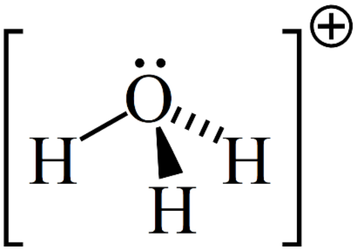
Acid-Base Equilibria



This booklet is designed to guide you through some of the principles involved in acid-base equilibria, particularly neutralisation, titrations curves, buffers and indicators.

Acid-Base Equilibria

What you should know already.

From GCSE Combined Science and earlier schooling, you will be aware;

1. we quantify acidity and alkalinity using the pH scale
2. the pH scale covers the range 1-14; 7 being considered neutral
3. there are families of bases including hydroxides, oxides and carbonates

From GCSE Chemistry, you will be aware of statements 1-3 plus;

4. acids are chemicals that release hydrogen ions, H^+, in aqueous solution
5. pH is related quantitatively to the concentrations of H^+ ions
6. if the concentration of H^+ ions is expressed as 10^{-x} mol dm^{-3}, then the pH has the value, x.
7. strength of acids is a measure if the extent of dissociation of the acid molecules in water
8. alkalis are water soluble bases that release hydroxide ions, OH^-, in aqueous solution
9. bases are chemicals that neutralise acids to produce salt and water

Calculation of pH

Water molecules naturally dissociate in water. This happens according to the following simplified equation:

$$H_2O_{(aq)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$

This equation represents how **Arrhenius** considered acid molecules to behave.

Arrhenius definition of acids:
Acids are chemicals that release hydrogen ions in solution.
Alkalis are chemicals that release hydroxide ions in solution.

This definition won Arrhenius the Nobel Prize in 1903!

However, it was limited in its scope and the definition had to be redefined to explain a far greater number of situations for which, the **Arrhenius** definition didn't work.

It is known that there are no 'free' $H^+_{(aq)}$ ions in solution. In fact, the dissociation is the result of a collision and reaction between 2 water molecules. This is known as autoionization.

$$H_2O_{(aq)} + H_2O_{(aq)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$$

This equation represents how Lowry and Brønsted (separately but around the same period) considered acids to behave.

H_3O^+ is known variously as hydroxonium ion, oxonium ion and hydronium ion. Make sure that you know what your exam board call it.

Lowry-Brønsted definition of acids and bases:

Acids are chemicals that donate hydrogen ions in solution.
Bases are chemicals that accept hydrogen ions in solution

In the second equation you can see that the water molecule doesn't simply release a hydrogen ion into solution, it only does it by donation to something else. In this case, the 'something else' is simply a dissolved water molecule. Be clear though, it is donating to another reactant (also a water molecule). If the molecule was dissolved in liquid ammonia, then it would protonate the ammonia molecules. Ammonia molecules would be the base in this situation because they accept the proton that water molecules are donating.

Can you see that an acid is only an acid if something is prepared to accept its proton? It's a 2-way process. By analogy, Mr Burns (Simpsons) could not describe himself as charitable or philanthropic if the only time he goes to the ***Springfield Charity Shop*** is when it is closed. You must actually **donate** the money to something. This is what Lowry and Brønsted realised. I consider it essential that you understand this, trivial as it seems. It is the foundation to acid-base reactions.

Now that I've said that the hydrogen ions are actually bonded to a water molecule in the form of the hydroxonium ion, I will go further to say that we will generally write H^+ rather than H_3O^+ because it's easier.

Going back to the dissociation of water, the amount of dissociation has been worked out.
The concentration of both H_3O^+ and OH^- ions is 1.00×10^{-7} mol dm^{-3}

$$@\ 25^{o}C;\ \ [H_3O^+_{(aq)}] = [OH^-_{(aq)}] = 1.00 \times 10^{-7}\ \text{mol dm}^{-3}$$

Specifying the temperature is essential as the values of the concentrations are dependent on temperature as we will see pretty soon.

Note that the $[H_3O^+_{(aq)}]$ and $[OH^-_{(\ aq)}]$ are both very small.

Let's consider a dilute solution of a strong monobasic (or monoprotic) acid, ***e.g.*** hydrochloric acid.

The concentration is 0.100 mol dm^{-3}

Stating that hydrochloric acid is a **strong acid** is saying that it **fully dissociates in water**. The truth is that it doesn't fully dissociate but it is so close to being fully dissociated that we assume that it is, to make the calculation easier. There are stronger acids than hydrochloric acid!

We can write an equation for the process.

dissolved acid molecule

$$HCl_{(aq)}\ +\ H_2O_{(aq)} \rightarrow H_3O^+_{(aq)} +\ Cl^-_{(aq)}$$

dissolved base molecule (which happens to be the same as the solvent)

If the acid fully dissociates, it will produce a solution that now contains a 0.100 mol dm^{-3} solution of [$H_3O^+_{(aq)}$].

So, the [H^+] = 0.100 mol dm^{-3} which we can write as 10^{-1} mol dm^{-3}

If we compare [H^+] in water and [H^+] in 0.100 mol dm^{-3} solution of hydrochloric acid, we see that the difference is enormous.

[H^+] in water 10^{-7} & 10^{-1} is the [H^+] in 0.100 mol dm^{-3} solution of hydrochloric acid

These concentrations vary over such a huge range, we use a simple mathematical operation to make the numbers simpler. We '**take logs**' of the values of the concentration.

The log (base 10) of a number, x, is the power that we raise 10 by to produce x.

For example,
log 100 = 2 This is because 100 = 10^2 so 2 is the power of 10
log 1 000 = 3 This is because 1000 = 10^3 so 3 is the power of 10
log 1 000 000 = 7 This is because 1 000 000 = 10^7 so 7 is the power of 10

log 126 = 2.10 This is because 126 = $10^{2.10}$ so 2.10 is the power of 10

We can do this for numbers **smaller than 1**.

log 0.100 = -1 This is because 0.100 = 10^{-1} so -1 is the power of 10
log 0.00100 = -3 This is because 0.00100 = 10^{-3} so -3 is the power of 10
log 0.0854 =-1.07 This is because 0.0854 = $10^{-1.07}$ so -1.07 is the power of 10

Now we know a little about logarithms, we can define pH

Definition of pH $\boxed{pH = -\log[H^+]}$

The negative sign in the definition simply ensures that pHs have a positive value.

We can now calculate the pH of the 0.100 mol dm^{-3} solution of hydrochloric acid.

$$pH = -\log[H^+] = -\log 0.100 \quad = 1.00$$

If this $HCl_{(aq)}$ was **diluted 10 times**, it would have a new concentration of 0.0100 mol dm^{-3}

$$pH = -\log[H^+] = -\log 0.0100 \quad = 2.00$$

For every 10 times dilution, the pH moves up by 1.00 units. This is a useful thing to remember!

Calculating the pH of a strong acid is straightforward. If you know the concentration of a **monobasic acid** (releases or donates 1 proton per molecule), you can assume that the concentration of the acid is the same as the concentration of H^+. Then you simply carry out the calculation:

$$pH = -\log [H^+]$$

If an acid is diprotic, *e.g.* $H_2SO_{4(aq)}$ you need to be a little careful. Some textbooks state that you can find [H^+] by simply doubling the concentration of the sulfuric acid. This is fundamentally wrong. The first proton that disassociates is strong, so it is true to say that **sulfuric acid is a strong acid.**
BUT, having lost one proton, the hydrogen sulfate ion (HSO_4^-) produced from the loss of the first proton, is actually a weak acid. This means that the total number of protons produced is not double the amount of sulfuric acid molecules. Make sure that you know what your exam board are expecting you to do if you get a problem like this one.

Calculating the pH of Strong Bases

We need to deal with the slightly more complicated matter of working out the pH for strong bases.

Let's begin by bringing back an equation from earlier:

$$H_2O_{(aq)} + H_2O_{(aq)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$$

This is clearly an equilibrium that lies well to the left. We know this because of the tiny concentration of $H_3O^+_{(aq)}$ and $OH^-_{(aq)}$

We can write an equilibrium expression for this in terms of concentrations.

$$K_c = \frac{[H_3O^+][OH^-]}{[H_2O][H_2O]}$$

The value of $[H_2O]$ is very large (55.6 mol dm^{-3}) and so it is approximately **constant** in this equilibrium. That means that we can combine $[H_2O]x[H_2O]$ with **Kc** to make a new constant, **K_W.**

$$K_W = [H_3O^+][OH^-]$$

We saw earlier that these concentrations are known at 25°C:

$$@\ 25^oC;\ [H_3O^+_{(aq)}] = [OH^-_{(aq)}] = 1.00 \times 10^{-7}\ \text{mol dm}^{-3}$$

So, we can work out the value of K_w

$$K_W = [H_3O^+][OH^-] = 1.00 \times 10^{-7} \times 1.00 \times 10^{-7} = 1.00 \times 10^{-14}\ \text{mol}^2\ \text{dm}^{-6}$$

This gives us an important relationship called the **IONIC PRODUCT of WATER.**
The value is temperature dependent because it is associated with an equilibrium constant K_W

@25°C $$K_W = [H_3O^+][OH^-] = 1.00 \times 10^{-14}\ \text{mol}^2\ \text{dm}^{-6}$$

This equation tells us that $[H_3O^+_{(aq)}]$ and $[OH^-_{(aq)}]$ are linked.

If you change either $[H_3O^+_{(aq)}]$ or $[OH^-_{(aq)}]$, then the other must be change so that the value of K_w **remains** 10^{-14} mol^{2}dm^{-6}

An increase in $[H_3O^+_{(aq)}]$ must cause a decrease in $[OH^-_{(aq)}]$ and vice versa.

However, it is not like a regular seesaw. If you increase $[H_3O^+]$ by 10 times then you must decrease $[OH^-_{(aq)}]$ by 10 times. Make sure that you understand that this equation is not suggesting that the total number of ions remains constant! It is the product of the two concentrations (hence the name of the constant).

This expression will now allow us to calculate the $[H_3O^+]$ if we are given the $[OH^-]$

For example:

Q. Calculate the pH of a 0.100 mol dm^{-3} solution of the strong base, sodium hydroxide, $NaOH_{(aq)}$.

A. If it's a strong base then the solution must contain a 0.100 mol dm^{-3} solution of hydroxide ions

$[OH^-] = 0.100$ mol dm^{-3} We need to find the value of $[H^+]$ so we can calculate a pH.

