The Neutralisation of Weak Acids and the Titration Curve

We have learned how to calculate the **pH of a simple solution of** weak acids such as ethanoic acid. I was very clear that the equation to use was:

$$K_a = \frac{[H^+]^2}{[HA]}$$

Now we need to complicate things a little by **adding a** strong base **to neutralise the solution of** weak acid. We can safely assume that addition of strong base will raise the pH (less acidic).

Let's work this through with an example.

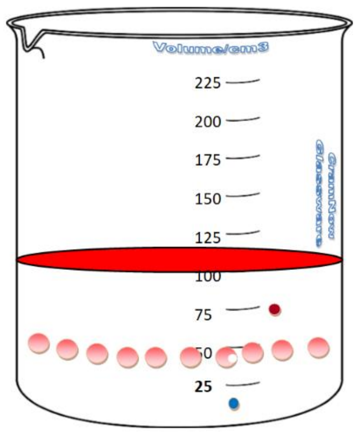
Let's begin by having **100cm^{-3} of ethanoic acid in a beaker**. This is effectively 10^{-3} mol of HA
We know that the Ka = 1.74x 10^{-5} mol dm^{-3}. We calculated the pH as 2.88.

A very small number of HA molecules are dissociated in the solution. This is represented by the diagram here. Note that this isn't quite in proportion because it is hard to illustrate the dissociation of such a small number of HA molecules and dissociated H^+ and A^- ions

Represent 1 x 10^{-3} mol undissociated HA **molecules.** These **don't contribute to the pH!**

Represent 1 x 10^{-3} mol dissociated A^- ions that we will assume **don't contribute to the pH** . (The truth is that they do but we can ignore this at A level.)

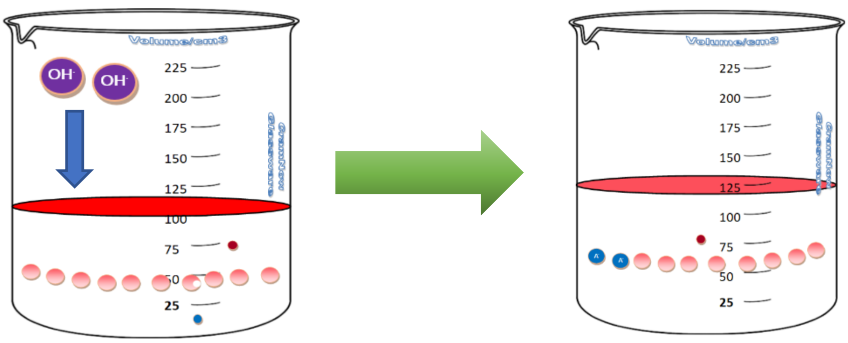
Represent 1 x 10^{-3} mol **dissociated H^+** ions that **do contribute to the pH.**



Let's now add 20cm^3 of 0.100 mol dm^{-3} NaOH solution.

This is a strong base and therefore, the OH^- ions are all 'available'. They will react 1:1 with the HA.
For every OH^- ion we add, there will be one HA molecule removed and 1 A^- ion produced.

Will represent 1 x 10^{-3} mol OH^- ions that we are going to add to the beaker.



Adding 2 x 10^{-3} mol of OH^- ions ( ) removes 2 x 10^{-3} mol of HA molecules ( ) to produce 2 x 10^{-3} mol of A^- ions ( )

We can now calculate a new pH as we have a value of Ka, and an amount of A^- and HA.

Recall

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

Rearranging we get:

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

We know the numbers of moles, n, of HA and A^- and we know the volume, v, of solution so we can find [HA] and [A^-].

$$\frac{[HA]}{[A^-]} = \frac{n_{HA}/V_{HA}}{n_{A^-}/V_{A^-}} = \frac{n_{HA}}{n_{A^-}}$$

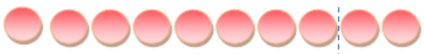
But you can see that the volumes cancel so we don't need to worry about volume!

