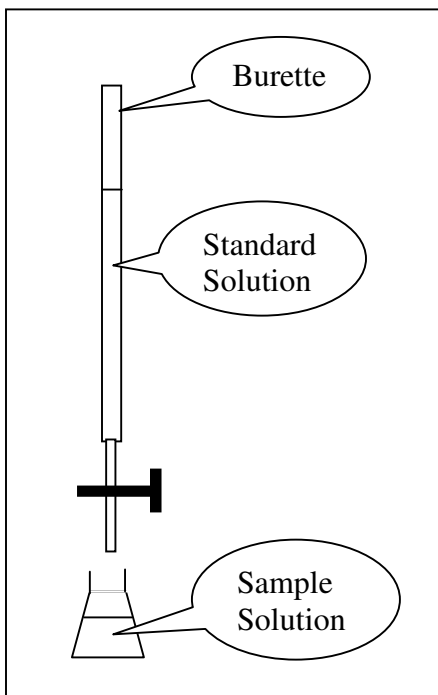


Practical Aspects of Titration

Remember, **standard solutions** are solutions of accurately known concentration. They are put into a burette and used to titrate solutions of unknown concentration (sample solutions)

Can solid NaOH be used to prepare a Standard Solution (by weighing it and dissolving it in a known volume of water)? _____ (See sample)

Answer: NaOH **cannot** be weighed accurately as it absorbs water and CO₂ from the air as it's being weighed. (it's **hygroscopic**)

There are 2 ways to prepare a standard solution accurately:

1. Use a **Primary Standard**

A **Primary Standard** has the following characteristics:

- It is obtained in pure and stable form & dissolves completely
- It does NOT absorb H₂O or CO₂ from the air. (non-hygroscopic)
- It has an accurately known molar mass
- It reacts quickly and completely with the sample

An accurately measured mass of the primary standard is weighed and dissolved in an accurately measured volume of water to obtain a solution

of accurately known concentration. (Standard Solution)

Eg.) 40.48 g of potassium hydrogen phthalate (KHC₈H₄O₄) is weighed out and dissolved in enough distilled water to make 1.000 L of solution. Find the [KHC₈H₄O₄]. (HINT: Use g → moles → M)

Some **Primary Standards** are:

- Na₂CO₃ (sodium carbonate)
- KHC₈H₄O₄ (potassium hydrogen phthalate)
- C₆H₅COOH (benzoic acid)

NEVER NaOH → remember, it is highly hygroscopic!

2. **Standardizing a Solution**

This is done by titrating a solution with a primary standard in order to find it's accurate concentration . The **standardized solution** can then be used to titrated other solutions.

Eg.) A Primary Standard Acid $\xrightarrow{\text{titrates}}$ A base solution (eg. NaOH) $\xrightarrow{\text{titrates}}$ Other acids of unknown conc.

Example:

It takes 4.02 mL of 0.200 M KHC₈H₄O₄ to titrate 10.00 mL of a solution of NaOH. Find the [NaOH]

The balanced equation for the reaction is : KHC₈H₄O₄ + NaOH → H₂O + KNaC₈H₄O₄

So the [NaOH] = _____ M

This standardized NaOH solution can now be used to titrate other acids of unknown concentration:

Eg.) It takes 28.54 mL of standardized 0.0804 M NaOH to titrate a 25.00 mL sample of an H₂SO₄ solution.

The balanced equation for this neutralization reaction is:

Calculate the [H₂SO₄].

Answer [H₂SO₄] = _____ M

Carefully read p. 164 – 165 in SW.

Do Ex. 121 – 123 on p. 165

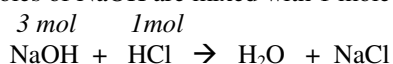
Finding the pH of Mixtures of Acids and Bases

Type 1 – When the mole ratio (coefficient ratio) is 1:1

NOTE: In acid base reactions, if one or both of the reactants are “strong” then the reaction will go to completion. Only when both reactants are “weak”, will you get an equilibrium situation. Titrations always require reactions which go to completion (single arrow), so acid/base titrations will always have either a strong acid, a strong base, or both.

Recall excess or “left over reactant” problems from Chem. 11? Read the following eg. & make sure you understand.

Eg.) If 3 moles of NaOH are mixed with 1 mole of HCl, what will happen?



What will happen here is: 1 mol of HCl will react with 1 mole of NaOH (1:1 coefficient ratio) to form 1 mol of H₂O and 1 mol of NaCl. 3 – 1 = 2 mol of NaOH will be left over. The NaOH is said to be IN EXCESS by 2 mol. The resulting solution, consisting of H₂O (neutral), NaCl (neutral) and left over NaOH (basic), will be **basic**. (All the HCl (limiting reactant) has been used up, so there is none of that left.)

Example Question:

10.00 mL of 0.100M NaOH is mixed with 25.00 mL of 0.100 M HCl. Find the pH of the final (resulting) mixture.

Solution: Balanced equation: NaOH + HCl → H₂O + NaCl

Initial moles of NaOH : 0.100 M x 0.01000 L = 0.00100 mol NaOH (3 SD's like the 0.100 M) (5 dec. places)

Initial moles HCl : 0.100 M x 0.02500 L = 0.00250 mol HCl (3 SD's like the 0.100 M) (5 dec. places)

Excess moles: HCl = 0.00150 mol HCl (5 dec. places) (3 SD's)

Volume of final mixture: 10.00 mL + 25.00 mL = 35.00 mL = 0.03500 L
 (2 dec. pl.) (2 dec. pl.) (2 dec. pl.) (4 SD's)
 (4 SD's)

[H₃O⁺] = [HCl] in the final mixture = $\frac{0.00150 \text{ mol (3 SD's)}}{0.03500 \text{ L (4 SD's)}} = 0.042857 \text{ M}$

3 SD's but DON'T round here. Leave it in your calculator, unrounded! For the next step

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (0.042857) = \underline{1.368} \text{ (rounded to 3 SD's)}$$

Remember, when adding or subtracting, use decimal places, when multiplying or dividing, use SD's.

When the base is in excess (eg. Excess NaOH):

$$\text{Moles NaOH in excess} \rightarrow ([\text{NaOH}] = [\text{OH}^-]) \rightarrow \text{pOH} \rightarrow \text{pH}$$

Try the following example. (Pay close attention to significant digits and decimal places, but don't round in your calculator until the last step.)

40.00 mL of 0.100 M NaOH is mixed with 25.00 mL of 0.100 M HCl. Calculate the pH of the solution resulting. Show all of your steps. Express your answer in the correct # of SD's as justified by the data.

Type 2 – When the mole ratio (coefficient ratio) is NOT 1:1

- Think of a **diprotic** acid as releasing **2 protons** (H^+ 's) to the base.

(NOTE: even though we learned that diprotic acids like H_2SO_4 , donate only 1 proton completely, that was to WATER, not to a STRONG BASE. A **STRONG BASE** will take **both** the protons from H_2SO_4 !)

- Dissociate bases to find out the number of OH^- ions they provide.
- Calculate excess moles of H^+ or OH^- rather than moles of acid or base as you did in type 1.

Eg.) 15.00 mL of 0.100 M H_2SO_4 is mixed with 12.50 mL of 0.200 M NaOH. Calculate the pH of the resulting solution.

Solution to Problem:

Balanced equation for the reaction: $\text{H}_2\text{SO}_4 + 2\text{NaOH} \rightarrow 2\text{H}_2\text{O} + \text{Na}_2\text{SO}_4$ (NOT a 1:1 reactant mole ratio!)

Dissociations: $\text{H}_2\text{SO}_4 \rightarrow 2\text{H}^+ + \text{SO}_4^{2-}$ $\text{NaOH} \rightarrow \text{Na}^+ + \text{OH}^-$

Initial moles of H^+ : $0.100 \text{ M} \times 0.01500 \text{ L} = 0.00150 \text{ mol } \text{H}_2\text{SO}_4 \times \frac{2 \text{ mol } \text{H}^+}{1 \text{ mol } \text{H}_2\text{SO}_4} = 0.00300 \text{ mol } \text{H}^+$ (3SD's \rightarrow 5 dps)

Initial moles OH^- : $0.200 \text{ M} \times 0.01250 \text{ L} = 0.00250 \text{ mol } \text{NaOH} \times \frac{1 \text{ mol } \text{OH}^-}{1 \text{ mol } \text{NaOH}} = 0.00250 \text{ mol } \text{OH}^-$ (3SD's \rightarrow 5 dps)

Excess moles H^+ = 0.00050 mol (5dp \rightarrow 2SD's)