Recall $K_w = [H^+][OH^-] = 1.00 \times 10^{-14}\ mol^2\ dm^{-6}$

Rearranging: $$\frac{K_w}{[OH^-]} = [H^+] = \frac{1.00 \times 10^{-14}\ mol^2\ dm^{-6}}{0.100\ mol\ dm^{-3}} = [H^+] = 1.00 \times 10^{-13}\ mol\ dm^{-3}$$

$pH = -\log 1.00 \times 10^{-13} = \underline{13.0}$

Have a go at the following:

1. Calculate the pH of a 0.100 mol dm^{-3} solution of $HNO_{3(aq)}$.

Answer________

2. Calculate the pH of a 0.0891 mol dm^{-3} solution of $HCl_{(aq)}$.

Answer________

3. Calculate the pH of a 4.51×10^{-3} mol dm^{-3} solution of $HNO_{3(aq)}$.

Answer________

4. Calculate the pH of a 8.24×10^{-2} mol dm^{-3} solution of $NaOH_{(aq)}$

Answer________

5. Calculate the pH of a 0.0224 mol dm^{-3} solution of $Ba(OH)_{2(aq)}$ (CARE!)

Answer________

There a many more self-marking pH questions on *CramNow*

Answers:
1. pH=1.00
2. pH=1.05
3. pH=2.35
4. pH=12.92
5. pH=12.65

Calculating the pH of Weak Acids

This is where things start to get interesting!

To calculate pH, we always need [H^+]. This allows us to plug it into the pH = -log[H^+] to get our pH.

However, with weak acids, the concentration of the weak acid does not immediately tell you the [H^+] .

The formation of the H^+ is the result of an equilibrium process. Unless we know the position of the equilibrium, we can't know what [H^+] is formed. We need to apply what we know of equilibrium law.

Let's use a general formula for an acid, **HA**. I have then chosen to use red HA to represent a strong acid and I have then chosen to use pink HA to represent a weak acid.

For a strong acid we can write:

$$\boxed{HA_{(aq)} + H_2O_{(aq)} \rightarrow H_3O^+_{(aq)} + A^-_{(aq)}}$$

For a weak acid we need to write:

$$\boxed{HA_{(aq)} + H_2O_{(aq)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}}$$

This is an equilibrium so we can write an expression for K_c:

$$\boxed{K_c = \frac{[H_3O^+][A^-]}{[HA][H_2O]}}$$

The value of [H_2O] **is very large and changes very little** by reaction with the weak acid. It is effectively a constant. Like before, we will combine [H_2O] with the constant K_c to make one **new constant, K_a**.

K_a is known as the **acid dissociation constant**. In general, we can write:

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

This is a very important equation that we will are going to use a lot!

Things to remember about Ka:

- the **smaller** the value of Ka, the **weaker** the acid
- values of Ka are **temperature dependant.**
- values of Ka cover a very **large range**.
- the large range of Ka values means that Ka are often converted into *p*Ka.
- *p*Ka**= -log** Ka (just like we did with *p*H!)
- the **smaller** the value of *p*Ka, the **stronger** the acid

Now we will apply this to a problem.

Q. *Calculate the pH of a 0.100 mol dm^{-3} solution of ethanoic acid. The value of Ka of ethanoic is 1.74 x 10^{-5} at 25^{o}C.*

A. The problem requires us to find a pH, as is often the case, so we will need to find a value of $[H^+]$.

We are given the Ka and we need $[H^+]$. That leaves us with **two unknown values**; [HA] and $[A^-]$

Let's deal first with the value of $[A^-]$.

Well this is not really a problem. Looking at the chemical equation for the dissociation of HA (shown above) we know that **for every** H^+ that is made by dissociation of HA, **we make one** A^-.

So, it is perfectly chemically sensible to write: $[H^+] = [A^-]$

This means that we can write:

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

That is one unknown dealt with.

Now we need to think about the equilibrium value of [HA].

This is where we are going to do a little bit of 'cheating'. But, the result of the cheating will be an answer that is almost exactly (to at least 5 significant figures!) the pH that we would obtain of we did this without cheating.

This is how we 'cheat'.

It is correct to assume that very little HA will dissociate because this is a pretty weak acid (the Ka is small). In fact, Ka values with values in the range 10^{-5} lead to around 1% dissociation. In our solution of ethanoic acid that is labelled as 0.100 mol dm^{-3}, only around 0.001 mol dm^{-3} of H^+ will be produced at equilibrium (clue to the pH that we are trying to calculate). At equilibrium, the value of [HA] will around be 0.099 mol dm^{-3}. Be clear, I am only suggesting that it is **approximately 0.099** mol dm^{-3} . We don't know what it is exactly. Now for the cheat.

We can say that the value of [HA] on the label will be very close to the equilibrium concentration of [HA] .

The **concentration on the label**. This is made by dissolving 0.100 mol of the pure acid in water to make 1.00 dm^{3} of aqueous solution.

$$\boxed{[HA] \approx [HA]_{equ}}$$

This is the concentration of HA **remaining at equilibrium** after dissolving 0.100 mol of the pure acid in water to make 1.00 dm^{3} of aqueous solution.

We can now do a bit of rearranging to get [H^+].

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

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

Taking the square root of both sides:

$$\boxed{\sqrt{K_a \times [HA]} = [H^+]}$$

There we have it. [H^+] can be calculated.

$$[H^+] = \sqrt{1.74 \times 10^{-5} \times 0.100} = 1.32 \times 10^{-3} \text{ mol dm}^{-3}$$

$$pH = -\log[H^+] = -\log 1.3 \times 10^{-3} = \underline{2.88}$$

Notice how the pH of 0.100 mol dm^{-3} ethanoic acid has a pH approximately 2 pH units different to the pH we calculated if we had the same concentration of the strong acid, HC*l* .This means that the ethanoic acid molecules are around 1% dissociated. Remember, for **every 1 pH unit rise (less acidic) there are 10x fewer H^+** ions per dm^3. So, 2 pH units difference means 100x fewer H^+ ions per dm^3. Therefore, 1% dissociated!

You should learn this equation!

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

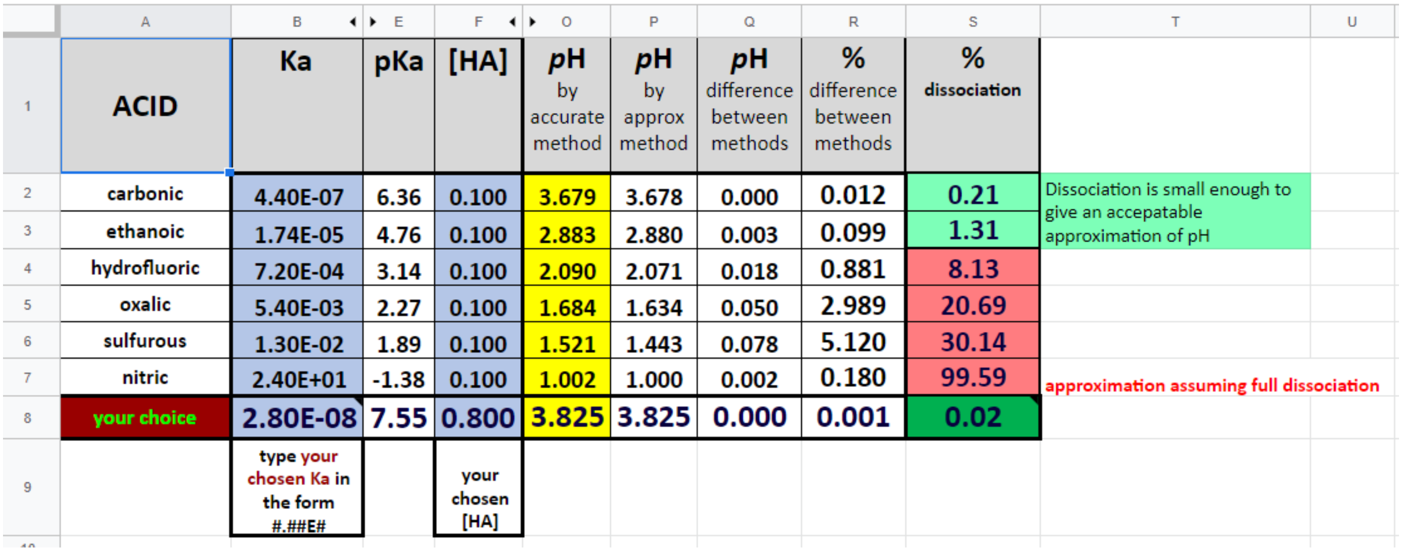
BUT you must be aware of its limitations. In my experience, students often try using this equation when it is the wrong equation to use. You must remember that this only works when you are trying to calculate the pH of a **simple solution of a** weak acid**. If there has been anything done to the acid, for example a base has been added, then the relationship [H^+] = [A^-] is no longer true** so we can't do this **[H^+]^2 trick.**

BE CAREFUL TO WORK OUT WHAT'S BEING ASKED IN THE QUESTION.

Also, you should remember that this is an approximation because of our simplification (cheat) where we approximated the [HA] by assuming very little dissociation. Sadly, not only does this give an inaccurate answer, the approximation method is limited to pretty weak acids (where Ka is around 10^{-5} or smaller). Many acids are weak but still too strong to use this approximation. That's a pretty grim state of affairs.

However, if you are really interested in doing this calculation correctly, you can have a look at the primer that I have written showing you how to do this **without making the assumption about [HA].** I have also made a spreadsheet that you can download and play with. You can dial in **Ka values** and **concentrations of your choice** and it will calculate the correct pH and the difference between the two methods.

The spreadsheet looks like this:



	A	B	E	F	O	P	Q	R	S	T	U
1	**ACID**	**Ka**	**pKa**	**[HA]**	***pH*** by accurate method	***pH*** by approx method	***pH*** difference between methods	**%** difference between methods	**%** **dissociation**		
2	**carbonic**	4.40E-07	6.36	0.100	3.679	3.678	0.000	0.012	0.21	Dissociation is small enough to give an accepatable approximation of pH	
3	**ethanoic**	1.74E-05	4.76	0.100	2.883	2.880	0.003	0.099	1.31		
4	**hydrofluoric**	7.20E-04	3.14	0.100	2.090	2.071	0.018	0.881	8.13		
5	**oxalic**	5.40E-03	2.27	0.100	1.684	1.634	0.050	2.989	20.69		
6	**sulfurous**	1.30E-02	1.89	0.100	1.521	1.443	0.078	5.120	30.14		
7	**nitric**	2.40E+01	-1.38	0.100	1.002	1.000	0.002	0.180	99.59	**approximation assuming full dissociation**	
8	**your choice**	**2.80E-08**	**7.55**	**0.800**	**3.825**	**3.825**	**0.000**	**0.001**	**0.02**		
9		**type your chosen Ka in the form #.##E#**		**your chosen [HA]**							

Some problems to have a go at:

1. Calculate the pH of a 0.100 mol dm^{-3} solution of benzoic acid. K_a for a benzoic acid is 6.3 x 10^{-5} mol dm $^{-3}$

Answer________

2. Calculate the value of K_a for the very weak acid, chloric (I) acid, if a 0.800 mol dm^{-3} solution has a pH of 3.825.