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

We need to find n_{HA} and n_{A^-}

This is how we do it:

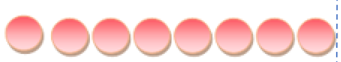
We assume the number of moles of HA at the start (the tiny amount of HA dissociation is igniored!):



n_{HA} = V x C = 100/1000 x 0.100 = 10.00 10^{-3} mol of HA at start

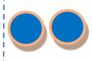
We know that number of moles of HA that have been neutralised by OH^-
This is the same as the number of moles of OH^- that were added.

n_{OH^-} = V x C = 20/1000 x 0.100 = 2.00 10^{-3} mol of OH^- added



n_{HA} - n_{OH^-} = 10.00 10^{-3} -2 .00 10^{-3} = **8.00 10^{-3} mol** of HA remaining

We know that number of moles of HA that have been destroyed must be the same as the number of moles of A^- that will have been made.
This is the same as the number of moles of OH^- that were added.



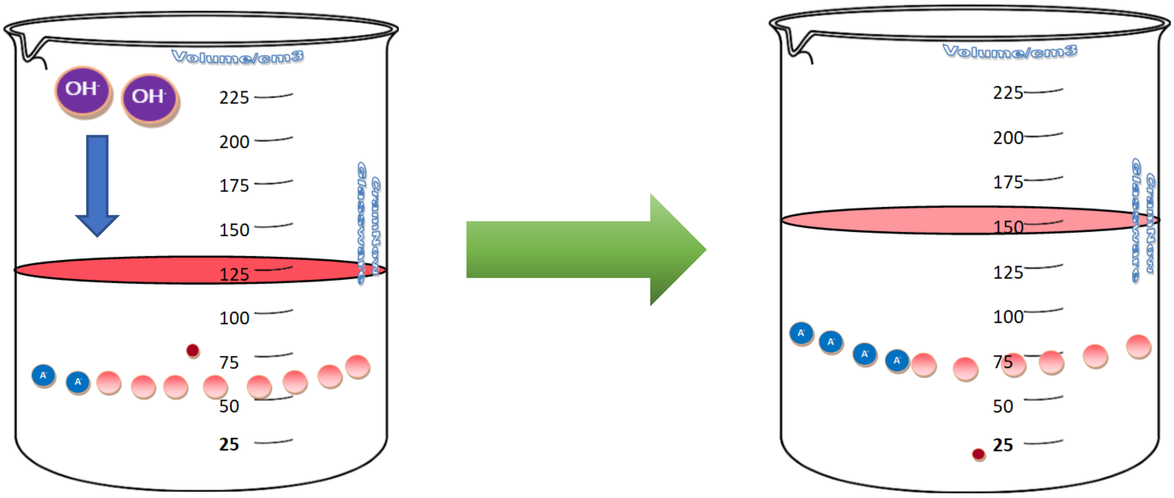
n_{A^-} = 2.00 10^{-3} mol of A^- made

$$[H^+] = K_a \frac{n_{HA}}{n_{A^-}} = (1.74 \times 10^{-5}) \times \frac{8.00\ 10^{-3}}{2.00\ 10^{-3}} = (1.74 \times 10^{-5}) \times 4 = 6.96 \times 10^{-5} \text{ mol dm}^{-3}$$

We are ready to finish the job by calculating pH pH= -log [H^+] = -log 6.96 x 10^{-5} = 4.16 = pH

We are now going to keep repeating this process by adding more sodium hydroxide(OH) to the beaker.

Let's pour in another $20 cm^3$ of 0.100 mol dm^{-3} NaOH solution.



It's probably worth reminding you of the fact the reaction produces molecules of water (which effectively contribute nothing to the pH).

