostly OH^- & CH_3COO^-

(4)

pH

(3)

$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$

(2)

mostly CH_3COOH & CH_3COO^-
some H^+

(1)

$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$

Volume NaOH added

B) Calculate the pH before any NaOH is added, point (1).

Because we haven't added any NaOH yet, this is just a weak-acid equilibrium problem.

	CH_3COOH (aq)	$\rightleftharpoons$	H+ (aq)	+	CH_3COO^- (aq)
I	1.0 M		0 M		0 M
C	− x		+ x		+ x
E	1.0 − x		x		x

Set up the K_a expression, approximate x to be small, and solve for pH:

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

$$1.76 \times 10^{-5} \approx \frac{x^2}{1.0}$$

$$x = 0.0041_{95} = [H^+]$$

$$pH = -\log[H^+]$$
$$= -\log(0.0041_{95})$$
$$pH = 2.38$$

C) Calculate the pH after 0.5 mL of 1.0 M NaOH is added.

Begin by figuring out the non-equilibrium reaction that takes place:

	CH_3COOH (aq)	+	OH^- (aq)	→	CH_3COO^- (aq)	+	H_2O (l)
I	0.0020 mol		0.0005 mol		0 mol		n/a
C	− 0.0005		− 0.0005		+ 0.0005		n/a
F	0.0015		0		0.0005		n/a

Apply the Henderson-Hasselbach equation and approximate x to be small:

$$pH = pK_a + \log\frac{[CH_3COO^-]}{[CH_3COOH]} \approx 4.75_4 + \log\left(\frac{0.0005 \text{ mol}/0.0025 \text{ L}}{0.0015 \text{ mol}/0.0025 \text{ L}}\right) = 4.28$$

D) How much (in moles) NaOH is required to get to point (2) where the pH = pK_a?

Begin by figuring out the non-equilibrium reaction that would take place:

	CH_3COOH (aq)	+	OH^- (aq)	$\rightarrow$	CH_3COO^- (aq)	+	H_2O (l)
I	0.0020 mol		x mol		0 mol		n/a
C	$- x$		$- x$		$+ x$		n/a
F	$0.0020 - x$		0		x		n/a

Because point (2) is well within the buffer region, we can apply the Henderson-Hasselbach equation:

$$pH = pK_a + \log\frac{[CH_3COO^-]}{[CH_3COOH]}$$

$$4.75_4 = 4.75_4 + \log\frac{x}{0.0020 - x}$$

$$0 = \log\frac{x}{0.0020 - x}$$

$$1 = \frac{x}{0.0020 - x}$$

$$x = 0.0010 \text{ mol } OH^-$$

E) Do you expect the pH at the equivalence point (point 3) to be <7, =7, or >7?

pH > 7 because this is a weak acid + strong base titration.

F) Calculate the pH at the equivalence point, point (3).

At the equivalence point, $n_{HA} = n_{OH^-}$:

	CH_3COOH (aq)	+	OH^- (aq)	$\rightarrow$	CH_3COO^- (aq)	+	H_2O (l)
I	0.0020 mol		0.0020 mol		0 mol		n/a
C	$- 0.0020$		$- 0.0020$		$+ 0.0020$		n/a
F	0		0		0.0020		n/a

We have only the conjugate-base left, which will undergo weak-base equilibrium. Note that the total volume is 4.0 mL because we would need to add 2.0 mL of 1.0 M NaOH to reach the equivalence point.

	CH_3COO^- (aq)	+	H_2O (l)	$\rightleftharpoons$	CH_3COOH (aq)	+	OH^- (aq)
I	0.50 M		n/a		0 M		0 M
C	$- x$		n/a		$+ x$		$+ x$
E	$0.50 - x$		n/a		x		x

Set up the K_b expression, approximate x to be small, and solve for pOH and pH:

$$K_b = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$

$$5.68_2 \times 10^{-10} \approx \frac{x^2}{0.50}$$

$$x = 1.6_8 \times 10^{-5} = [OH^-]$$

$$pOH = -\log[OH^-] = -\log(1.6_8 \times 10^{-5}) = 4.77_3$$

$$pH + pOH = 14$$
$$pH = 14 - 4.77_3$$
$$pH = 9.23$$

G) Calculate the pH after 3.0 mL of NaOH is added, point (4).

After the equivalence point, the pH will be dependent on excess NaOH:

	CH_3COOH (aq)	+	OH^- (aq)	$\rightarrow$	CH_3COO^- (aq)	+	H_2O (l)
I	0.0020 mol		0.0030 mol		0 mol		n/a
C	$- 0.0020$		$- 0.0020$		$+ 0.0020$		n/a
F	0		0.0010		0.0010		n/a

We can determine pOH directly and then pH:

$$pOH = -\log[OH^-] = -\log\left(\frac{0.0010 \text{ mol } OH^-}{0.0050 \text{ L}}\right) = 0.69_9$$

$$pH + pOH = 14$$
$$pH = 13.30$$

H) Go back to the diagram above. Circle the region in which you would find a buffer solution. What do you notice about the pH in this range? Does the pH-dependence make sense?

In the region around pH = pK_a, we have a buffer. You can see the titration curves flattens out here, which tells us the pH is fairly constant regardless of the addition of NaOH.