Answer________

3. Calculate the concentration of propanoic acid (pK_a = 4.88 care!) required to produce a *p*H=2.88.
   (This was the same pH that was produced by a 0.100 mol dm $^{-3}$ solution of ethanoic acid)

Answer________

Each of these problems requires the equation for weak acids to be rearranged.

You will find many more self-marking questions on weak acid pH calculations on *CramNow*

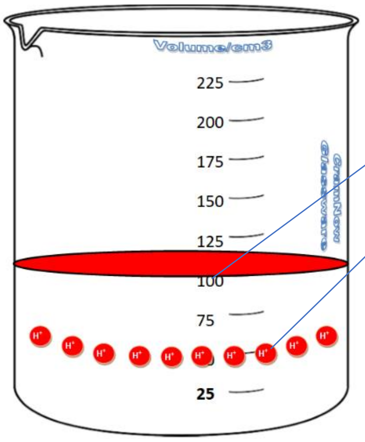
The Neutralisation of Strong Acid by Strong Base and the Titration Curve

For this, we will consider how the pH changes as we progressively neutralise hydrochloric acid by adding sodium hydroxide.

Let's begin by having **100cm^{3} of hydrochloric in a beaker**. The concentration is 0.100 mol dm^{-3}

This is represented by the following diagram

In these diagrams H^+ represents 1 x 10^{-3} mol **dissociated** H^+ ions that **contribute to the pH**.



volume of solution = 0.100 dm^{-3}

moles of H^+, n_{H^+} = 10.0 x 10^{-3} mol

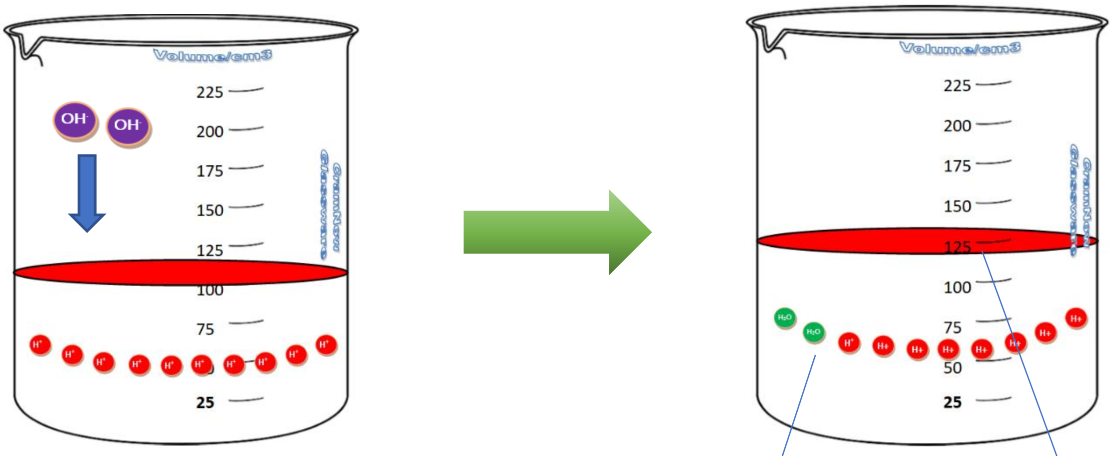
$[H^+]$ = $\frac{10.0 \times 10^{-3}\ \text{mol}}{0.100\ \text{dm}^{-3}}$ = **1.00 x 10^{-1}** mol dm^{-3}

pH = -log $[H^+]$ = -log **1.0 x 10^{-1}** = <u>1.00</u> = pH

Let's now add 20cm^{3} of 0.100 mol dm^{-3} NaOH solution. This will increase the volume by 20cm^{3}.

OH^- Represents 1 x 10^{-3} mol OH^- ions that are added to the beaker.

As the OH^- ions meet the H^+ ions, there is a reaction that produces H_2O

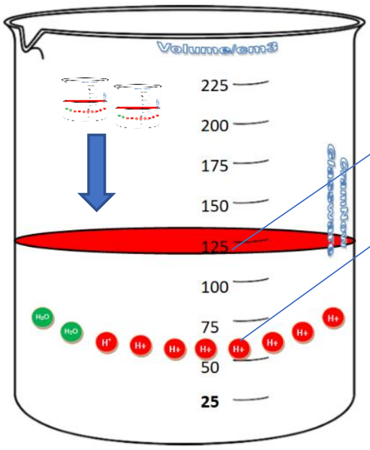


Two obvious things have happened.

The number of H^+ **ions has been reduced** and the **volume has increased**.

It seems logical that **both changes** must make the **solution less acidic** and **increase the pH**.

We need to be able to calculate the new pH. This is done below.



new volume = 0.120 dm^{-3} (100cm^3 + 20cm^3!)

new n_{H^+} = n_{H^+} before addition – n_{OH^-} added

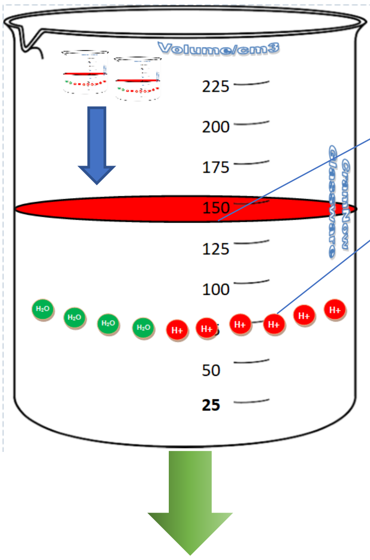
= 10 x 10^{-3} mol – 2.0 x 10^{-3} mol

= 8 x 10^{-3} mol of H^+

$[H^+]$ = $\frac{8 \times 10^{-3}\ \text{mol}}{0.120\ \text{dm}^{-3}}$ = 6.67 x 10^{-2} mol dm^{-3}

pH = -log $[H^+]$ = -log 6.67 x 10^{-2} = 1.18 = pH

Let's repeat this by adding a **further 20cm^3 of 0.100 mol dm^{-3} NaOH solution**. You do the calculations.



new volume =

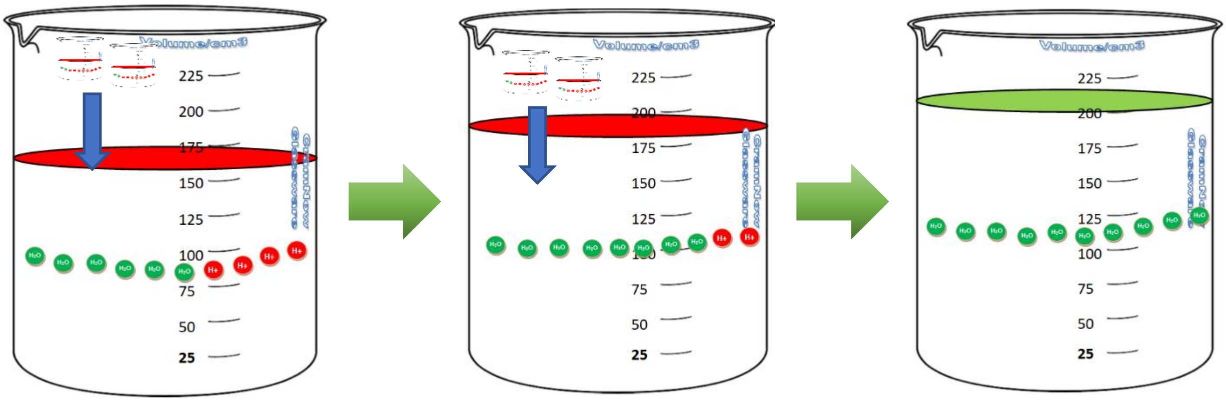
new n_{H^+} = n_{H^+} before addition – n_{OH^-} added

= .... - ....

= ....mol of H^+

new $[H^+]$ = ____________ =...................mol dm^{-3}

pH = -log $[H^+]$ = -log .... = ... = pH



new volume = ...

new n_{H^+} = ...

$[H^+]$ =...............

pH =...............

new volume = ...

new n_{H^+} = ...

$[H^+]$ =...............

pH =...............

new volume = ...

new n_{H^+} = care! Not 0!

$[H^+]$ =think!........

pH =think!........

Fill in the blank boxes in the table below.

ADDITION of OH^- UP TO EQUIVALENCE POINT

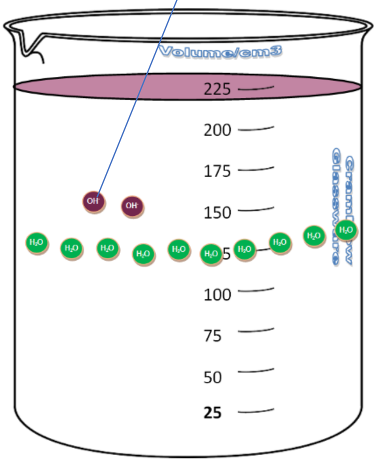
total volume of 0.100 M NaOH added/cm^3	0.0	20.0	40.0	60.0	80.0	90.0	95.0	99.0	99.5	99.9	100
pH	1.00	1.18	1.37	1.60	1.95						equiv. point

These are the answers that you should have calculated on the previous page

The **equivalence point** where all of the hydrochloric acid has been neutralised. There is only a neutral salt solution at this point.