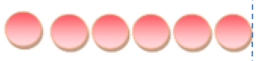
We again need to find the new n_{HA} and n_{A^-}

We know that number of moles of HA at the start of the second addition:

n_{HA} = V x C = 100/1000 x 0.100 = 8.00 10^{-3} mol of HA at before further addition

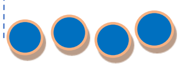
We know that number of moles of HA that have been neutralised by OH^-
This is the same as the number of moles of OH^- that were added:

n_{OH^-} = V x C = 20/1000 x 0.100 = 2.00 10^{-3} mol of OH^- added



n_{HA} - n_{OH^-} = 1.00x10^{-3} - 2 .00 10^{-3} = **6.00 10^{-3} mol** of HA remaining

We know that number of moles of HA that have been destroyed must be the same as the number of moles of A^- that will have been made.
This is the same as the number of moles of OH^- that were added.



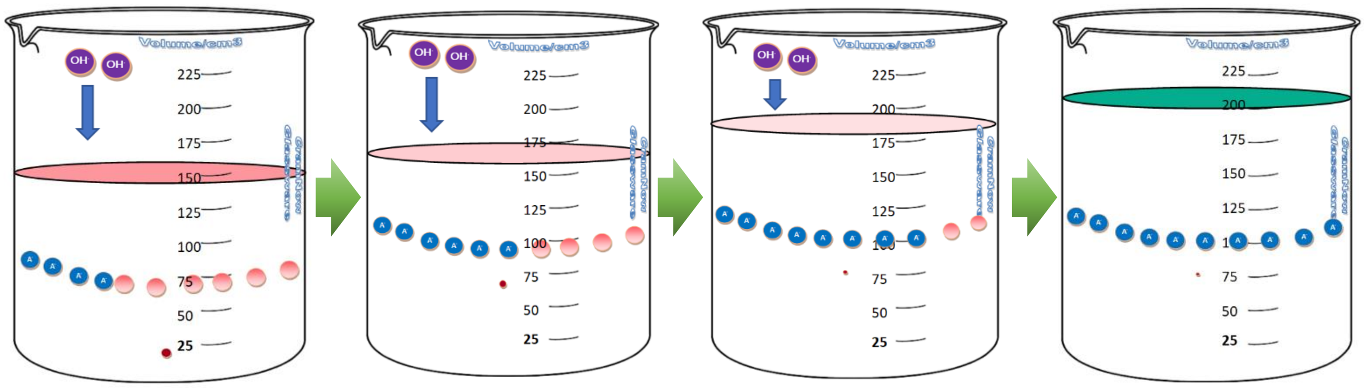
n_{A^-} . . . . . . = **4.00 10^{-3}** mol of A^- now present in beaker.

$$[H^+] = K_a \frac{n_{HA}}{n_{A^-}} = (1.74 \times 10^{-5}) \times \frac{6.00\ 10^{-3}}{4.00\ 10^{-3}} = (1.74 \times 10^{-5}) \times 6/4 = 2.61 \times 10^{-5} \text{ mol dm}^{-3}$$

We are ready to finish the job by calculating pH pH= -log [H^+] = -log 2.61 x 10^{-5} = **4.58 = pH**

We have now added $40cm^3$ of NaOH and the pH has risen by around 1.7 units.

Continuing the process but repeatedly adding further 20cm^3 volumes of NaOH . . . .



n_{HA} =6.00 10^{-3} mol n_{A^-} =4.00 10^{-3} mol pH =4.58 = pH	n_{HA} =4.00 10^{-3} mol n_{A^-} =6.00 10^{-3} mol pH =4.94 = pH	n_{HA} =2.00 10^{-3} mol n_{A^-} =8.00 10^{-3} mol pH =5.36 = pH	n_{HA} =0.00 10^{-3} mol n_{A^-} =10.00 10^{-3} mol pH =? This is not 7 as you may be thinking. Complete 'neutralisation' of a weak acid does not create a solution of that that has pH of 7*

We have just used the following equation to calculate [H$^+$].
However, you may find the following equation more useful.
It is essentially the same equation but has had -log$_{10}$ taken of both sides and so the equation produces a pH directly.
Some students prefer this second form of the equation.
It's just a matter of choice.