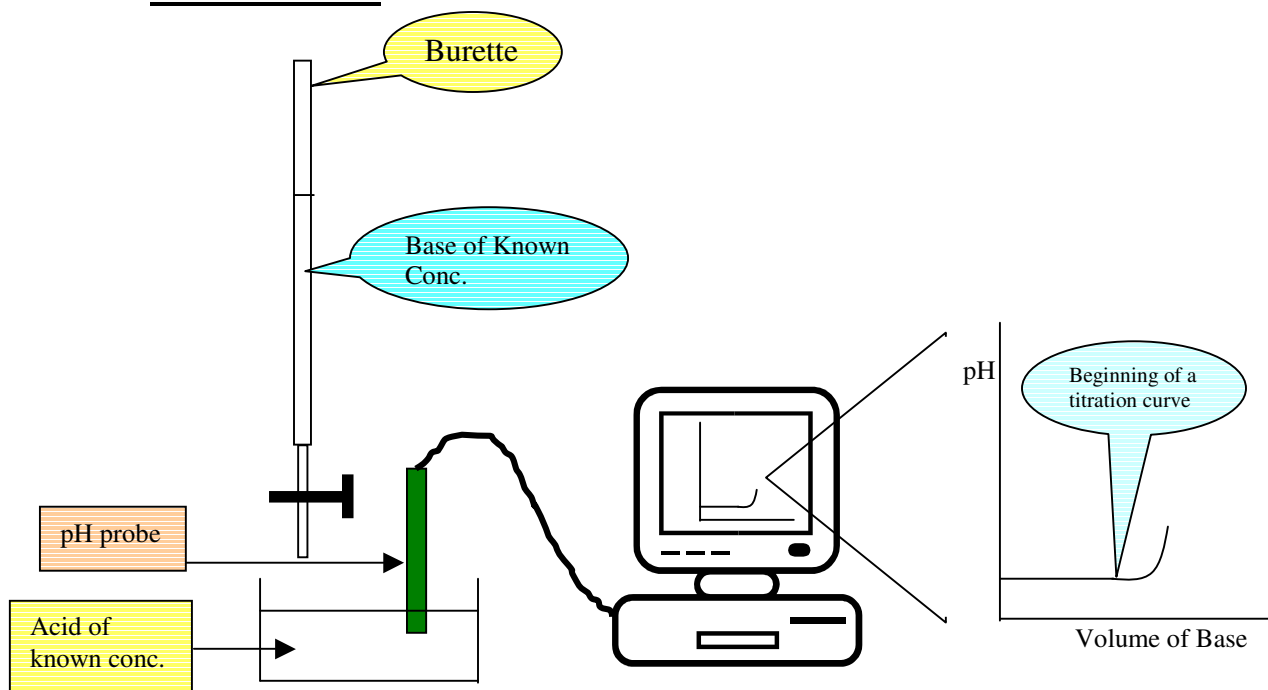
Volume of final mixture: 15.00 mL + 12.50 mL = 27.50 mL = 0.02750 L
 (2 dec. pl.) (2 dec. pl.) (2 dec. pl.) (4 SD's)
 (4 SD's)

$[\text{H}_3\text{O}^+] = [\text{H}^+]$ in the final mixture = $\frac{0.00050 \text{ mol (2 SD's)}}{0.02750 \text{ L (4 SD's)}} = \underline{0.0181818 \text{ M}}$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (0.0181818) = \underline{1.74} \text{ (rounded 2 SD's)}$$

Do Ex. 58, 59 and 60 on p. 143 of SW.

Titration Curves



A base of known concentration is slowly added to a measured volume of an acid of known concentration. Meanwhile, the pH of the mixture is monitored by a pH probe attached to a computer. The computer plots a graph of pH vs. Volume of Base Added. The curve on the graph that results from this is called a **titration curve**.

You will be doing this as a lab. However, you will also be expected to be able to *calculate* the pH's needed to plot a **titration curve** for a Strong Acid—Strong Base titration.

Strong Acid—Strong Base (SA/SB) Titration Curves

We can calculate the pH of the mixture in the beaker throughout the titration. First, we separate the process into 4 stages:

1. Acid before any base is added
2. Base added but acid in excess
3. Equivalence (Stoichiometric) Point
4. Base in excess

Stage 1—Acid before any base is added

The beaker contains 25.00 mL of 0.100 M HCl. Calculate the pH.

HCl is a SA, so $[H_3O^+] = [acid] = 0.100 M$

and $pH = -\log(0.100) = \underline{1.000}$

Stage 2—Base added but acid in excess

5.00 mL of 0.100 M NaOH is added to 25.00 mL of 0.100 M HCl. Find the pH of the resulting solution.

Solution: Balanced equation: $\text{NaOH} + \text{HCl} \rightarrow \text{H}_2\text{O} + \text{NaCl}$

Initial moles of NaOH: $0.100 \text{ M} \times 0.00500 \text{ L} = 0.000500 \text{ mol NaOH}$ (3 SD's like the 0.100 M) (6 dec. places)

Initial moles HCl: $0.100 \text{ M} \times 0.02500 \text{ L} = 0.00250 \text{ mol HCl}$ (2 SD's like the 0.100 M) (5 dec. places)

Excess moles: $\text{HCl} = 0.00200 \text{ mol HCl}$ (5 dec. places) (3 SD's)

Volume of final mixture: $5.00 \text{ mL} + 25.00 \text{ mL} = 30.00 \text{ mL} = 0.03000 \text{ L}$
 (2 dec. pl.) (2 dec. pl.) (2 dec. pl.) (4 SD's)
 (4 SD's)

$[\text{H}_3\text{O}^+] = [\text{HCl}] \text{ in the final mixture} = \frac{0.00200 \text{ mol (3 SD's)}}{0.03000 \text{ L (4 SD's)}} = 0.06667 \text{ M}$

3 SD's but DON'T round here. Leave it in your calculator, unrounded, for the next step.

$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (0.06667) = \underline{1.176}$ (rounded to 3 SD's)

Stage 3—Equivalence (Stoichiometric) Point

25.00 mL of 0.100 M NaOH is added to 25.00 mL of 0.100 M HCl. Find the pH of the resulting solution.

Solution: Balanced equation: $\text{NaOH} + \text{HCl} \rightarrow \text{H}_2\text{O} + \text{NaCl}$

Initial moles of NaOH: $0.100 \text{ M} \times 0.02500 \text{ L} = 0.00250 \text{ mol NaOH}$ (3 SD's like the 0.100 M) (5 dec. places)

Initial moles HCl: $0.100 \text{ M} \times 0.02500 \text{ L} = 0.00250 \text{ mol HCl}$ (2 SD's like the 0.100 M) (5 dec. places)

Excess moles: $\text{Neither HCl nor NaOH is in excess}$

However, 0.00250 moles of H_2O and 0.00250 moles of NaCl have been produced:

	NaOH	$+$	HCl	\rightarrow	H_2O	$+$	NaCl
<i>Initial moles</i>	0.00250		0.00250		0		0
<i>Change in moles</i>	-0.00250		-0.00250		+ 0.00250		+ 0.00250
<i>Final moles</i>	0		0		0.00250		0.00250

The NaOH and the HCl have completely neutralized each other. There is no SA or SB left!

The two substances which remain are H_2O \rightarrow which is **neutral** and won't affect pH.

And the *salt* $\text{NaCl}_{(\text{aq})} \rightarrow \text{Na}^+_{(\text{aq})} + \text{Cl}^-_{(\text{aq})}$

The cation from a SB (eg. any alkali ion) is always NEUTRAL!

The anion from a SA (top 5 on right) is always NEUTRAL!

THE SALT FORMED FROM A **SA-SB** TITRATION IS ALWAYS **NEUTRAL**

Since there is no SA, no SB and just H_2O and a NEUTRAL salt, the pH of the solution formed will be **7.00**

At the Equivalence (Stoichiometric) Point of a SA—SB Titration, the pH is always = 7.00

Stage 4—Base in Excess

26.00 mL of 0.100 M NaOH is added to 25.00 mL of 0.100 M HCl. Find the pH of the resulting solution.

Solution: Balanced equation: $\text{NaOH} + \text{HCl} \rightarrow \text{H}_2\text{O} + \text{NaCl}$

Initial moles of NaOH: $0.100 \text{ M} \times 0.02600 \text{ L} = 0.00260 \text{ mol NaOH}$ (3 SD's like the 0.100 M) (5 dec. places)

Initial moles HCl: $0.100 \text{ M} \times 0.02500 \text{ L} = 0.00250 \text{ mol HCl}$ (2 SD's like the 0.100 M) (5 dec. places)

Excess moles: $\text{NaOH} = 0.00010 \text{ mol NaOH}$ (5 dec. places) (2 SD's)

Volume of final mixture: $26.00 \text{ mL} + 25.00 \text{ mL} = 51.00 \text{ mL} = 0.05100 \text{ L}$
 (2 dec. pl.) (2 dec. pl.) (2 dec. pl.) (4 SD's)
 (4 SD's)

$[\text{OH}^-] = [\text{NaOH}] \text{ in the final mixture} = \frac{0.00010 \text{ mol (2 SD's)}}{0.05100 \text{ L (4 SD's)}} = 0.00196 \text{ M}$

2 SD's but DON'T round here. Leave it in your calculator, unrounded! For the next step

$\text{pOH} = -\log [\text{OH}^-] = -\log (0.00196) = 2.70757$ (leave unrounded in calculator)

$\text{pH} = 14.000 - \text{pOH} = \underline{\underline{11.29}}$

Now, round to 2 SD's

Notice how adding just 1.00 mL extra 0.100 M NaOH, made the pH shoot up from 7.00 to 11.29 (a jump of over 4 pH units!)