We need to consider what would happen to the pH if we continue to add more OH^- ions beyond the equivalence point.
If we pour in another 20cm^3 of 0.100 mol dm^{-3} NaOH solution, the situation will be the one 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 x 10^{-3}** mol of OH^-

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

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

pH = -log [H^+]= -log 1.10x10^{-11} = <u>10.9</u> = 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 x 10^{-3}** mol of OH^-

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

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

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

pH = -log [H$^+$]= -log **6.00 x 10^{-13}**= <u>12.2</u>= pH

Below is a continuation of the table from earlier. 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 STRONG ACID (hydrochloric acid) ‘versus’ STRONG BASE (sodium hydroxide)

Graph paper is on the following page

STRONG ACID (hydrochloric acid) ‘versus’ STRONG BASE (sodium hydroxide)

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:

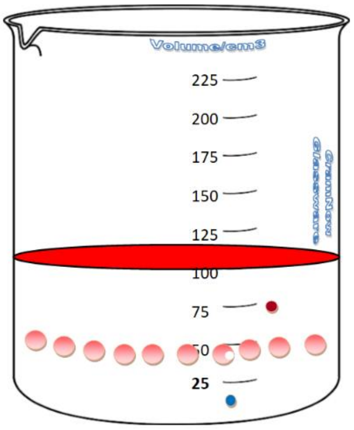
$$\boxed{K_a = \frac{[H^+]^2}{[HA]}}$$

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



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

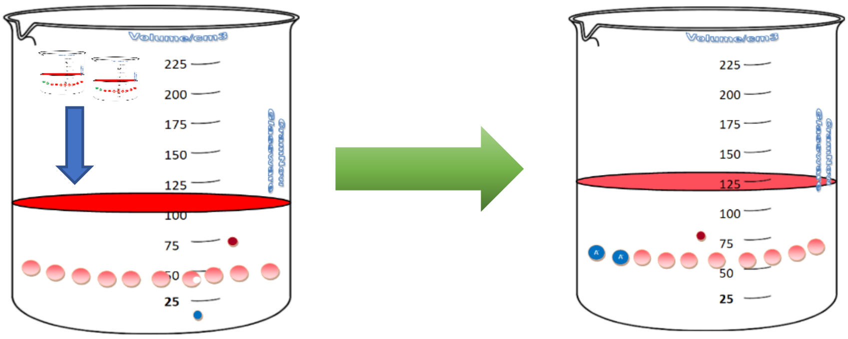
A- Represent 1 x 10^{-3} mol dissociated A^- ions that we will assume **don't contribute to the pH** . (The truth is that they do but we can ignore this at A level.)

H^+ 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.

OH^- 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:

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

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

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^-].

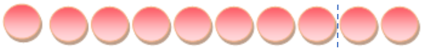
$$\frac{[HA]}{[A^-]} = \frac{n_{HA}/V_{HA}}{n_{A^-}/V_{A^-}} = \frac{n_{HA}}{n_{A^-}}$$

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

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!):



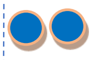
n_{HA} = V x C = 100/1000 x 0.100 = $10.00\ 10^{-3}$ mol of HA at start

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.



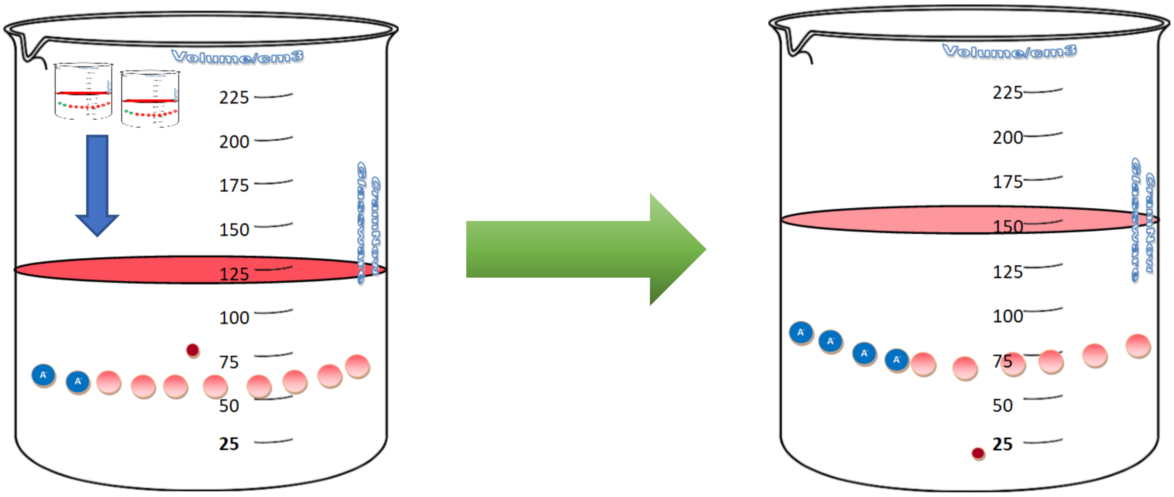
n_{A-} = $2.00\ 10^{-3}$ mol of A^- made

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

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

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

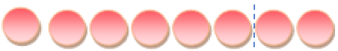
Let's pour in another 20cm^3 of 0.100 mol dm^{-3} NaOH solution.



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^-}

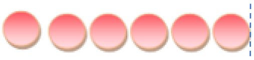
We know that number of moles of HA at the start of the second addition:



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

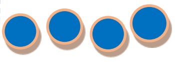
We know that number of moles of HA that have been neutralised by OH$^-$
This is the same as the number of moles of OH$^-$ that were added:

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.



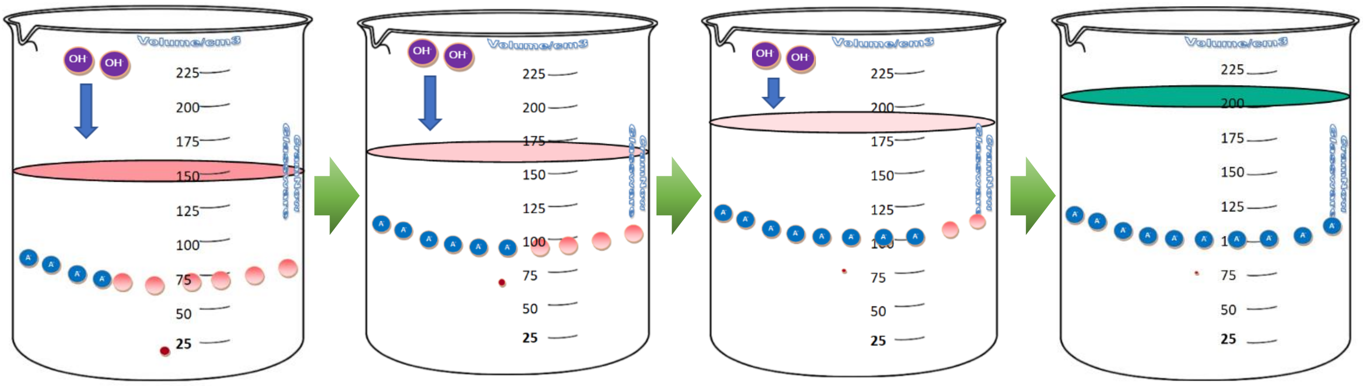
n_{A^-} . . . . . . = 4.00 10^{-3} mol of A$^-$ now present in beaker.

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

We are ready to finish the job by calculating pH pH= -log [H$^+$] = -log 2.61 x 10^{-5} = $\underline{4.58}$ = 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' gives acceptable accuracy between about 20-80% neutralisation.

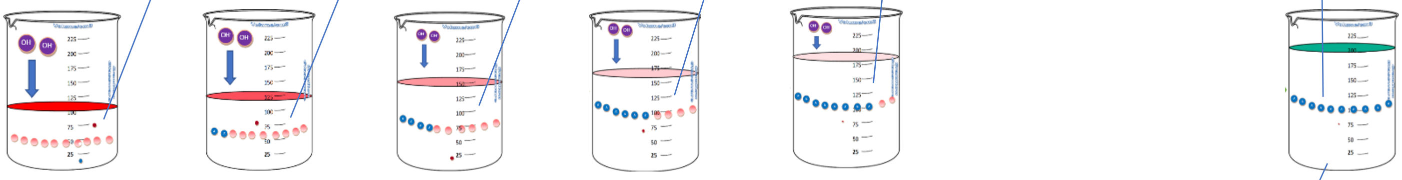
Doing it Yourself

This type 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'

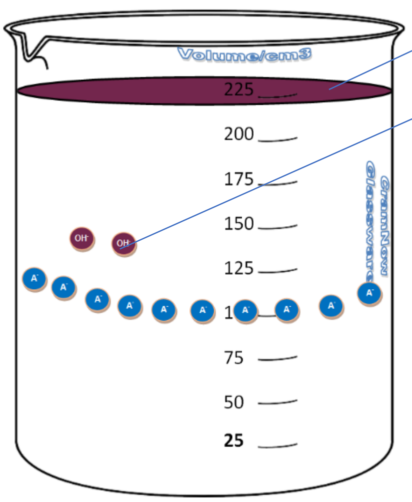
We need to consider what would happen to the pH if we continue to add more OH^- ions beyond the equivalence point.

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!**)

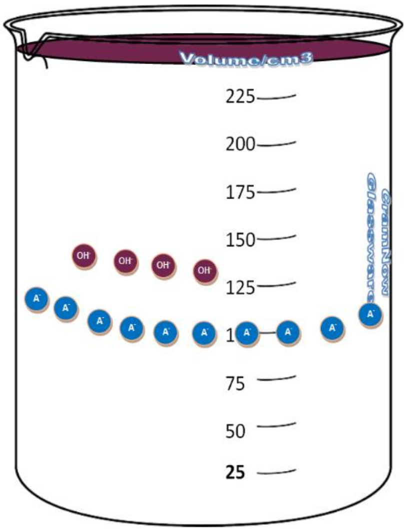
n_{OH^-} added = (20/1000) x 0.100 mol dm^{-3}
= **2.0 x 10^{-3}** mol of OH^-

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

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

pH = -log [H$^+$] = -log 1.10x10^{-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 x 10^{-3}** mol of OH^-

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

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

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

pH = -log [H$^+$] = -log **6.00 x 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 **Na**OH 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)