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

take -log$_{10}$ of both sides and rearrange

This equation is known as the '*Henderson-Hasselbalch'* equation.

$$pH = pK_a + \log\left(\frac{n_{A^-}}{n_{HA}}\right)$$

Remember this equality, explained early!

$$\left(\frac{[A-]}{[HA]}\right) = \left(\frac{n_{A^-}}{n_{HA}}\right)$$

Personally, I like it because it clearly demonstrates the link between pH and the **ratio of** HA : A$^-$
I also think that it makes the explanation and understanding of **buffers** a bit easier too.
It still has limitations because it assumes **no natural dissociation** of [HA]. This is fine when a reasonable amount of neutralisation has occurred, but it fails when there has been a small amount of neutralisation by strong base. Try this on your calculator! See what pH you obtain when you have added 1.00cm^3 of NaOH to the ethanoic acid. It also doesn't work very close to and including complete neutralisation. Think why?
For an acid with pKa of around 5, the 'H-H' equation gives acceptable accuracy between about 20-80% neutralisation.

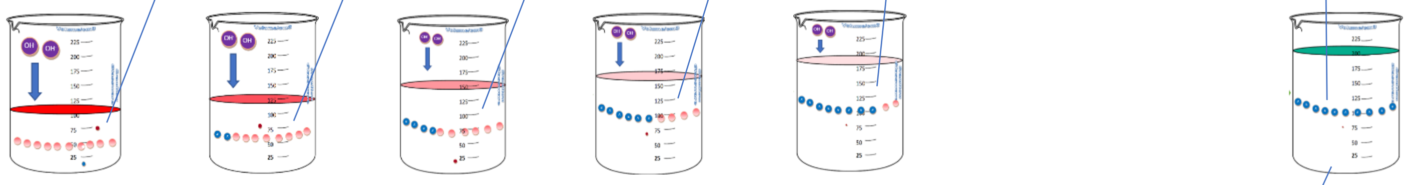
Doing it Yourself

These types of calculation is common in A level chemistry questions so you need to be confident in completing them.
Check that you can do these calculations yourself!
There is a table below with blanks where you need to calculate the pH.

I have included a box for the ratios of HA : A^- because I think this reinforces what's happening as we progressively neutralise the acid by adding the strong base NaOH

ADDITION of OH^- UP TO EQUIVALENCE POINT

total volume of 0.100 M NaOH added/cm^3	0.0	10.0	20.0	30.0	40.0	50.0	60.0	70.0	80.0	90.0	95.0	99.0	99.5	100
ratio HA : A^-	Very big		8:2		6:4		4:6		2:8					0
pH	2.88		4.16		4.58		4.94		5.36					



This beaker contains 100% A^- because all the HA has been neutralised.
But A^- is the conjugate base (or salt) of a weak acid HA and so the salt is weakly basic! Therefore, the pH is not 7! Therefore, I have blanked out the box. There is way to calculate the pH of this solution. The method is covered in the primer 'Calculating the pH of Bases and Salts'

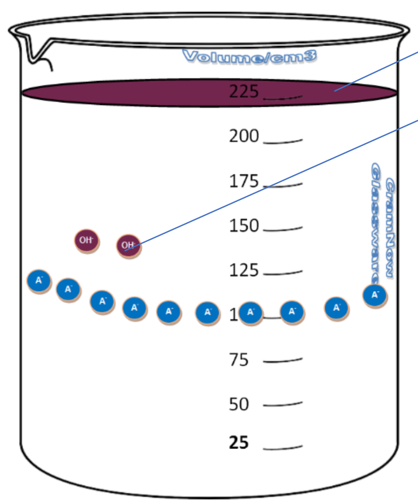
We need to consider what would happen to the pH if we continue to add more OH^- ions beyond the equivalence point.

The conjugate base, A^-, can be considered to have no effect on the pH.

(The truth is that it does, because it is the **conjugate base of a weak acid** so this is a 'non-neutral salt'. If you are interested, there is a primer in *CramNow* showing you how to calculate the pH of weak bases and salt solutions like this.)