Plotting a SA—SB Titration Curves

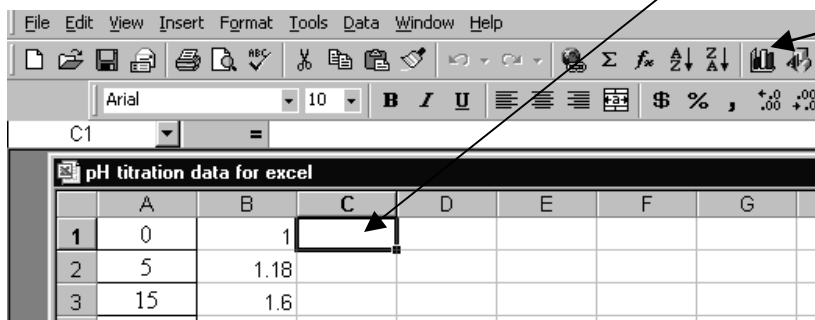
Using the processes outlined in “Stage 1 to Stage 4” above, calculate the pH of the resulting solutions formed by adding the given volumes of 0.10 M NaOH to 25.00 mL of 0.10 M HCl. Work out your answers on a separate sheet (or on your calculator) and record them in the following table:


Volume of 0.10 M NaOH (mL)	Volume of 0.10 M HCl (mL)	pH of Resulting Solution	
0.00	25.00		No base added
5.00	25.00	1.18	
15.00	25.00		Base added Acid in excess
20.00	25.00		
24.00	25.00		
24.50	25.00		
24.90	25.00		Equivalence Pt.
25.00	25.00		
25.10	25.00		Base in excess
25.50	25.00		
26.00	25.00	11.29	
30.00	25.00		
40.00	25.00		
50.00	25.00		

Check with the teacher to make sure your pH values are correct! Then go on to the next step:

Now, go to a computer and make a graph with Volume of NaOH on the “X” axis and pH on the “Y” axis. You can use Microsoft Excel and follow the instructions below:

1. Log on
2. Go to “Start” then “Programs” and select “Microsoft Excel”.
3. Enter the values for “Volume of 0.10M NaOH” from the table in Column “A” (**No words!**)
4. Enter the values for pH (to 2 decimal places) in column “B” (**No words!**)
5. When finished entering numbers, click in the cell “C 1”



6. Now click the “Chart Wizard” icon near the top of the screen.
7. Select “XY (Scatter)”
8. When the “Chart Sub-Types” box comes up, click on the MIDDLE LEFT box 
9. Click the “Next” button at the bottom of the screen.

10. When the next thing comes up, click the “Next” button again. Click “Titles” if it isn’t already selected.
11. In the “Chart Title:” enter “Strong Acid-Strong Base Titration Curve followed by your names”
12. In the “Value (X) axis:” box, enter “Volume of NaOH”
13. In the “Value (Y) axis:” box, enter “pH”
14. Click the “Legend” tab at the top, then click in the box that says “Show Legend” to remove the checkmark
15. Now, click the “Next” button at the bottom
16. **IMPORTANT:** Click the little round button next to “As New Sheet”
17. Now click “Finish”
18. Save and Print enough copies of the graph for the people in your group.
19. Keep it. Your teacher will have you add some important information to it.

Do Experiment 20-H—Using the pH Probe and Computer to do a Strong Acid—Strong Base Titration. See the internet site: <http://wwwchem.uwimona.edu.jm:1104/software/titr.html> !

Weak Acid—Strong Base Titration Curves

Again, this type of titration has the 4 stages:

1. Acid before any base is added
2. Base added but acid in excess
3. Equivalence (Stoichiometric) Point
4. Base in excess

When the acid in the beaker is WEAK, stages 1-3 are different than in a SA-SB titration.

Stage 1 – Only the Acid is present, but it is a WEAK acid, so the $[H_3O^+]$ is NOT equal to [acid]
To find $[H_3O^+]$ and pH, you have to use an ICE table.

Eg. Find the pH of 25.00 mL of 0.10 M CH₃COOH before any base is added to it.

Solution:

$$\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CH}_3\text{COO}^-$$

[I]	0.10		0	0
[C]	-x		+x	+x
[E]	0.10 - x		x	x

1. Ka expression: $K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$

$$K_a = \frac{(x)(x)}{0.10 - x}$$

Assume $0.10 - x \cong 0.10$

$$K_a \cong \frac{x^2}{0.10}$$

$$\text{So } x^2 = 0.10 K_a$$

$$\begin{aligned} [\text{H}_3\text{O}^+] = x &= \sqrt{0.10 K_a} \\ &= \sqrt{0.10 (1.8 \times 10^{-5})} \end{aligned}$$

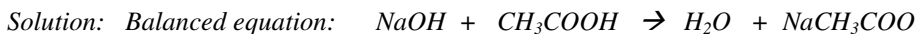
$$[\text{H}_3\text{O}^+] = 1.34164 \times 10^{-3} \text{ M}$$

$$\text{pH} = 2.87$$

We see that for a **WEAK Acid-Strong Base** Titration, the pH before the base is added is **higher** (eg. 2.87) than it was for a SA-SB Titration (where the pH before the base is added was 1.00) For the same concentration, the **weaker** the acid, the **HIGHER** the pH will start out!

Stage 2—Base Present with Acid in Excess

Eg. 10.00 mL of 0.100 M NaOH is added to 25.00 mL of 0.10 M CH₃COOH.



Initial moles of NaOH: $0.100 \text{ M} \times 0.01000 \text{ L} = 0.00100 \text{ mol NaOH}$

Initial moles CH₃COOH: $0.100 \text{ M} \times 0.02500 \text{ L} = 0.00250 \text{ mol CH}_3\text{COOH}$

Excess moles: $\text{CH}_3\text{COOH} = 0.00150 \text{ mol CH}_3\text{COOH}$

But, this time we must consider the salt (NaCH₃COO) that is produced → because it is **NOT neutral!**

$$\text{NaOH} + \text{CH}_3\text{COOH} \rightarrow \text{H}_2\text{O} + \text{NaCH}_3\text{COO}$$

<i>Initial moles</i>	0.00100	0.00250	0	0
<i>Change in moles</i>	-0.00100	-0.00100	+0.00100	+0.00100
<i>Final moles</i>	0	0.00150	0.00100	0.00100

A Weak Acid

The salt of it's Conjugate Base

What we are left with is a mixture of a Weak Acid (CH_3COOH) and the Salt of It's Conjugate Base (NaCH_3COO)

A mixture of a Weak Acid and a Weak Base (the Salt of It's Conjugate Base) is called a **BUFFER SOLUTION**.

As we will see later, a **Buffer Solution** is a solution which maintains the pH at a fairly Constant value. This causes the Titration Curve to decrease in slope during this stage. The area on the curve is called the "Buffer Region".

(In Chem. 12, we will not need to be able to calculate the pH in a Buffer Solution.)

Stage 3—Equivalence (Stoichiometric) Point

Eg. 25.00 mL of 0.100 M NaOH is added to 25.00 mL of 0.10 M CH_3COOH .

Solution: Balanced equation: $\text{NaOH} + \text{CH}_3\text{COOH} \rightarrow \text{H}_2\text{O} + \text{NaCH}_3\text{COO}$

Initial moles of NaOH: $0.100 \text{ M} \times 0.02500 \text{ L} = 0.00250 \text{ mol NaOH}$

Initial moles CH_3COOH : $0.100 \text{ M} \times 0.02500 \text{ L} = 0.00250 \text{ mol CH}_3\text{COOH}$

Excess moles: *neither NaOH nor CH_3COOH is in excess*

But, this time we must consider the salt (NaCH_3COO) that is produced \rightarrow because it is **NOT neutral!**

	NaOH	$+$	CH_3COOH	\rightarrow	H_2O	$+$	NaCH_3COO
<i>Initial moles</i>	0.002500		0.00250		0		0
<i>Change in moles</i>	-0.00250		-0.00250		+ 0.00250		+ 0.00250
<i>Final moles</i>	0		0		0.00250		0.00250

Negligible compared to water already present

We have produced 0.00250 moles of the salt NaCH_3COO (CH_3COO^-)

This salt that is produced (NaCH_3COO) dissociates to form Na^+ (spectator) and CH_3COO^- which undergoes **base hydrolysis** in water.

The total volume of our solution is $25.00 + 25.00 = 50.00 \text{ mL} = 0.05000 \text{ L}$.

So the $[\text{CH}_3\text{COO}^-] = \frac{0.00250 \text{ mol}}{0.05000 \text{ L}} = 0.0500 \text{ M}$

The K_b for $\text{CH}_3\text{COO}^- = 1.0 \times 10^{-14} / 1.8 \times 10^{-5} = 5.556 \times 10^{-10}$

We can now use the hydrolysis equation and an ICE table to calculate the $[\text{OH}^-]$ and then pOH and then pH:

	$\text{CH}_3\text{COO}^- + \text{H}_2\text{O}$	\rightleftharpoons	$\text{CH}_3\text{COOH} + \text{OH}^-$
[I]	0.0500		0 0
[C]	-x		+x +x
[E]	$0.0500 - x$		x x

K_b expression: $K_b = \frac{[\text{CH}_3\text{COOH}] [\text{OH}^-]}{[\text{CH}_3\text{COO}^-]}$

$K_b = \frac{x^2}{0.0500 - x}$ Assume $0.0500 - x \approx 0.0500$

$$K_b \cong \frac{x^2}{0.0500}$$

$$\text{So } x^2 = 0.0500 K_b$$

$$[\text{OH}^-] = x = \sqrt{0.0500 K_b}$$

$$[\text{OH}^-] = \sqrt{0.0500 (5.556 \times 10^{-10})} = 5.270 \times 10^{-6} \text{ M} \rightarrow \text{pOH} = 5.278 \rightarrow \text{pH} = 8.72$$

For a WA/SB Titration, the pH at Equivalence Point is ALWAYS > 7

This is because, when a Weak Acid reacts with a Strong Base, you always produce the conjugate base of the weak acid, which is BASIC.