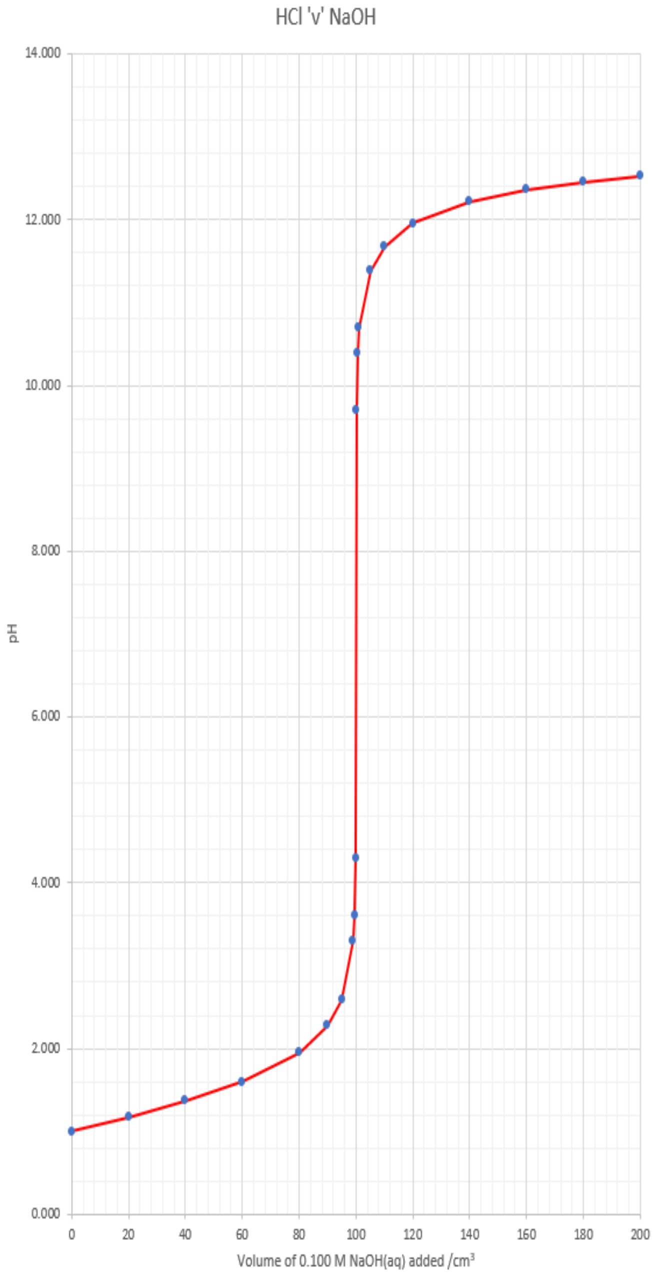
Graph paper is on the following page.

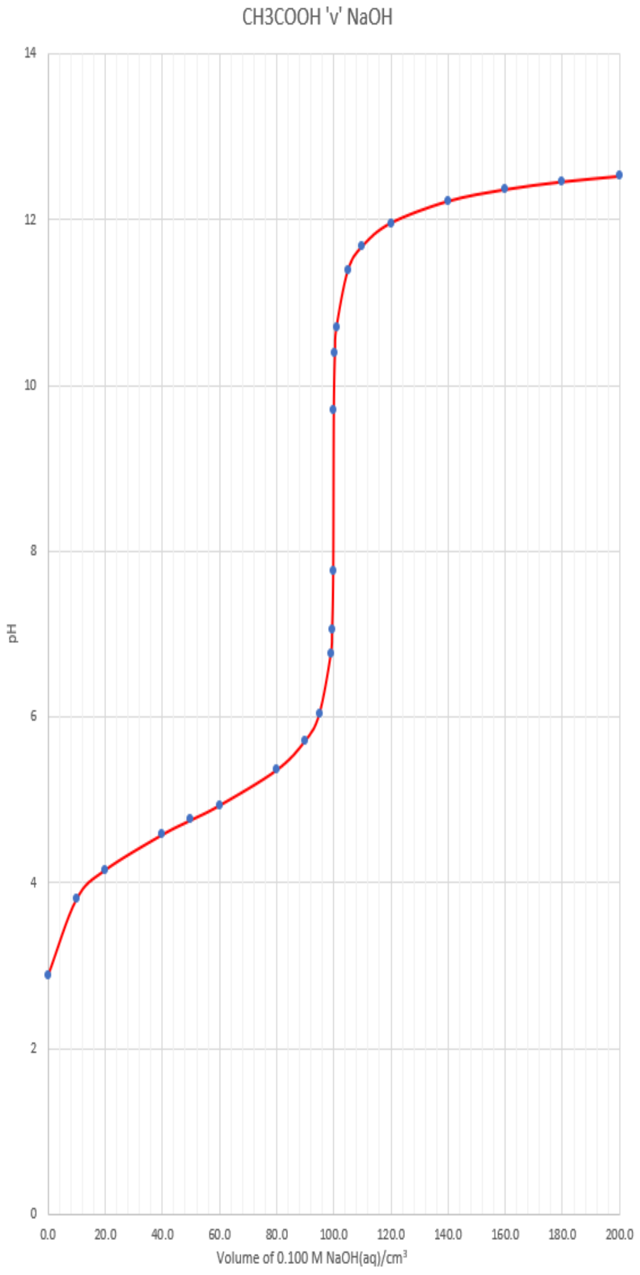
WEAK ACID (ethanoic acid) ‘versus’ STRONG BASE (sodium hydroxide)

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.





The Effect of Temperature on pH

A very common misconception regarding pH is that neutral solutions are defined as those with a pH of 7. This seems to be drummed into school students so much that it's hard to stop them believing this definition.

It is true that a solution is neutral when the pH is 7, **but only at 25°C!**

The pH of a neutral solution varies significantly if the temperature rises or falls.

Consider the following equilibrium:

$$\boxed{H_2O_{(aq)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}}$$

We could assume that the ΔH = +ve (endothermic in forwards direction) as bonds have been broken.

The Lowry-Brønsted equation for this is:

$$\boxed{H_2O_{(aq)} + H_2O_{(aq)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}}$$

It's not quite as clear-cut when we represent this in a Lowry-Brønsted equation as a bond was broken in the H_2O molecule, but a bond was made in the H_3O^+ ion. But this bond that is formed is very weak as you may intuitively suspect. This process is, indeed, **endothermic in the forward direction.**

Le Chatelier's Principle would predict that a rise in temperature would shift the equilibrium to the right-hand side leading to greater dissociation of water molecules.

The [H^+] must rise and the pH must fall! BUT, you must not assume that a fall in pH means that the solution becomes acidic.

It remains neutral because [H^+] = [OH^-]. **Both values are bigger.**

Some examples of pH at different temperatures

Temperature/°C	pH
0	7.47
25	7.00
50	6.63
100	6.14

Conjugate Acids and Bases

According to the Lowry- Brønsted theory of acids and bases, for a molecule to behave as an acid, it must be in the presence of a base that it can **donate** a proton to.

When we dissolve a strong acid in water, the acid fully protonates the water molecules which are behaving as a base.

$$\boxed{HCl_{(aq)} + H_2O_{(aq)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}}$$

Strictly speaking, this is an equilibrium that lies so far to the right-hand side that we say that the reaction goes to completion. Once the dissolved HCl molecule has donated its proton, it would seem sensible to assume that the Cl^- has no 'desire' to take it back.

Now compare this to the situation with a typical weak acid such as ethanoic acid.

$$\boxed{CH_3COOH_{(aq)} + H_2O_{(aq)} \rightleftharpoons H_3O^+_{(aq)} + CH_3COO^-_{(aq)}}$$

In this case, the ethanoic acid is far more reluctant to donate its proton. Furthermore, water isn't that great at accepting a proton from the acid. So, it seems reasonable to think that ethanoic acid molecules that have lost their proton (the ethanoate ions) may be reasonably 'keen' to get them back again from the water molecules that are holding onto them (H_3O^+) and become ethanoic acid molecules again.

That means that on the right-hand side of this equilibrium, we have another acid (H_3O^+) and another base (CH_3COO^-). This second pair of acid and a base are called the conjugate acid and conjugate base of the acid and base on the left.

H_3O^+ is the **conjugate acid** of H_2O (a conjugate pair)

CH_3COO^- is the **conjugate base** of CH_3COOH (a conjugate pair)

In general, we can write the following for all acids in water:

$$\boxed{HA_{(aq)} + H_2O_{(aq)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}}$$

The **stronger the acid HA**, the **weaker its conjugate base** (also often called **salt**).
A moderately weak acid, such as ethanoic acid with have a conjugate base (or salt) that has some base strength! In fact, a 0.100 mol dm^{-3} solution of the salt sodium ethanoate has a pH of about 9.4. It's an alkaline salt! Many salts are **NOT NEUTRAL**!

Strong acids (assumed to be 100% dissociated) have conjugate bases that have no measurable base strength. However, it is wrong to assume that a typical weak acid will have a strong conjugate base. Only if the acid is extremely weak (**very high pKa**) would its conjugate base be considered strong.
Ethanol is never normally considered to be an acid. But it is an extremely weak acid! It has a pKa of 16.0. Its conjugate base is the ethoxide ion ($CH_3CH_2O^-$).This is considered to be a strong base and produces highly alkaline solutions when the salt (sodium ethoxide, for example) is added to water.

Showing How Conjugate Bases (Salts) Produce Alkaline Solutions

If we take sodium ethanoate salt and put some into water, it reacts with the water to form an equilibrium. The Na^+ ions have been left out as they are only spectator ions!

This raises the $[OH^-]$ which raises the pH above 7

$$CH_3COO^-_{(aq)} + H_2O_{(aq)} \rightleftharpoons CH_3COOH_{(aq)} + OH^-_{(aq)}$$

BASE ACID CONJUGATE ACID CONJUGATE BASE

For HC*l*, the equilibrium position lies so far to the right that we don't consider it to be an equilibrium (which it strictly is).

The conjugate base of HC*l* is the Cl^- ion and we don't think of this to be basic in any way. That's why a 0.100 mol dm^{-3} solution of NaC*l* has a pH of 7.

Another way of expressing this is to say that the equilibrium when NaC*l* is dissolved in water lies **completely to the left.**

Cl^- ion accepts no protons from water and so no extra OH^- ions are produced and the salty solution remains neutral at pH 7 (@25°C)

This has no effect on $[OH^-]$ so the solution remains pH 7

$$Cl^-_{(aq)} + H_2O_{(aq)} \leftarrow HCl_{(aq)} + OH^-_{(aq)}$$

BASE ACID CONJUGATE ACID CONJUGATE BASE

We can write a general equation to represent the ACID-BASE conjugate pairs idea.

