Titration

1. What is a titration?

   A titration is when a solution of unknown concentration is reacted with a solution of known concentration. This reaction will tell you more information about the unknown solution.

   In the context of a homework or exam question, it may just indicate that you are reacting two substances.

2. What is the equivalence point?

   The point in a titration where the reacts have perfectly reacted (i.e. there is no limiting or excess reactant).

   $$moles\ of\ base = moles\ of\ acid$$

3. For a strong acid and weak base reaction the equivalence point has a pH < 7.

   a. Why?

   $$HA_{(aq)} + B_{(aq)} \rightleftharpoons A^-_{(aq)} + HB^+_{(aq)}$$

   At the equivalence point the moles of HA = moles of B. Which would make one assume neutralization and thus a pH = 7. However, because a weak base is being titrated – it's conjugate that is formed (BH^+) has a measurable amount of strength as an acid. Meaning that after the first reaction has occurred – there will be a second reaction...

$$BH^+ \rightleftharpoons B_{(aq)} + H^+_{(aq)}$$

This formation of H^+ leads to an acidic pH indicated by a value less than 7.

4. For a strong base and weak acid reaction the equivalence point has a pH > 7.

    a. Why?

    $$HA_{(aq)} + OH^-_{(aq)} \rightleftharpoons A^-_{(aq)} + H_2O_{(l)}$$

    At the equivalence point the moles of HA = moles of B. Which would make one assume neutralization and thus a pH = 7. However, because a weak acid is being titrated – it's conjugate that is formed (A^-) has a measurable amount of strength as a base. Meaning that after the first reaction has occurred – there will be a second reaction...

    $$A^-_{(aq)} + H_2O_{(l)} \rightleftharpoons HA_{(aq)} + OH^-_{(aq)}$$

    This formation of OH^- leads to a basic pH indicated by a value greater than 7.

5. Determine the pH of the following solutions

    a. 1.00 L solution of 1.00M HNO_2 and 1.50M $NaNO_2$.
       ($K_a = 4 \times 10^{-4}$).

This is a buffer solution. HNO_2 is a weak acid and the salt contains its conjugate base NO_2^-. This means that we can use the Henderson-Hasselbalch equation to solve for the pH.

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

$$pH = - \log (4 \times 10^{-4}) + \log \frac{(1.50M)}{(1.00M)}$$

$$\boxed{pH = 3.57}$$

b. The solution in part a after 0.200 moles HCl has been added.

Whenever you add a strong acid or base to a solution that contains weak substances, it is helpful to write a list of the major species in solution. "Major Species" are substances that are found in the solution in the greatest quantity. Strong substances and salt always fully dissociate into its ions. Weak substances primarily stay intact. Also, remember water will always be a major species as we are dealing with aqueous solutions.

In this solution the major species are:

spectators

$$HNO_2, \; Na^+, \; NO_2^-, \; \boxed{H^+}, \; Cl^-, \; H_2O$$

best weak base in solution
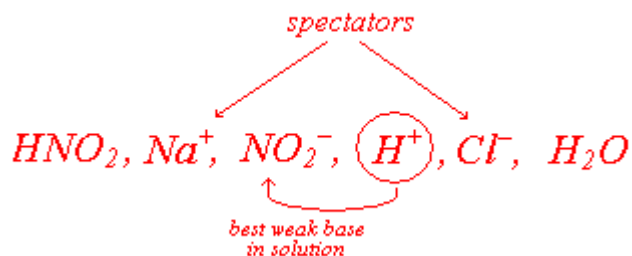
The strongest acid/base in solution takes priority. In this case, H^+ is the strongest substance in the solution. It is going to react with the best base in solution, which in this case is, NO_2^-.

Remember that strong substances react to completion that means you
would use stoichiometry as your calculation methods and

stoichiometry is in terms of units of moles.

Thus the first step in the calculation involves the following reaction along with a stoichiometry chart – similar to the ICE chart.