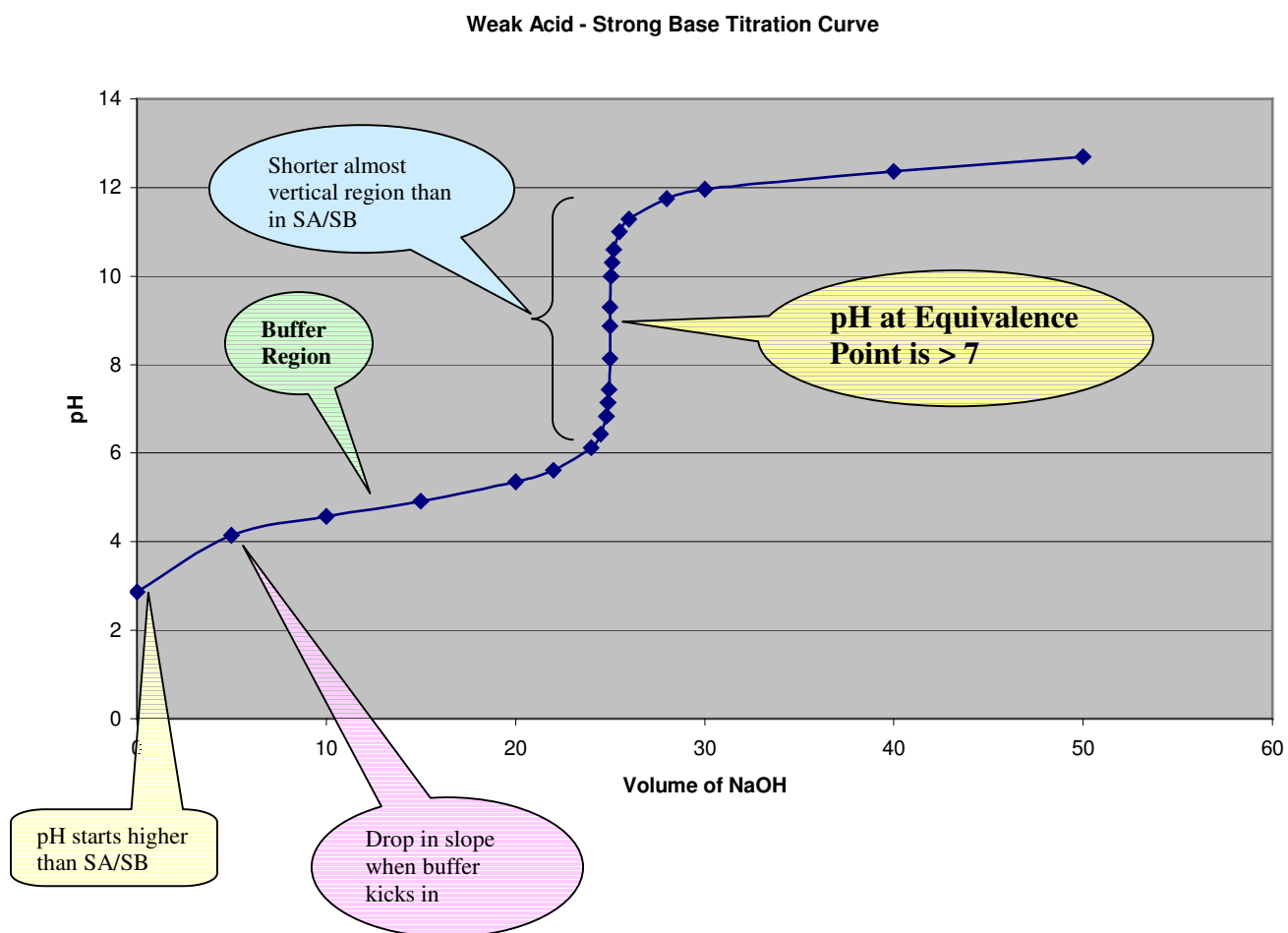
Remember: For a SA/SB Titration, the salt produced has the conjugate base of a STRONG ACID, which is always Neutral → so **for a SA/SB Titration, the pH at EP (SP) is ALWAYS = 7.00**

Stage 4 – Base in excess:

Looking at the Balanced equation: $\text{NaOH} + \text{CH}_3\text{COOH} \rightarrow \text{H}_2\text{O} + \text{NaCH}_3\text{COO}$

Once NaOH is in Excess, you will have some STRONG BASE (NaOH) and some WEAK BASE (CH_3COO^-) in the resulting mixture. The OH^- contributed by the weak base (CH_3COO^-) was significant *when there was no other base present (EP)*, but once a **strong base (NaOH)** is present, the OH^- contributed by the weak base is *insignificant* compared to that produced by the NaOH. So the titration curve past the EP for a WA/SB Titration is the same as it is for a SA/SB Titration (where NaOH is in excess)

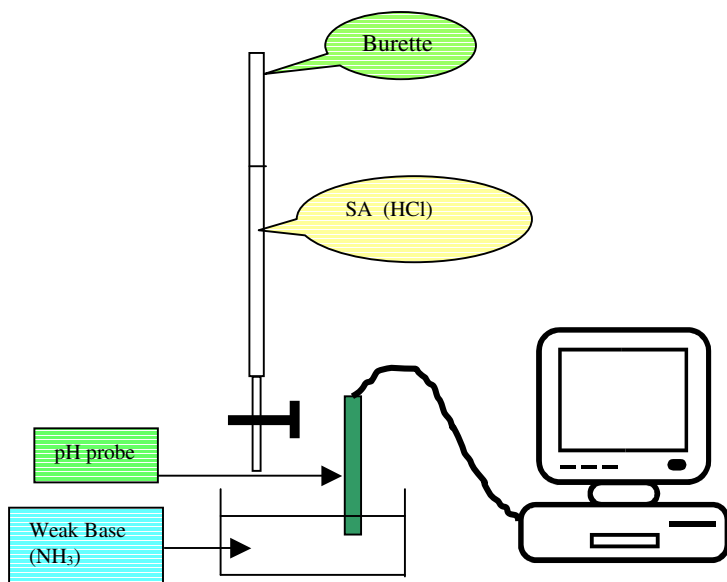
See the next page for a graph for the titration of CH_3COOH with NaOH (A Weak Acid/Strong Base Titration):



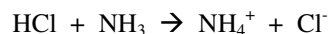
See the next page for a Strong Acid-Weak Base Titration Curve...

Strong Acid—Weak Base Titration Curves

In this type of titration, the Standard Solution is usually the Strong Acid and the Sample is usually the Weak Base. Therefore, the SA will be in the burette and the WB will be in the beaker:



An example of a SA/WB Titration could be done with the strong acid HCl and the weak base NH₃.



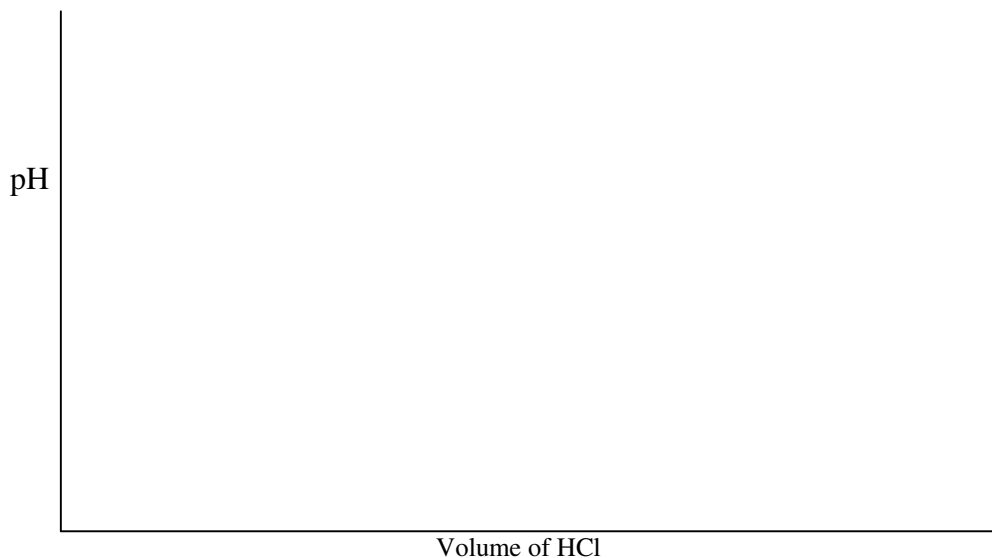
The pH will start out high (base), but not too high (weak)

When HCl is added but the NH₃ is still in excess, we will have a mixture of NH₃ (a weak base) and NH₄⁺ (a weak acid) which is a buffer. So again, we will have a buffer region as the pH goes down.