If we pour in another $20cm^3$ of 0.100 mol dm^{-3} NaOH solution, the situation will be that in the diagram below.

Excess OH^- ions that have no H^+ (from the original acid) to react with.
This has **increased the OH^- ion concentration and increased the volume.**



new volume = 0.220 dm^{-3} ($200cm^3$ + $20cm^3$!)

n_{OH^-} added= (20/1000) x 0.100 mol dm^{-3}

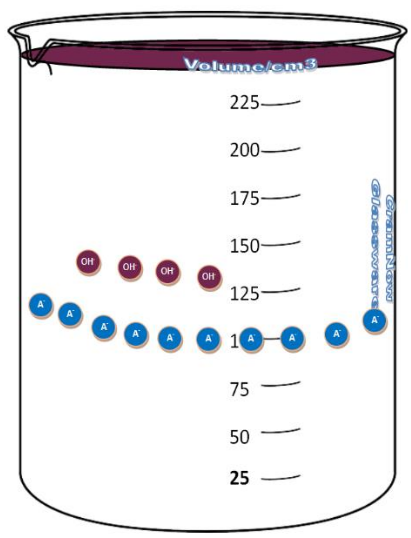
= 2.0×10^{-3} mol of OH^-

$[OH^-] = \frac{2.0 \times 10^{-3} \text{ mol}}{0.220 \text{ dm}^{-3}} = 9.09 \times 10^{-3} \text{ mol dm}^{-3}$

$[H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{9.09 \times 10^{-3}} = 1.10 \times 10^{-11}$

pH = -log $[H^+]$= -log 1.10×10^{-11} = 10.9 = pH

If we continued adding $20cm^3$ samples of 0.100 mol dm^{-3} NaOH to this solution, the concentration of OH^- **would continue to grow** and **so would the volume (we'd need a larger beaker!).**
After a further $20cm^3$ samples of 0.100 mol dm^{-3} NaOH solution has been added, the pH will be:



new volume = 0.240 dm^{-3} ($220cm^3$ + $20cm^3$!)

n_{OH^-} added= (20/1000) x 0.100 mol dm^{-3}

= 2.0×10^{-3} mol of OH^-

new n_{OH^-} = 4.0×10^{-3} mol of OH^-

$[OH^-] = \frac{4.0 \times 10^{-3} \text{ mol}}{0.240 \text{ dm}^{-3}} = 1.67 \times 10^{-2} \text{ mol dm}^{-3}$

$[H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{1.67 \times 10^{-2}} = 6.00 \times 10^{-13} \text{ mol dm}^{-3}$

pH = -log $[H^+]$= -log 6.00×10^{-13}= 12.2= pH

This is the same set of calculations that we carried out for additions of 0.100 mol dm^{-3} NaOH to this solution beyond the equivalence point for the addition to hydrochloric acid.

This is a continuation of the table from above. **Fill in the missing blanks.**

ADDITION of OH^- BEYOND EQUIVALENCE POINT

total **volume** of 0.100 M NaOH added/cm^3	100	100.1	100.5	101.0	105.0	110.0	120.0	140.0	160.0	180.0	200
pH	7.00 equiv. point						10.9	12.2			

You now should have a full set of pHs for a large range of volumes of 0.100 mol dm^{-3} NaOH solution from $20.0cm^3$ to $200cm^3$.

This data should now be plotted on graph paper with volume of NaOH solution on the x axis and pH on the y axis.

This will produce a **pH titration curve** for a WEAK ACID (ethanoic acid) 'versus' STRONG BASE (sodium hydroxide)

Graph paper is on the following page.

WEAK ACID (ethanoic acid) 'versus' STRONG BASE (sodium hydroxide)

Your graphs of

- STRONG ACID (hydrochloric acid) 'versus' STRONG BASE (sodium hydroxide)
- WEAK ACID (ethanoic acid) 'versus' STRONG BASE (sodium hydroxide)
  should look like these!

You can use the graphs to check your calculations of pH in the tables.