①

	$H^+_{(aq)}$	$NO_2^-_{(aq)}$	$HNO_2_{(aq)}$
	$H^+_{(aq)}$ +	$NO_2^-_{(aq)}$ →	$HNO_2_{(aq)}$
mol_i	0.200mol	1.50 mol	1.00 mol
change	-0.200 mol	-0.200 mol	+0.200 mol
final	0	1.30 mol	1.20 mol

The change row is determined by the limiting reactant. Because there is a 1:1 mole ratio between reactants, you can determine the limiting reactant by simply looking at the moles of each. The reactant with smallest number of moles is the limiting factor. So you subtract that number of moles from everything on the reactant side… and because there is a 1:1 mole ratio between reactants and products, you add that many moles to the product side.

To determine how to proceed with the calculation of pH, you will need to determine what kind of solution is present after the first reaction. This information is found in the final row of the chart above. Looking at the chart you will notice that you do not have any of the strong acid left, but there is a mixture of weak acid and conjugate base in the solution. This means that the resulting solution is a buffer.

Because this solution is a buffer, we can use the Henderson-Hasselbalch equation in step 2 to calculate the pH of the solution.

②
$$pH = pK_a + \log \frac{[base]}{[acid]}$$

$$pH = -\log(4 \times 10^{-4}) + \log\frac{(1.30 \ mol)}{(1.20 \ mol)}$$

$$\boxed{pH = 3.43}$$

You may have noticed that I plugged moles into the equation instead of concentration. The reason that I can do this is because the acid and base are in the same solution… which means that they have the same value for volume.

Remember that $M = \frac{mol}{L}$ So if they are in the volume the L cancels out when you divide one molarity by the other… thus plugging the number of moles results in the same answer as plugging in molarity.

 If this is not something that you are totally comfortable with… then it is totally fine to convert moles → molarity by diving the moles by the total volume of solution. And then plugging that value into the Henderson equation.

6. Determine the pH of the following solutions

   a. 25.0g of NH_3 and 40.0g NH_4NO_3 in 501.0 mL of water. $(K_a = 5.6 \times 10^{-10})$

      This is a buffer solution. NH_3 is a weak base and the salt contains its conjugate acid NH_4^+. This means that we can use the Henderson-Hasselbalch equation to solve for the pH. We will just need to convert to the correct units first.

$$25.0 \ g \ NH_3 \ \frac{1 \ mol}{17.04g} = 1.467 \ mol \ NH_3$$

$$40.0 \ g \ NH_4NO_3 \ \frac{1 \ mol}{80.06 \ g} = 0.50 \ mol \ NH_4NO_3$$

Because the NO_3^- is just a spectator ion, we are only really interested in the amount of conjugate base this salt provides, we switch from moles of NH_4NO_3 to moles of NH_4^+.

$$pH = -log \ (5.6 \ x \ 10^{-10}) + log\frac{(\frac{1.47 \ mol}{0.50 \ L})}{(\frac{0.50 \ mol}{0.50 \ L})} = -log \ (5.6 \ x \ 10^{-10}) + log \ \frac{(1.47 \ mol)}{(0.50 \ mol)}$$

$$pH = \boxed{9.72}$$

As you can see the volumes cancel out – this illustrates the idea described in question above – since the volumes will ultimately cancel out, it is valid to simply plug in moles.

b. The solution in part a after 0.02 mol of NaOH has been added.

Remember whenever you add a strong acid or base to a solution that contains weak substances, it might be helpful to write out your list of major species.

The major species in solution are:

$$NH_3, \quad NH_4^+, \quad NO_3^-, \quad Na^+, \quad \boxed{OH^-}, \quad H_2O$$

spectator ions

best weak acid in solution
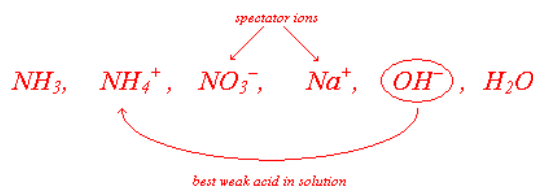
The strongest acid/base in solution takes priority. In this case OH^- is the strongest substance in solution. It is going to react with the best acid in solution, which in this case is, NH_4^+.