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

ACID 1 BASE 2 CONJUGATE ACID 2 CONJUGATE BASE 1

Conjugate Pairs

Here's an interesting example from organic chemistry:

Nitric 'acid' behaving as a base! This must be done with little or **no water** or the H_2O will compete for the proton because it's a better base than HNO_3!

$$HNO_3 + H_2SO_4 \rightleftharpoons H_2NO_3^+ + HSO_4^-$$

B2 A1 CONJ. A2 CONJ. B1

The $H_2NO_3^+$ then decomposes to give the nitronium cation NO_2^+

Acid and Base Buffering

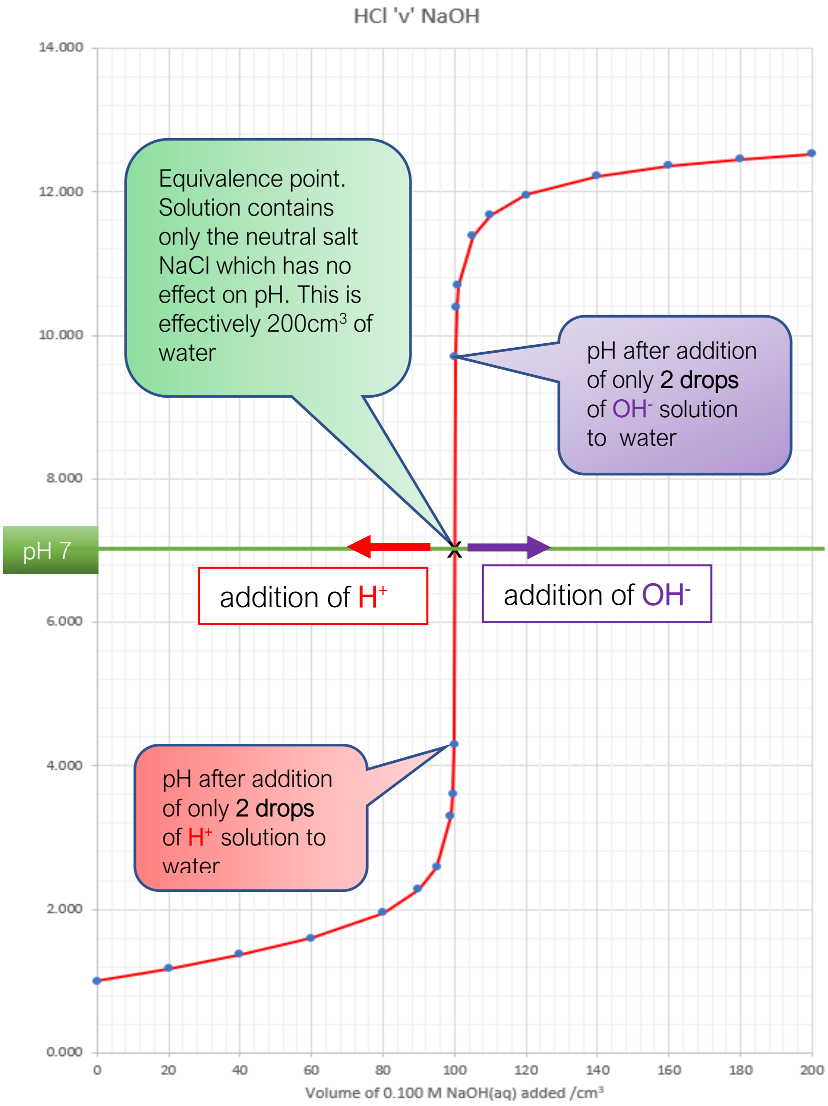
If you are studying A Level biology, you will be familiar with the term ‘Buffer’. Many simple biological systems are grown in buffered media.

Let’s begin by **defining a buffer**. Then we can find out how they work and carry out some calculations.

> Buffer solutions are chemical systems that suffer only a small change in pH when relatively small amounts of acids or bases are added to them.

With this definition, there is no suggestion of how much acid or base can be added before the pH begins to change rapidly. Assume that it is a relatively small amount.

You may think that if you add a very small volume of acid or base to water, you will only get a small change in pH . It seems intuitive that this would be the case. But, this really isn’t the case because of the logarithmic relationship between [H^+] and pH. This is easier to see on the graph showing the titration curve from the strong acid ‘v’ strong base.



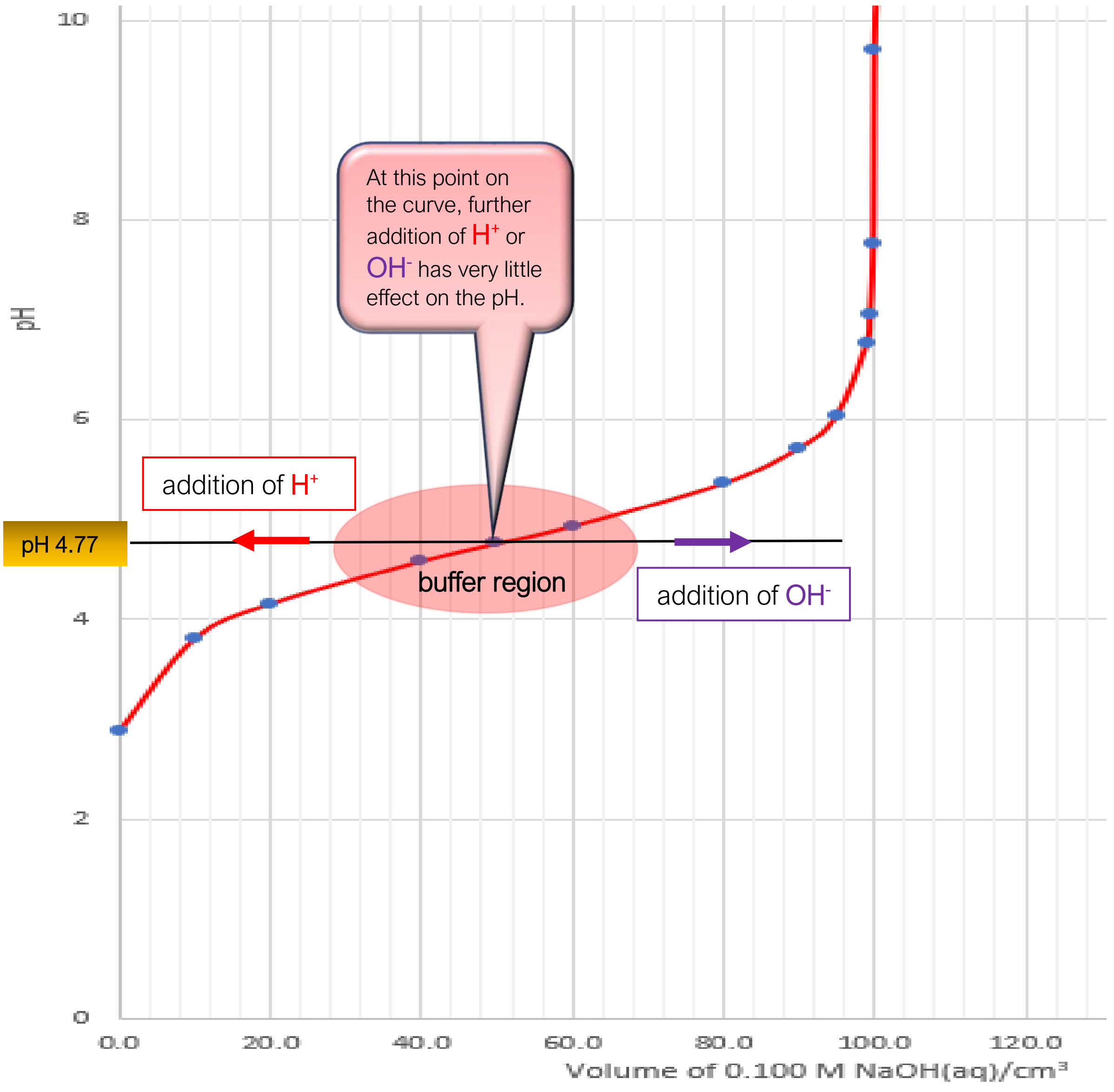
Clearly, tiny additions of acid or base have drastic effect on the pH of water.

Let's consider the blood flowing around your veins.

Blood has many jobs to perform but one involves carrying all sorts of molecules around, dissolved within it. There are many acidic and basic metabolites that are being pumped out and carried from an organ such as the liver, to organs such as the kidney. Humans are extremely sensitive to the pH in our blood. Anything outside of the range 7.2-7.6 and we are in deep trouble that could be lethal.

And yet, we maintain a healthy pH balance in our blood of around 7.4. Our blood must have chemicals dissolved within it that help to maintain a pH close to this figure of 7.4. There must be some buffering going off. I will come back to this soon.

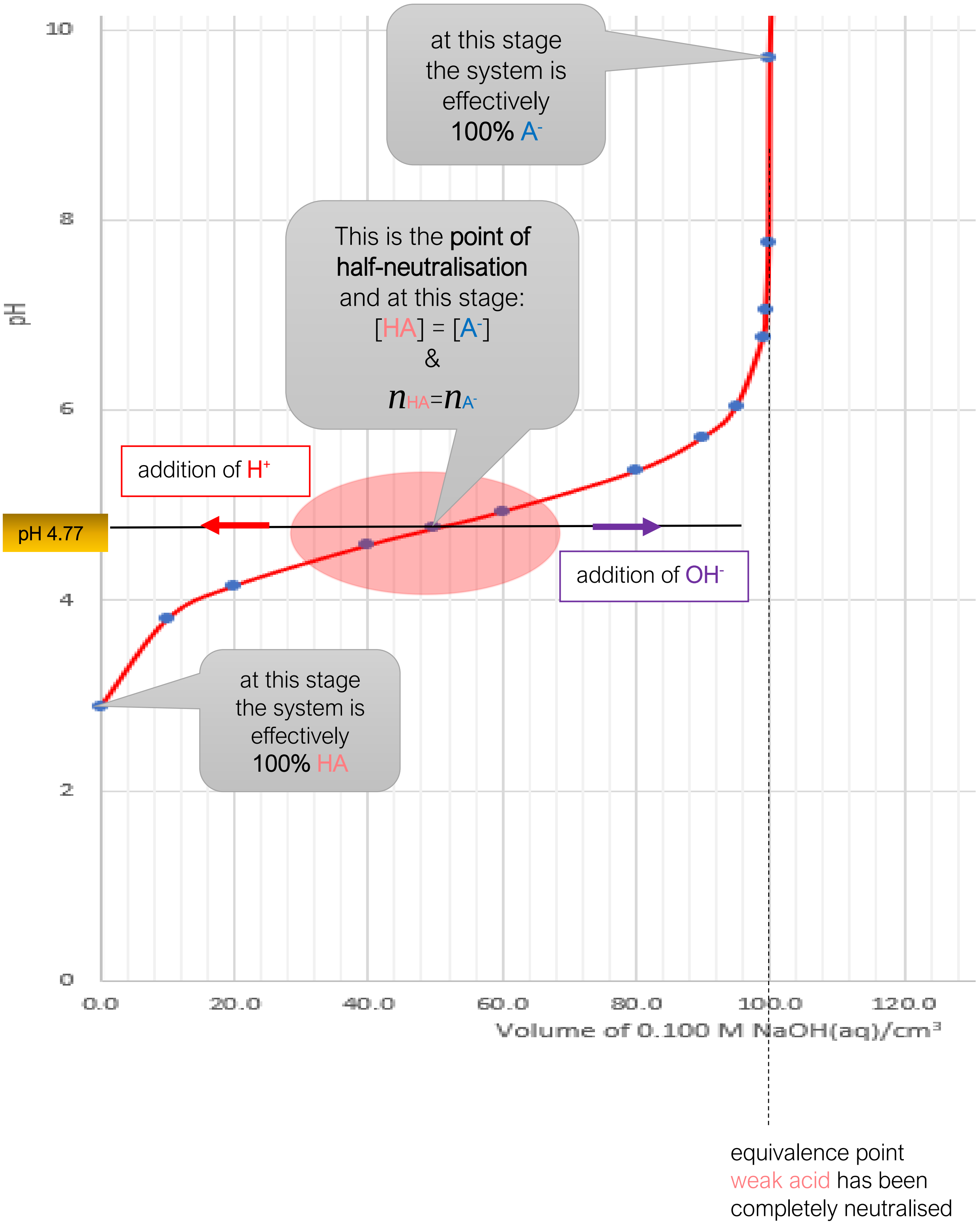
To illustrate the effect on the pH of a buffer by adding some acid or base, I will bring back a section of the titration curve for ethanoic acid 'v' sodium hydroxide (weak acid 'v' strong base)



Now that we can ‘see’ how this works, we need to understand why the curve rises and falls so gently at this point.