At the equivalence point in this titration, all of the HCl and NH₃ will be gone and only NH₄⁺ (a weak acid) and Cl⁻ (a neutral spectator) will remain. Because there is a WEAK ACID (NH₄⁺) present, the pH will be LESS THAN 7. (but not really low)

Once the Acid (HCl) is in excess, the pH will continue to go down.

Read the information above and see if you can make an informed guess at what the Titration Curve for this SA/WB Titration would look like. Label the Equivalence Point. When you are finished, check with the teacher!



Summary of pH at Equivalence (Stoichiometric) Points for the three types of Titrations:

Reactants	Salt Formed is...	pH at Equivalence Point
Strong Acid – Strong Base	Neutral (conjugate base of SA)	= 7.00
Weak Acid – Strong Base	Basic (conjugate base of WA)	> 7.00
Strong Acid – Weak Base	Acidic (conjugate acid of WB)	< 7.00

Make sure you study and KNOW this table. It is very important!

Indicators for Titrations

Indicators can be used to tell you when you have reached the Equivalence (Stoichiometric) Point in a Titration.

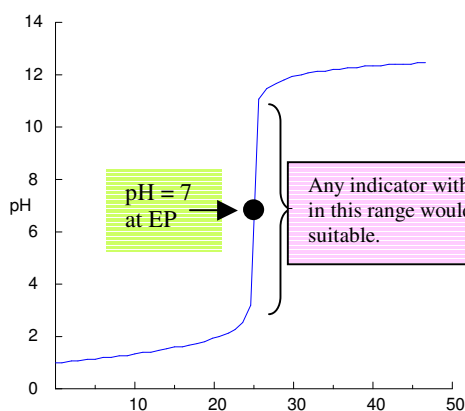
However, different indicators must be used for different types of titrations.

Ideally, the pH at the Transition Point (pKa) of the Indicator will be the same as the pH at the Equivalence Point of the titration. Or:

$$\text{pKa (indicator)} = \text{pH at EP of Titration}$$

To choose the best indicator for a particular titration, have the titration curve and the indicator table handy:

For example, for a SA-SB Titration Curve:



Bromocresol green	3.8 – 5.4	yellow to blue
Methyl red	4.8 – 6.0	red to yellow
Chlorophenol red	5.2 – 6.8	yellow to red
Bromthymol blue	6.0 – 7.6	yellow to blue
Phenol red	6.6 – 8.0	yellow to red
Neutral red	6.8 – 8.0	red to amber
Thymol blue	8.0 – 9.6	yellow to blue
Phenolphthalein	8.2 – 10.0	colourless to pink
Thymolphthalein	9.4 – 10.6	colourless to blue

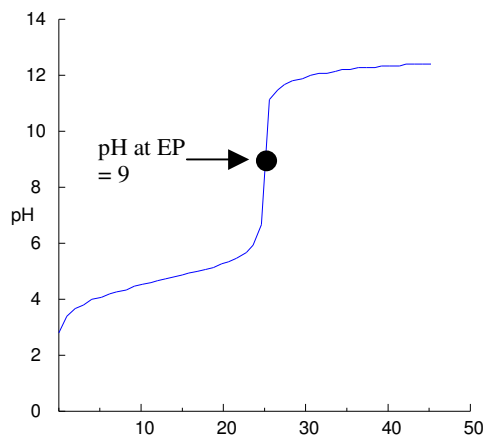
The **best** indicators are the ones which have the **pH at EP within their Transition Range**. So the best indicators for the SA-SB Titration above would be Bromthymol Blue (Range 6.0 – 7.6), Phenol Red (Range 6.6 – 8.0) or Neutral Red (Range 6.8 – 8.0) as these all have pH = 7 within their transition ranges.

However, looking at the graph, there is an almost vertical line from pH 3 to pH 11 on the graph. This means that VERY LITTLE volume change of base would give a **huge** change in pH. It probably takes only a few drops to get the pH to change from 3.0 to 11.0! Any of the indicators Bromocresol Green to Thymolphthalein would change colour in that pH range, so they would all work for this one.

Next, we will look at a WA – SB Titration:

See the next page....

For a **WA-SB Titration Curve**:



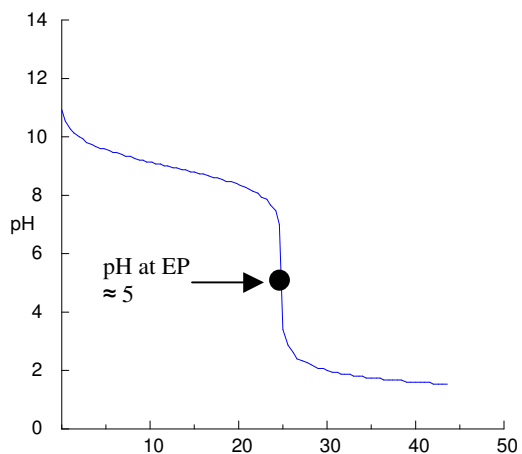
Neutral red	6.8 – 8.0	red to amber
Thymol blue	8.0 – 9.6	yellow to blue
Phenolphthalein	8.2 – 10.0	colourless to pink
Thymolphthalein	9.4 – 10.6	colourless to blue
Alizarin yellow	10.1 – 12.0	yellow to red
Indigo carmine	11.4 – 13.0	blue to yellow

For a WA-SB Titration Curve, the almost vertical section is shorter (than for the SA-SB Curve). This means you have a narrower range of suitable indicators. For this particular titration, any indicator which has pH = 9 within its Transition Range is suitable.

Indicators Suitable for **this** WA – SB Titration would include _____,

or _____

Now for a **SA – WB Titration Curve**:

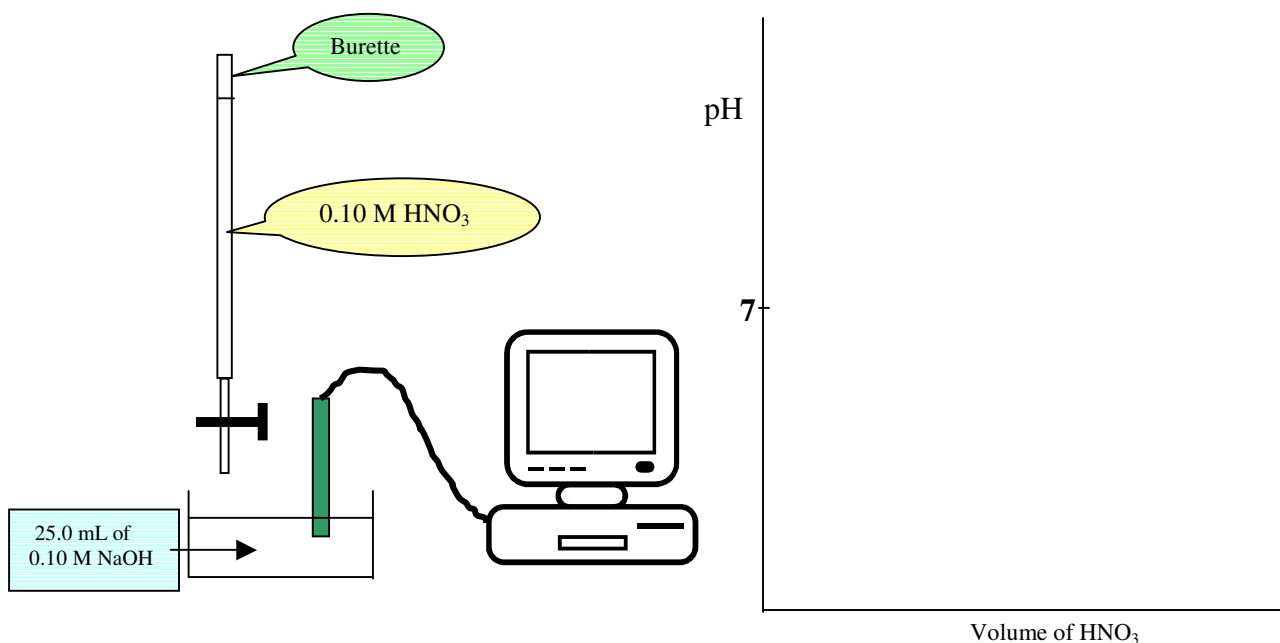


Orange IV	1.4 – 2.8	red to yellow
Methyl orange	3.2 – 4.4	red to yellow
Bromocresol green	3.8 – 5.4	yellow to blue
Methyl red	4.8 – 6.0	red to yellow
Chlorophenol red	5.2 – 6.8	yellow to red
Bromthymol blue	6.0 – 7.6	yellow to blue
Phenol red	6.6 – 8.0	yellow to red

Indicators Suitable for **this** SA – WB Titration would include _____

or _____

Question: Draw the titration curve you would expect would result from the following titration. Get the shape and the important points (pH at beginning, pH at EP, pH at the end etc.) as close as you can:



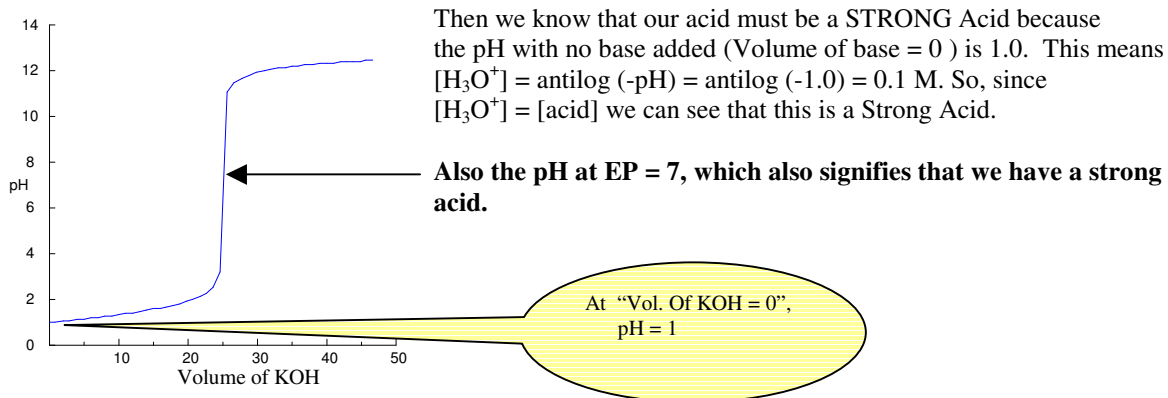
Name an indicator which would be suitable for this titration. _____

As you pass through the Equivalence (Stoichiometric) point in this titration, the colour of your indicator would change from _____ to _____ (to _____)

Using Titration Curves in Questions and Calculations

If we have a strong base (eg. NaOH or KOH) in the burette ("Volume of base" is on "X" axis), we can tell by the shape and by the pH at the beginning (Volume of Base = 0) whether the acid is Strong or Weak (given the [acid])

For example, if we have a 0.10 M acid in the beaker and 0.10 M KOH in the burette and the titration curve looks like:



By using the pH at “Volume of Base = 0”, we can calculate the K_a for a Weak Acid we are titrating. Look at the following example in which a 0.10 M Weak Acid is being titrated with 0.10 M NaOH.

Notice that the pH at “Volume of Base = 0” is about 2.5

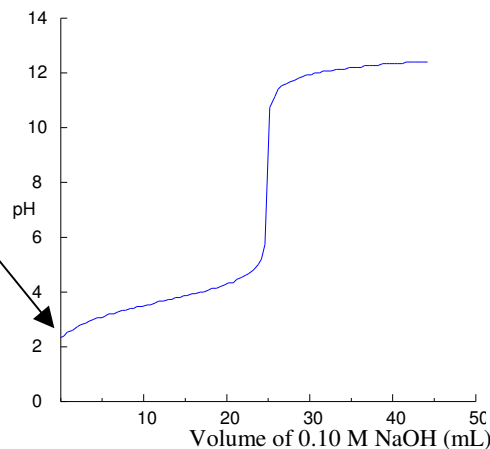
Since $\text{pH} = 2.5$, $[\text{H}_3\text{O}^+] = \text{antilog}(-2.5)$
 $= 3.16 \times 10^{-3} \text{ M}$

Using $[\text{H}_3\text{O}^+] = \sqrt{C_o K_a}$

We can rearrange and solve for K_a :

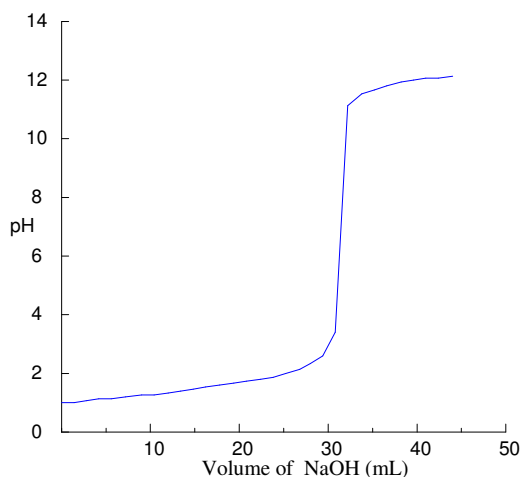
(squaring both sides:) $[\text{H}_3\text{O}^+]^2 = C_o K_a$

$$\text{so } K_a = \frac{[\text{H}_3\text{O}^+]^2}{C_o} = \frac{(3.16 \times 10^{-3})^2}{0.10} = \underline{\underline{1 \times 10^{-4}}}$$



We can also use a titration curve to find the Volume of Base when the Equivalence point is reached. By knowing the [acid], we use this “Volume of Base” to calculate the concentration of the Base. Look at the following example:

When titrating a 25.0 mL sample of 0.10 M HCl with a solution of NaOH, the following titration curve was obtained. Calculate the [NaOH] in the burette:

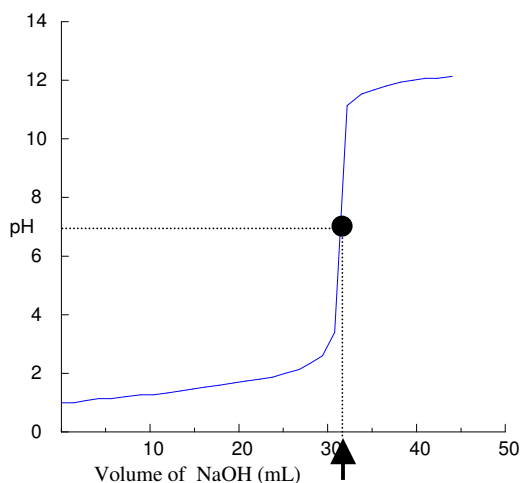


We see that the Volume of NaOH needed to reach the Equivalence Point is approximately 32 mL.

Given this and the information at the beginning of the question, calculate the [NaOH] in the burette:

Calculation:

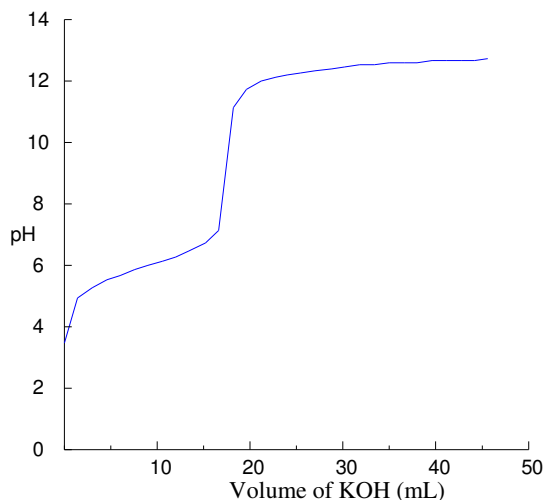
We know that this is a SA-SB titration, so at the EP, $\text{pH} = 7$. Also, the EP is always in the center of the “almost vertical” region. We mark the EP and draw a straight line down to see where it hits the “Volume of Base” axis. This will give us the Volume of NaOH needed to reach the equivalence point:



$$[\text{NaOH}] = \underline{\hspace{2cm}} \text{ M}$$

Question:

The following titration curve results from titrating 25.0 mL of a 0.10 M Weak Acid HA with a Strong Base KOH:



a.) Use this graph to estimate the K_a of the acid HA.

b.) Use this graph to calculate the $[KOH]$.

More Practical Things about Titrations

Selecting Solutions for Acid-Base Titrations

If you are titrating an **acid**, make sure you use a **base** so that your titration reaction is a **neutralization**. It should have at least one STRONG reactant so it will go to completion.

For example, if you are titrating the acid CH_3COOH (WA), use a **STRONG BASE** like NaOH, KOH etc. You could **not** use another acid (like HCl etc.). Also, since CH_3COOH is a WEAK acid, you **cannot** use a weak base (like NH_3)

Also, the concentration of your standard should be *relatively close to* the concentration of the solution you are titrating so that the volumes used are comparable. (So you don't need "buckets" or "a fraction of a drop")

Here is an example of a multiple choice question:

In titrating 25.00 mL samples of NH_3 which is approximately 0.1 M, which of the following solutions should be used to determine the $[NH_3]$?

- a) 0.00100M HCl b) 0.125 M HCl c) 6.00 M HCl d) 12.0 M HCl e) 0.100M NaOH

Too dilute. You would need too much volume

Right. HCl is a Strong Acid and conc. is close to 0.1 M

Too concentrated. You would need too little volume

Much too concentrated. You would need too little volume

You can't titrate a WB with a SB. You need a SA.

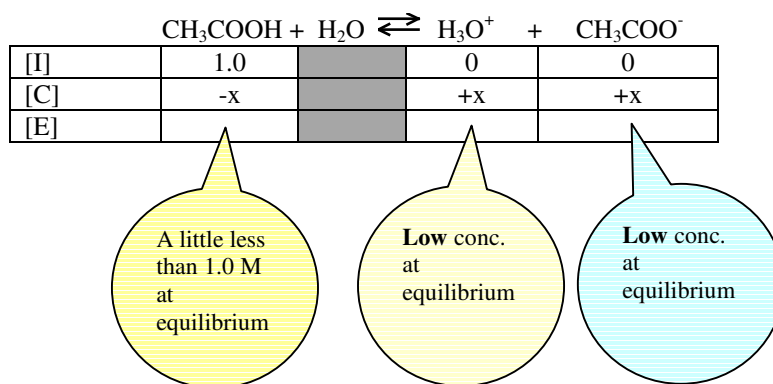
Buffer Solutions

A **buffer solution** is a solution which *resists* changes in pH when a *small* amount of **acid** or **base** is added. Or we could say it *minimizes* the change in pH when acid or base is added.