Remember that reactions involving strong substances happen to

completion. This means that you are going to be using stoichiometry (and units of mols) to calculate.

①

	$OH^-_{(aq)}$	+	$NH_4^+{}_{(aq)}$	→	$NH_{3\ (aq)}$	+	$H_2O_{(l)}$
mol_i	0.02 mol		0.50 mol		1.47 mol		——
change	-0.02 mol		-0.02 mol		+0.02 mol		——
final	0		0.48 mol		1.49 mol		——

Looking at the chart you will notice that you do not have any of the strong acid left, but there is a mixture of weak acid and conjugate base in the solution. This means that the resulting solution is a buffer. Because this solution is a buffer, we can use the Henderson-Hasselbalch equation in step 2 to calculate the pH of the solution.

$$pH = -\log(5.6 \times 10^{-10}) + \log \frac{(1.49)}{(0.48)} = \boxed{9.74}$$

7. Calculate the pH when 80. mL of 0.25M KOH is added to 40. mL of 0.50M HClO. (K_a = 3 x 10^{-8})

When you first start these problems determine whether you have a buffer – that'll let you know whether or not you may use the Henderson-Hasselbalch equation in the initial step.

This solution is not a buffer as the salt des not contain the conjugate base of HClO. So the first step would be to determine the major species in solution.

Major species in solution:

spectator

$HClO$, K^+ , $\widehat{OH^-}$, H_2O

Best weak acid
in solution
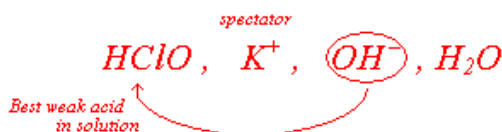
Because there is a strong base in solution, it takes priority. So we are going to look at the reaction between hydroxide and the best acid in solution, HClO. Because this is a strong reaction, we are going to complete a stoichiometry calculation which means we need to determine the moles of HClO and OH⁻ in solution.

$$0.080 \; L \; \frac{0.25 \; mol \; OH^-}{L \; of \; sol'n} = 0.02 \; mol \; OH^-$$

$$0.040 \; L \; \frac{0.50 \; mol \; HClO}{L \; of \; sol'n} = 0.02 \; mol \; HClO$$

Now that we have the moles of each in solution we can plug into the stoichiometry chart.

①

	$OH^-_{(aq)}$ +	$HClO_{(aq)}$ →	$ClO^-_{(aq)}$ +	$H_2O_{(l)}$
mol_i	0.02 mol	0.02 mol	0	——
change	-0.02 mol	-0.02 mol	+0.02 mol	——
final	0	0	0.02 mol	——

If we now take a look at what is left in solution after the strong reaction has taken place, we notice that the only species left are H_2O and ClO^-. This is the equivalence point of the titration (where moles of acid equal moles of base) so we are only left with the conjugate in solution after the reaction has run to completion. This means that the next reaction we have to look at is the equilibrium reaction between ClO^-(a conjugate base) and H_2O. Because this is an equilibrium reaction we will use an ICE chart to solve.

ICE charts are in terms of molarity so we will need to begin by converting from moles of ClO^- to [ClO^-]. Remember that we will have to divide the moles of ClO^- by the sum of the two volumes of solution added.

$$\frac{0.02 \; mol \; ClO^-}{0.120 \; L \; of \; sol'n} = 0.167 \; M$$

Now we can plug into the ICE chart.