The gentle incline occurs when the weak acid has been half-neutralised by a strong base.

A this point of half-neutralisation half of the HA molecules (ethanoic acid) have been neutralised to produce an equal concentration of the conjugate base, A^- (ethanoate ions)



We can calculate the pH at this point. I prefer the 'Henderson-Hasselbalch' equation for these calculations.

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

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

we saw that $n_{HA} = n_{A^-}$
so log 1 = 0

$$pH = pK_a + 0$$

pK_a of ethanoic acid is 4.76

$$pH = \underline{4.76}$$

This is an important fact to note!

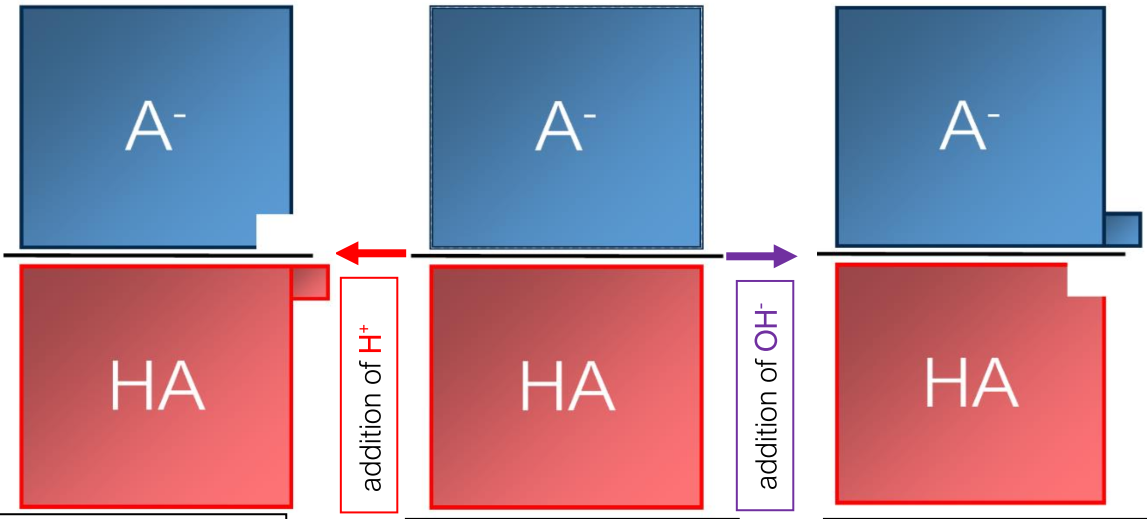
at the point of half-neutralisation
$pH = pK_a$

When the ratio of $n_{HA} : n_{A^-}$ is close to 1:1 then the system buffers very well.
Both the **concentrations are approximately equal,** and both are **large.**

Addition of H^+ **or** OH^- has very little effect on the ratio of $n_{HA} : n_{A^-}$

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

This is illustrated in the diagram below
Addition of small amount of H^+ or OH^- has a tiny impact on the pH



$$pH = pK_a + \log\frac{19}{21}$$

$$pH = 4.76 + (-0.04)$$

$$pH = \underline{4.72}$$

$$pH = pK_a + \log\frac{20}{20}$$

$$pH = 4.76 + (0.00)$$

$$pH = \underline{4.76}$$

$$pH = pK_a + \log\frac{21}{19}$$

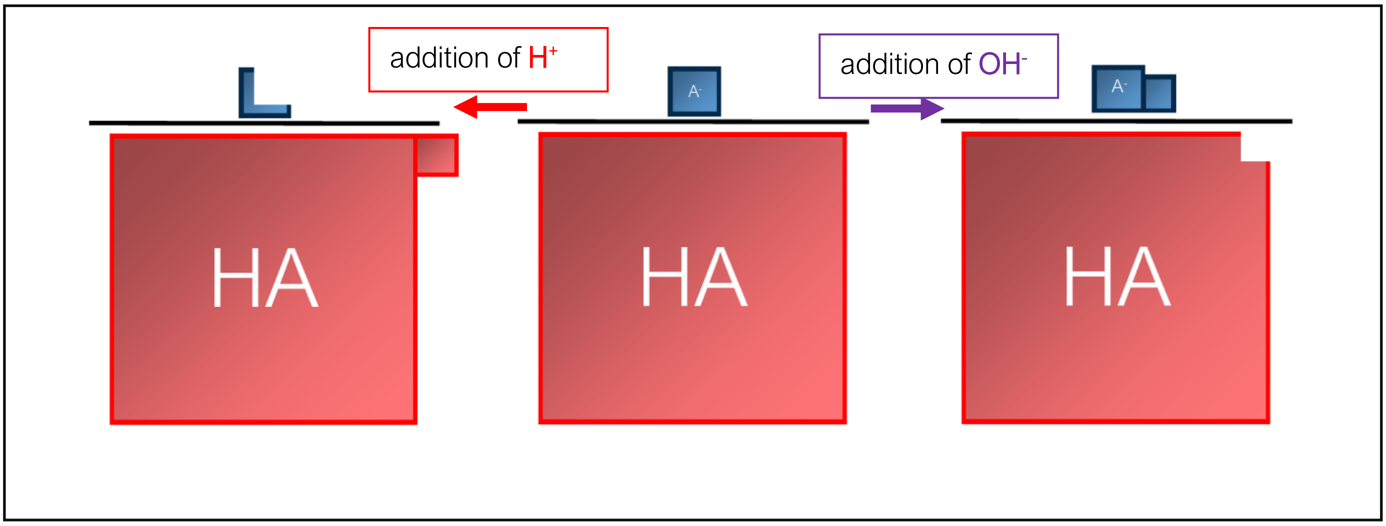
$$pH = 4.76 + (0.04)$$

$$pH = \underline{4.80}$$

NARROW pH range

Large amount of HA but a small amount of A^-

pH changes significantly after additions of small amounts of acid or base.



$$\text{pH} = \text{p}K_a + \log \frac{1}{21}$$
$$\text{pH} = 4.76 + (-1.32)$$
$$\text{pH} = \underline{3.44}$$

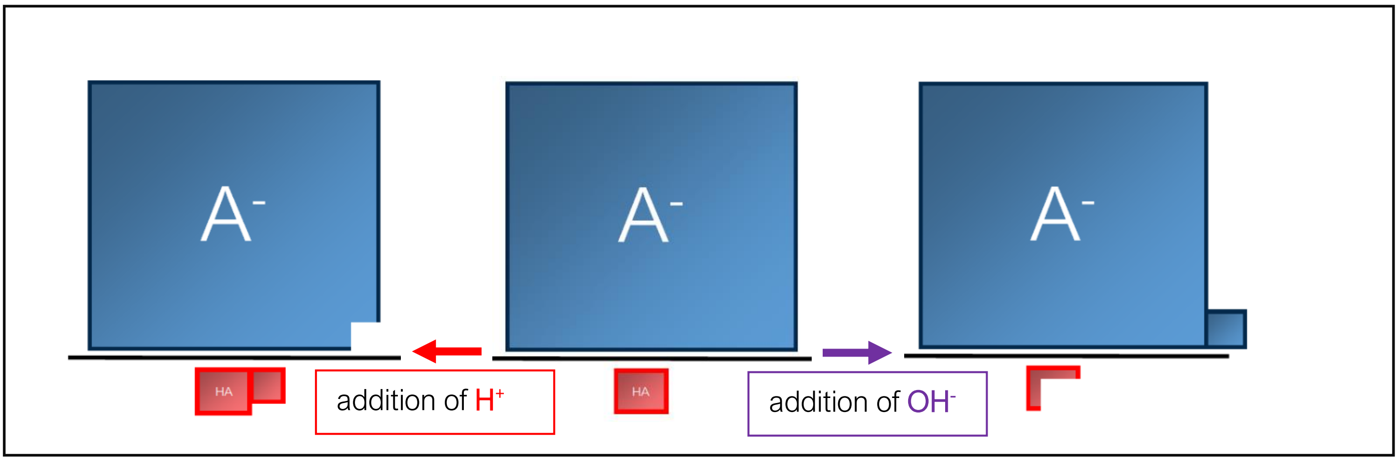
$$\text{pH} = \text{p}K_a + \log \frac{2}{20}$$
$$\text{pH} = 4.76 + (-1.00)$$
$$\text{pH} = \underline{3.76}$$

$$\text{pH} = \text{p}K_a + \log \frac{3}{19}$$
$$\text{pH} = 4.76 + (-0.80)$$
$$\text{pH} = \underline{3.96}$$

WIDER pH RANGE

Large amount of A^- but a small amount of HA

pH changes significantly after additions of small amounts of acid or base.



$$\text{pH} = \text{p}K_a + \log \frac{19}{3}$$
$$\text{pH} = 4.76 + (+0.80)$$
$$\text{pH} = \underline{5.56}$$

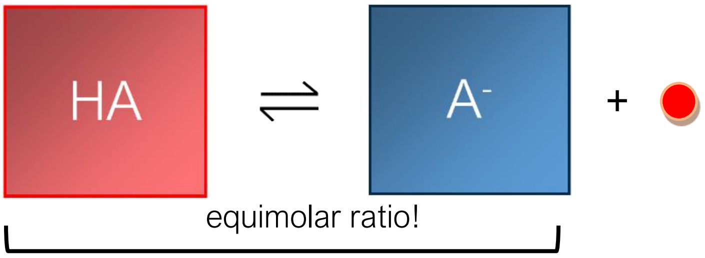
$$\text{pH} = \text{p}K_a + \log \frac{20}{2}$$
$$\text{pH} = 4.76 + (+1.00)$$
$$\text{pH} = \underline{5.76}$$

$$\text{pH} = \text{p}K_a + \log \frac{21}{1}$$
$$\text{pH} = 4.76 + (+1.32)$$
$$\text{pH} = \underline{6.08}$$

WIDER pH RANGE

For a buffer to perform at its best, there needs to be large and equal concentrations of both the weak acid and its conjugate base.

