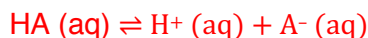1. A 0.050 M solution of weak acid, HA, has a pH = 2.23 at 25 °C.

    A) Write a balanced chemical equilibrium equation for this system/reaction.

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

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

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

    C) At equilibrium, determine the value of $[H^+]$ (or $[H_3O^+]$).
        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 would decrease the concentrations, and $Q_a < K_a$. The system will respond by shifting equilibrium to the side with a greater number of moles (to the right) in order to increase the concentrations. Therefore, percent ionization would increase, and pH increases because of dilution.

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:

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

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

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

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

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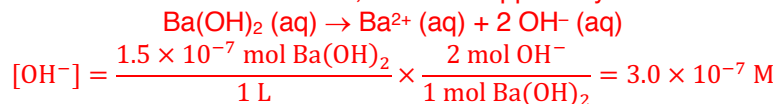$$pH = 14 - 5.04_9$$
$$pH = 8.95$$

3. What is the pH of a 1.5×10^{-7} M solution of $Ba(OH)_2$? 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 <u>pH ~7 because it's very dilute</u> here. Because the solution is dilute, the dominant process is actually the acid-base equilibrium of water itself! However, we start with some initial amount of OH⁻, which is supplied by the dissociation of $Ba(OH)_2$:

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

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

Set up an ICE chart for the acid-base 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		3.0×10^{-7} + x

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

$$K_w = [H^+][OH^-] \qquad\qquad pH = -\log[H^+]$$
$$1.0 \times 10^{-14} = (3.0 \times 10^{-7} + x)(x) \qquad\qquad = -\log(3.0_3 \times 10^{-8})$$
$$x = 3.0_3 \times 10^{-8} = [H^+] \qquad\qquad pH = 7.52$$

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

       H_2SeO_4 H_2SO_4 H_2SeO_3 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.

The salt dissociates completely via: $NaNO_2$ (aq) → 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
"E"	0.131_6		0		0.138_4

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

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
E	0.108_4		0		0.161_6		n/a

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

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, write the chemical species you would expect to find in solution.
   I did point (1) for you in the form of an equilibrium expression.
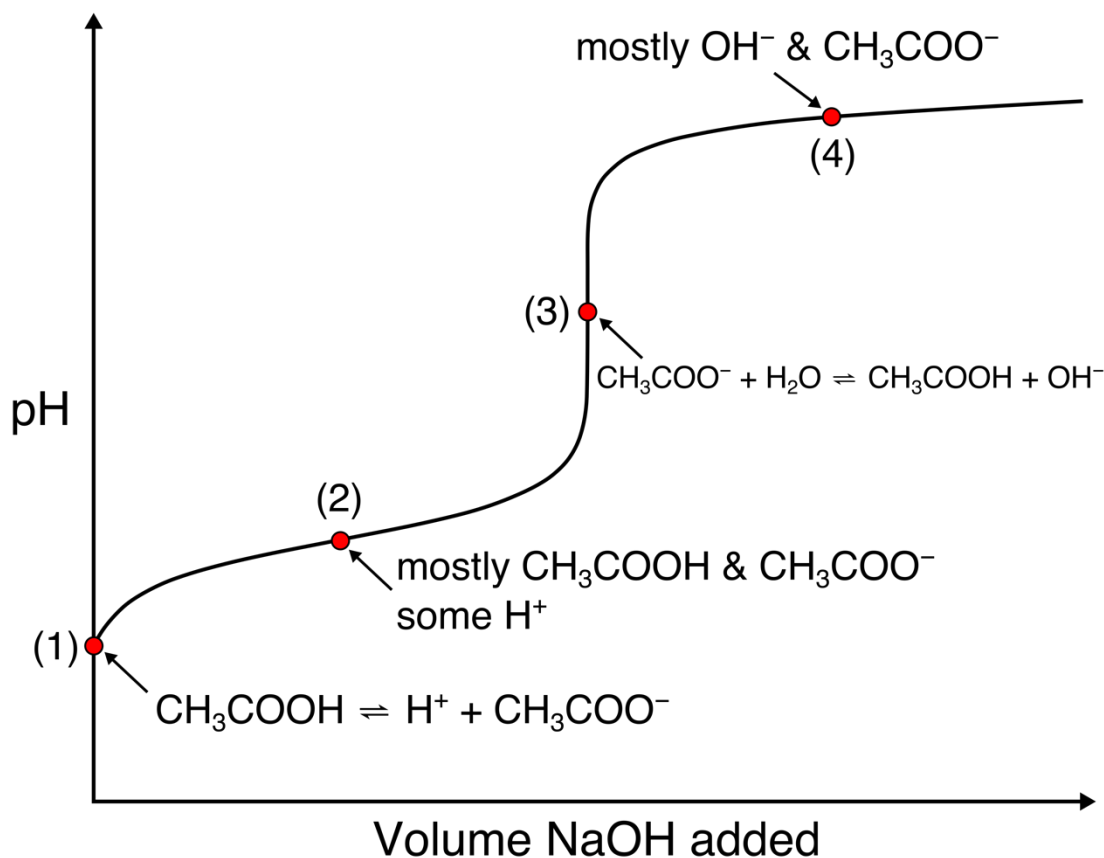
B) Calculate the pH before any NaOH is added, point (1).
   Because we haven't added any NaOH yet, this is just a weak-acid equilibrium problem.

	CH_3COOH (aq)	⇌	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 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
"E"	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 NaOH is required to get to point (2) if the pH = pK_a?

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

	CH_3COOH (aq)	+	OH^- (aq)	⇌	CH_3COO^- (aq)	+	H_2O (l)
I	0.0020 mol		x mol		0 mol		n/a
C	− x		− x		+ x		n/a
"E"	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 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)	⇌	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
"E"	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)	⇌	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:

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

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

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

$$pH + pOH = 14$$

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

$$pH = 14 - 4.77_3$$

$$pH = 9.23$$

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)	⇌	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
"E"	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.