Weak Acid Equilibria and the Common Ion Effect

Say you had some 1.0 M acetic acid (CH_3COOH) solution.

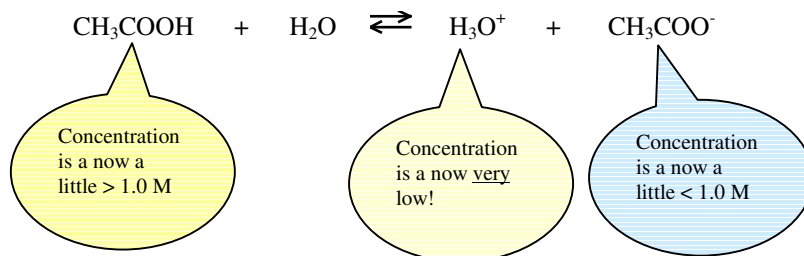
This equilibrium becomes established:



Since CH_3COOH is a WEAK acid, the $[\text{H}_3\text{O}^+]$ and $[\text{CH}_3\text{COO}^-]$ are quite **low** at equilibrium.

Now, lets add some sodium acetate (NaCH_3COO) to the equilibrium mixture so that $[\text{CH}_3\text{COO}^-]$ is 1.0 M.

When we do this the $[\text{CH}_3\text{COO}^-]$ obviously goes up. However, by LeChatelier's Principle, the equilibrium will shift to the LEFT, causing $[\text{H}_3\text{O}^+]$ to decrease and $[\text{CH}_3\text{COOH}]$ to increase



So what we have produced is a solution that has a fairly high ($\approx 1\text{M}$) of a **WEAK ACID** (CH_3COOH) and a **WEAK BASE** (CH_3COO^-) in the same solution. This is how a **buffer solution** is prepared.

Since the acid and the base are both WEAK, they don't neutralize each other like a mixture of a SA and SB would. They co-exist in this equilibrium unless disturbed!

There are two kinds of **Buffer Solutions**:

- A **Weak Acid** and the **Salt of It's Conjugate Base** (WASCB) eg. 1.0 M CH_3COOH & 1.0 M NaCH_3COO
- A **Weak Base** and the **Salt of It's Conjugate Acid** (WBSA) eg. 1.0 M NH_3 & 1.0 M NH_4Cl

The first type (WASCB) or Acidic Buffers are useful as buffers in the acidic range (solutions in which pH is 7 or lower)

The second type (WBSCA) or Basic Buffers are useful as buffers in the basic range (solutions in which pH is 7 or higher)

Any weak acid and a salt containing its conjugate base will work as an Acidic Buffer.

Any weak base and a salt containing its conjugate acid will work as a Basic Buffer.

Here are a few examples of buffer solutions:

Some Acidic Buffers (WASCB)	Some Basic Buffers (WBSCA)
1.0 M HNO ₂ & 1.0 M KNO ₂	1.0 M NH ₃ & 1.0 M NH ₄ Cl
0.1 M NaH ₂ PO ₄ & 0.1 M Na ₂ HPO ₄	1.0 M NH ₃ & 1.0 M NH ₄ NO ₃
0.2 M H ₂ C ₂ O ₄ & 0.20 M NaHC ₂ O ₄	1.0 M N ₂ H ₄ & 1.0 M N ₂ H ₅ Br

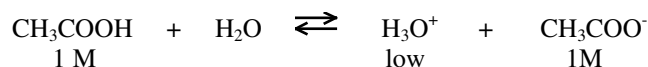
NOTE: Buffers **CANNOT** be prepared using any **STRONG ACIDS** or **STRONG BASES!!!** Strong acids and bases are too reactive, and will not remain in an equilibrium mixture. They will react!
So mixtures like 1.0 M HCl and 1.0 M NaCl or 1.0 M CH₃COOH and 1.0 M NaOH CANNOT be Buffers!



How Buffers Work to Minimize the Change in pH When Acids or Bases are Added

Consider the buffer solution made up of 1M CH₃COOH and 1M NaCH₃COO.

The equation representing the equilibrium present in this buffer solution is (*just the same as the ionization of the weak acid, CH₃COOH*):

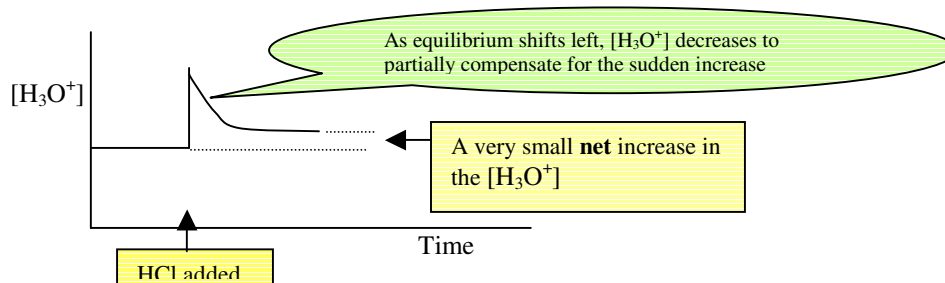


Now, we add a small amount of HCl to this solution.

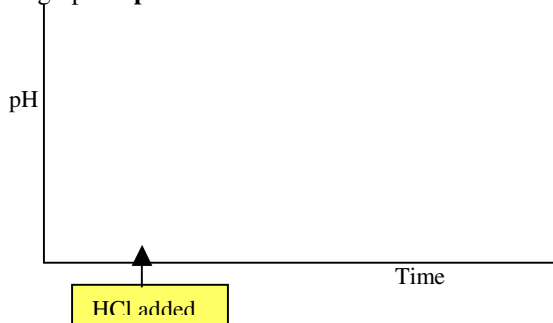
The HCl produces H₃O⁺, so the [H₃O⁺] will immediately **increase**. (and the pH will go down).

However, since this is an equilibrium and there is plenty of CH₃COO⁻ available, the equilibrium will **SHIFT to the LEFT** and [H₃O⁺] will go back down again (but not quite to its original value)

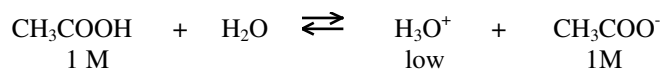
This can be shown on a graph of [H₃O⁺] vs. Time:



Draw a graph of **pH vs. Time** when a small amount of HCl is added to the buffer above (Explain each part)

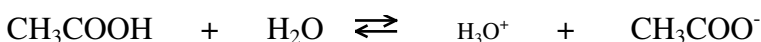


Using the same buffer solution:

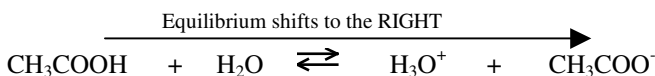


This time we add a small amount of base NaOH:

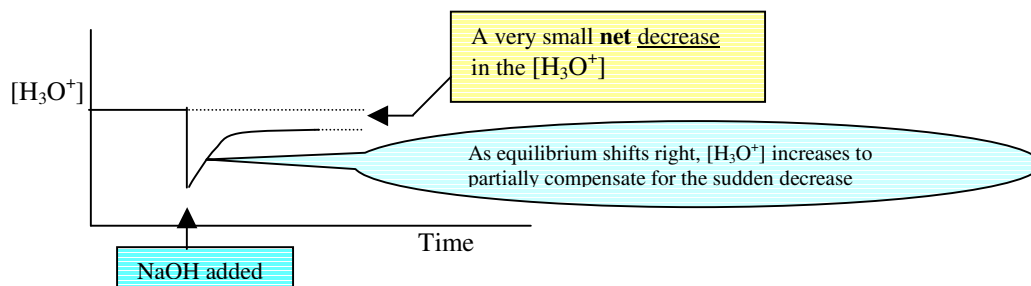
The NaOH produces OH^- which neutralizes H_3O^+ so the $[\text{H}_3\text{O}^+]$ will immediately **decrease**. (and the pH will go up).



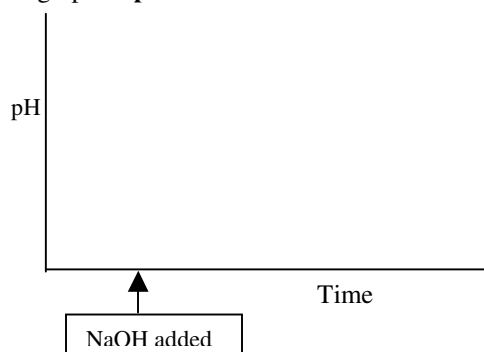
However, since this is an equilibrium and there is plenty of CH_3COOH available, the equilibrium will **SHIFT to the RIGHT** and $[\text{H}_3\text{O}^+]$ will go back up again (but not quite to its original value)



This can be shown on a graph of $[\text{H}_3\text{O}^+]$ vs. Time:



Draw a graph of **pH vs. Time** when a small amount of NaOH is added to the buffer above (Explain each part)



So, in summary, this buffer maintains a relatively constant pH when a small amount of acid or base is added to it!

This is the function of a buffer solution!

Basic Buffers work using the same principles. Work through the example by filling in the blanks.....