②

	$ClO^-_{(aq)}$	+	$H_2O_{(l)}$	⇌	$OH^-_{(aq)}$	+	$HClO_{(aq)}$
I	0.167 M		——		0		0
C	-x		——		+x		+x
E	0.167 – x		——		x		x

$$\frac{x^2}{0.167 - x} = K_b$$

Remember that this is K_b because we are looking at a reaction of a base producing OH^-. So we will need to solve for K_b using the relationship:

$$K_a \; x \; K_b = K_w$$

Looking up the K_a value of the weak acid HClO, 3.0 x 10^{-8} we can plug in and solve.

$$K_b = \frac{1.0 \; x \; 10^{-14}}{3.0 \; x \; 10^{-8}} = 3.33 \; x \; 10^{-7}$$

Because K_b is such a small number we can make the small K, small x approximation and we have the equation:

$$\frac{x^2}{0.167} = 3.33 \; x \; 10^{-7}$$

Solving for x we get

$$x = 2.36 \times 10^{-4} = [OH^-]$$
$$pOH = -\log(2.36 \times 10^{-4}) = 3.63$$
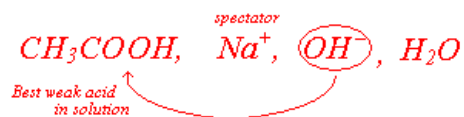$$pH = 14 - 3.63 = \boxed{10.37}$$

8. Calculate the pH for 100.0 mL of 0.400M CH_3COOH with 300. mL of 0.200M NaOH.

Once again, determine whether you have a buffer – that'll let you know whether or not you may use the Henderson-Hasselbalch equation in the initial step.

This solution is not a buffer as the salt des not contain the conjugate base of CH_3COOH . So the first step would be to determine the major species in solution.

Major species in solution:

$$CH_3COOH, \quad \underset{\substack{\text{Best weak acid} \\ \text{in solution}}}{} Na^+, \quad \overset{spectator}{\boxed{OH^-}}, \quad H_2O$$

Because there is a strong base in solution, it takes priority. So we are going to look at the reaction between hydroxide and the best acid in solution, CH_3COOH. Because this is a strong reaction, we are going to complete a stoichiometry calculation which means we need to determine the moles of CH_3COOH and OH^- in solution.

$$0.3000L \; \frac{0.200 \, mol \, OH^-}{L \, of \, sol'n} = 0.0600 \, mols \, OH^-$$

$$0.1000 \, L \; \frac{0.400 \, mol \, CH_3COOH}{L \, of \, sol'n} = 0.0400 \, mols \, CH_3COOH$$

Now that we have the moles of each in solution we can plug into the stoichiometry chart.

(1)

	$OH^-_{(aq)}$	$+ CH_3COOH_{(aq)} \rightarrow$	$CH_3COO^-_{(aq)} +$	$H_2O_{(l)}$
mol_i	0.0600 mol	0.0400 mol	0	—
change	-0.0400 mol	-0.0400 mol	$+0.0400 \text{ mol}$	—
final	0.02 mol	0	0.0400 mol	—

 If we now take a look at what is left in solution after the strong reaction has taken place, we notice that the only species left are OH^- (a strong base) and CH_3COO^- (a weak base). We have now gone past the equivalence point.

As both of these remaining species are bases – they will not react with each other. So there is no equilibrium reaction or buffer solution to examine.

So in order to determine the pH, what do we look at? Do we need to examine the contribution to pH from both the weak and strong base? We do not – the strong base will override any affect that the weak base would make. So whenever we have a mixture of acids or bases (in the context of this class) and need to determine the pH – we will look only at the pH due to the strongest base in the solution.

In this case we are looking at the pH value based on the [OH⁻] remaining in solution.

$$[OH^-] = \frac{0.02 \text{ mols } OH^-}{0.400 \text{ L}} = 0.05 \text{ M } OH^-$$

Now we can use the concentration of hydroxide to solve for the pH.

$$pH = 14 - pOH = 14 - (-\log(0.05)) = \boxed{12.699}$$