Eg.) A buffer solution is prepared using 1M NH_3 and 1M NH_4Cl (WBSCA)

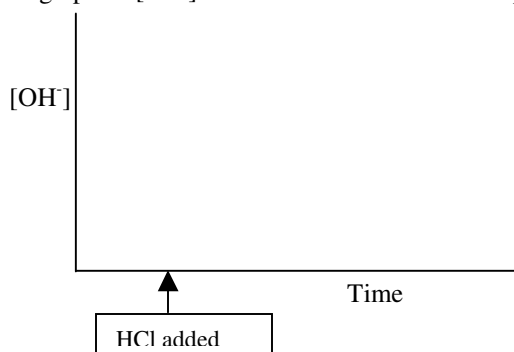
a) Write the **equilibrium equation** describing this buffer.

b) When a small amount of HCl (SA) is added, the $[\text{OH}^-]$ quickly _____creases (the pH goes ____)

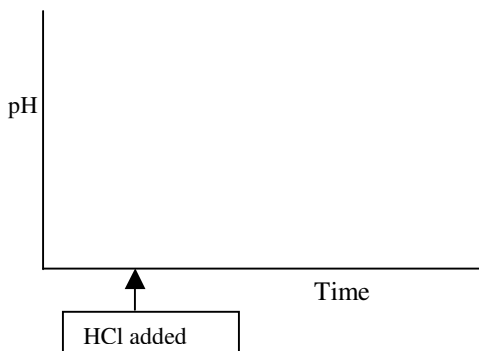
c) As a result, the equilibrium shifts to the _____, and the $[\text{OH}^-]$ gradually _____creases. (the pH goes back _____)

d) So, as a result of adding HCl, there was a small **net** _____crease in the $[\text{OH}^-]$ (a small **net** ____ crease in pH)

e) Draw a graph of $[\text{OH}^-]$ vs. Time to illustrate what happened in b \rightarrow d. Label each part.



f) Draw a graph of pH vs. Time to illustrate what happened in b \rightarrow d.



Eg.) A buffer solution is prepared using 1M NH_3 and 1M NH_4Cl (WBSCA)

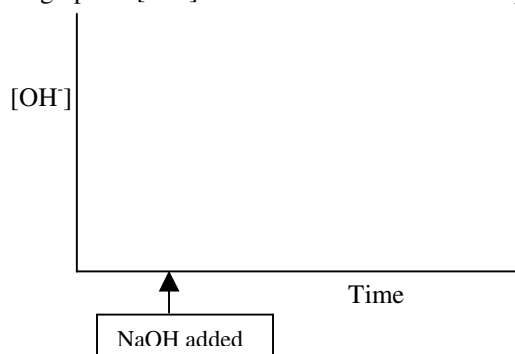
a) Write the **equilibrium equation** describing this buffer.

b) When a small amount of NaOH (SB) is added, the $[\text{OH}^-]$ quickly _____ creases (the pH goes _____)

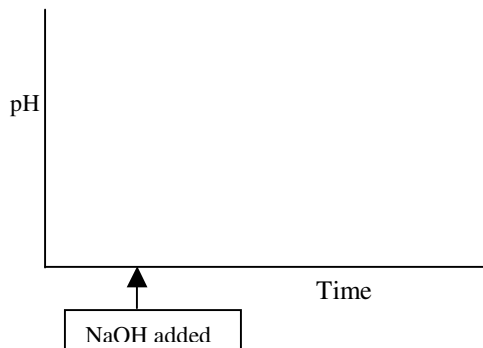
c) As a result, the equilibrium shifts to the _____, and the $[\text{OH}^-]$ gradually _____ creases. (the pH goes back _____)

d) So, as a result of adding NaOH, there was a small **net** _____ crease in the $[\text{OH}^-]$ (a small **net** _____ crease in pH)

e) Draw a graph of $[\text{OH}^-]$ vs. Time to illustrate what happened in b \rightarrow d. Label each part.



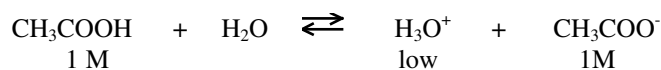
f) Draw a graph of pH vs. Time to illustrate what happened in b \rightarrow d.



So, in summary, this buffer _____ when a small amount of acid or base is added to it!

Limitations of Buffers

Say we have a buffer solution prepared using 1M CH₃COOH and 1M NaCH₃COO. The equilibrium describing this buffer solution is:

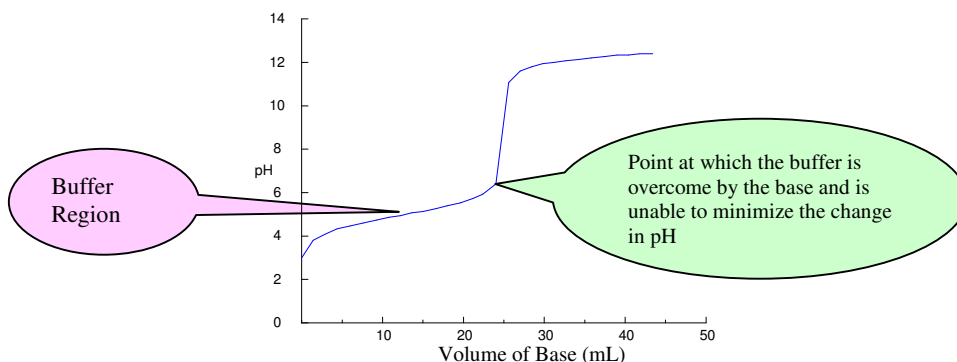


Let's say we add 1.5 moles of HCl to 1 Litre of this solution. The [H₃O⁺] will immediately go up to 1.5 M. This is more than the 1 M CH₃COO⁻ can handle (react with). There will still be an **excess** of H₃O⁺ large enough to bring the pH **down** significantly.

In the above case we have **overcome** the limitations of our buffer and it cannot hold the pH relatively constant any more.

Buffers only maintain a relatively constant pH when **SMALL** amounts of acid or base are added to them!

Looking at the “buffer region” of the titration curve for a WA-SB titration illustrates how the buffer “loses control” of the pH when the [base] overcomes the buffer:

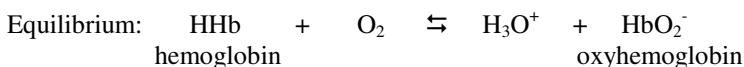
**Uses of Buffers**

- Calibration of pH meters
- Control of pH in industrial reactions
- Used in maintaining water quality
- Pools and hot tubs
- Wine making
- pH balanced shampoos and deodorants
- Soil pH
- Minimizing effects of acid rain

Biological Buffer Systems

-see p. 182-183 of SW.

For Hemoglobin to work properly, the pH of the blood needs to stay very close to 7.35



When you inhale the [O₂] in lungs is high. This diffuses through the thin alveoli walls into the blood. So the equilibrium above shifts to the **RIGHT**, producing more oxyhemoglobin.

This “oxygenated” blood then takes the oxyhemoglobin to the cells of the body where [O₂] is low. (O₂ is used up during cellular respiration.) Because [O₂] is low, the equilibrium shift to the **LEFT**, releasing O₂ to the cells where it can be used for cellular respiration.

This equilibrium must be in a delicate balance for it to work properly.

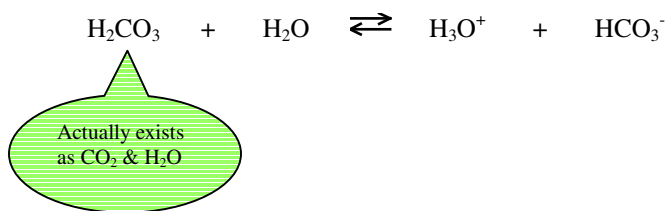
If $[\text{H}_3\text{O}^+]$ is **too high** (pH **too low**), the equilibrium cannot shift right enough in the lungs and cannot form enough oxyhemoglobin. This condition is called **acidosis** (pH < 7.2)

If $[\text{H}_3\text{O}^+]$ is **too low** (pH **too high**), the equilibrium cannot shift left enough in the cell and cannot release enough oxygen. This condition is called **alkalosis** (pH > 7.5)

Both of these conditions can be deadly.

Buffer Systems in the Blood

CO_2 is produced during cellular respiration. It dissolves in the blood and can be thought of as a solution of “carbonic acid” (H_2CO_3). Also present in our blood stream is “bicarbonate” (HCO_3^-) which is the conjugate base of H_2CO_3 . So we have an acidic (WASCB) buffer system in our blood stream:

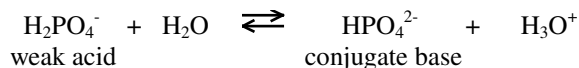


When the $[\text{H}_3\text{O}^+]$ tends to fluctuate in our blood, this buffer maintains the pH as close as possible to 7.35

When a person “hyperventilates”, too much CO_2 is lost and this equilibrium shifts to the left, decreasing the $[\text{H}_3\text{O}^+]$ and therefore increasing the pH. This can cause the person to “black out”.

CO_2 can be brought back up by “bag breathing” in a paper bag.

Another biological buffer system in the body (this one mainly in cells) is the $\text{H}_2\text{PO}_4^- / \text{HPO}_4^{2-}$ system:



Read though the rather chemically interesting “chicken farmer” exercise 143 on page 183 of SW.

Do Experiment 20-F – Buffers (lab or demonstration depending on time available)

Do “Questions from Provincials for Unit 4”

Test on Unit 4—Acids Bases and Salts.