Chemically, we can write:



If OH^- ions are added, they react with the H^+ ions. These H^+ ions are rapidly **replaced** because there is a large reservoir of HA that dissociates to produce more (equilibrium shifts to the right) . The $[H^+]$ and so the pH remains approximately constant.

If H^+ ions are added they react with the large reservoir of conjugate base A^-. They react to make more undissociated HA (equilibrium shifts to the left) . The $[H^+]$ and so the pH remains approximately constant.

An Alternative Way to produce a Buffer Mixture

There is another way to make an equimolar solution of weak acid and conjugate base which is a little easier than 'half-neutralising' a weak acid.

Instead, we can simply add the pure conjugate base (the salt of the acid).

In the case of ethanoic acid, we can work out the number of moles of ethanoic acid molecules that we have and then add the same number of moles of sodium ethanoate by simply weighing out the salt.

Here is a question that we can work through:

Q. Calculate the mass of sodium ethanoate that would need to be added to $25 cm^3$ of $0.200 mol dm^{-3}$ ethanoic acid solution to produce the optimum buffering.

A. First we should calculate the number of moles of CH_3COOH we have.

n CH_3COOH = v x c = 25/1000 x 0.200 = **5.0×10^{-3}** mol

We now need the **same number of moles** of its salt CH_3COONa = **5.0×10^{-3}** mol

The molar mass of CH_3COONa = **82** g/mol

The mass of CH_3COONa = 82 x 5.0×10^{-3} = 0.41g

The problem could be extended to ask

Q. Calculate the new pH if $5.0 cm^3$ of $0.100 mol dm^{-3}$ HC*l* was added to the buffer mixture in the earlier part of the question.

A. You should assume that the added acid will **protonate the conjugate base**, CH_3COO^- .
This will reduce the moles of CH_3COO^- and increase the number of moles of CH_3COOH

We need of work out the moles of HC*l* added.

n HC*l* 5.0cm^3 x 0.100 mol dm-3 = 1.0 x 10^{-3} mol

New n CH_3COOH = 5.0 x 10^{-3} mol + 1.0 x 10^{-3} mol = 6.0 x 10^{-3} mol

New n CH_3COO^- = 5.0 x 10^{-3} mol - 1.0 x 10^{-3} mol = 4.0 x 10^{-3} mol

We can now plug these numbers into our 'Henderson-Hasselbalch' buffer equation.

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

$$pH = pK_a + \log \frac{4.0 \times 10^{-3}}{6.0 \times 10^{-3}}$$

$$pH = 4.76 + \log \frac{4.0 \times 10^{-3}}{6.0 \times 10^{-3}} = 4.59$$

Choice of Buffer

Different circumstances will require buffering at different pHs.

So, how do you choose the correct weak acid to make your buffer?

We need to recall one very important fact about buffers. That is:

At the point of half-neutralisation, the pH = pKa

This is when a buffer is working at its best and has the best buffering capacity. If we want to buffer at a specific pH, then we need to select a **weak acid whose pKa is the same as the pH that we are aiming for.**

If we half-neutralise it (or add a molar equivalent of the salt) then we will achieve a buffer system that will have the desired pH.

If the pH is a little higher or lower than the pKa of the weak acid that we can get hold of, then a little adjustment of the n_{HA} : n_A will hit the desired pH. This is demonstrated in the section on 'Blood Buffering'

A buffer does not need to be an exact 1:1 ratio of n_{HA} : n_A!

If we need a **buffer in the alkaline region**, then we take a weak base and half-neutralise with a strong acid.

e.g. ammonia (weak base) and ammonium chloride (conjugate acid). This creates a pH of 9.3
NH_3 NH_4^+

(**9.3 is the pKa** of ammonium chloride which is a weak acid in the conjugate pair with ammonia!)

Blood Buffering

As was mentioned earlier, blood performs many functions including transporting a vast number of dissolved chemicals. Most of them are acidic but some are basic. We know that even tiny amounts of acid or base added to water have a drastic effect on the pH.

Healthy blood has a pH of 7.40 and must remain in a very narrow pH range of 7.35 - 7.45.

The only way that the pH can be maintained is if the blood contains a buffering system.

The weak acid that performs this job is a very simple, naturally occurring and abundant weak acid called carbonic acid $H_2CO_{3(aq)}$. Fizzy drinks are loaded with carbonic acid which decomposes naturally to give $CO_{2(aq)}$ and $H_2O_{(aq)}$*. Carbon dioxide isn't very soluble in water so comes out of solution to produce bubbles of gas.

Carbonic acid is formed when $CO_{2(g)}$ dissolves in water to form a solution $CO_{2(aq)}$ and then reacts with water.

$$\boxed{CO_{2(aq)} + H_2O_{(aq)} \rightleftharpoons H_2CO_{3(aq)}}$$

It shouldn't surprise you to learn that there is a plentiful supply of each chemical in blood. Carbon dioxide produced by respiration and inhalation, is dissolved in the blood.

carbonic acid dissociates according to the following equation:

$$\boxed{\underset{\text{carbonic acid}}{H_2CO_{3(aq)}} \rightleftharpoons \underset{\text{hydrogen carbonate}}{HCO_3^-{}_{(aq)}} + H^+_{(aq)}}$$

hydrogen carbonate is produced by the kidneys. So, both the acid and its conjugate base are available to be added to the equilibrium, when required.

The pKa of carbonic acid is 6.10 (@37°C!)

If you could only remember one fact associated with buffers, it would be good to remember that the pH at half-neutralisation is the same value as the pKa of the half-neutralised weak acid. When the weak acid is half-neutralised, there is an **equimolar mixture of the weak acid and its conjugate base (its salt).**

From these statements, it should be clear that in the case of carbonic acid in blood, it can't be in equal concentrations with its conjugate base because that would give a pH of 6.10! You'd die.

So, we need to calculate the ratio of $HA : A^-$ that will produce the desired pH of 7.40.

The 'Henderson-Hasselbalch' equation is ideal for this, in my opinion.

$$\boxed{pH = pK_a + \log\left(\frac{n_{A^-}}{n_{HA}}\right)} \qquad \boxed{7.40 = 6.10 + \log\left(\frac{n_{HCO_3^-}}{n_{H_2CO_3}}\right)}$$

required pH-pKa = 7.40- 6.10=1.30

This tells us the difference between the required blood pH of 7.40 and the pKa of carbonic acid is +1.30
This difference needs to be made up by:

$$\log\left(\frac{n_{HCO_3^-}}{n_{H_2CO_3}}\right)$$

$$\log\left(\frac{n_{HCO_3^-}}{n_{H_2CO_3}}\right) = +1.30$$

$$\text{So,}\quad 10^{1.30} = \frac{n_{HCO_3^-}}{n_{H_2CO_3}} = 20.0 \quad \text{therefore,}\quad 20.0 \times nH_2CO_3 = nHCO_3^-$$

$n_{HCO_3^-}$ must be 20.0 times bigger than $n_{H_2CO_3}$ to achieve a pH of 7.40

This ratio, being so far from 1:1 means that the buffering capacity isn't great but, during periods when the H^+ levels rise (acidosis) then the following equilibrium shifts to the left:

$$\boxed{H_2CO_{3(aq)} \rightleftharpoons HCO_3^-{}_{(aq)} + H^+{}_{(aq)}}$$

The rising $H_2CO_{3(aq)}$ levels are then reduced by the equilibria that are coupled to this:

Exhaled more rapidly

Rising H^+ levels (acidosis)

$$\boxed{CO_{2(g)} \rightleftharpoons CO_{2(aq)} + H_2O_{(aq)} \rightleftharpoons H_2CO_{3(aq)} \rightleftharpoons HCO_3^-{}_{(aq)} + H^+{}_{(aq)}}$$

$CO_{2(g)}$ is exhaled more rapidly so $H_2CO_{3(aq)}$ decomposes (Le Chateliers Principle!) and the $[H_2CO_{3(aq)}]$ is therefore reduced. When the opposite occurs (alkalosis), the reverse sequence happens.

When climbing at high altitude, where atmospheric oxygen levels become dangerously low, the body tries to compensate by rapid breathing (hyperventilation). An unwanted side-effect is that more $CO_{2(g)}$ is expelled from the lungs dragging each of the equilibria above, to the left. This reduces the $[H^+]$ and therefore the pH rises. The blood becomes too alkaline. This is known as **alkalosis** and is a dangerous consequence of high altitude climbing that has proven lethal on many occasions.

* $CO_{2(g)}$ it isn't very soluble so in the case of fizzy drink manufacture, the equilibrium is shifted to the right by raising the concentration of the carbon dioxide. This is easily done by raising the pressure of the gas. Once the carbonic acid solution is produced, the high concentrations of carbonic acid are maintained as long as the pressure of carbon dioxide remains high. When the cap is screwed onto the fizzy drink container, the small gap above the liquid contains a small volume of carbon dioxide at high pressure. Removal of the cap releases this high-pressure carbon dioxide and the system is no longer in equilibrium. Carbonic acid starts to decompose to replace the carbon dioxide that is lost from the bottle. It can never restore the equilibrium because the system has become an **open system** so equilibrium is impossible. The drink eventually becomes flat as the system tries, in vain, to restore an equilibrium.

ACID-BASE Indicators: What they are and how they are used.

Read the following statements and consider whether they are true or false

- Indictors are used to indicate the pH of a solution.
- Indicators exhibit one colour in acidic solutions and another colour in alkaline solution.

In fact, the answer to both questions is **false**.

Many students think that the answer to these questions is true. This misunderstanding results from their early exposure to the chemistry of acids and alkalis. The indicator that most students come across, earlier in school, is Universal indicator. This is actually a mixture of several indicators chosen to give a range of colours (all colours of the rainbow). We can all recall the colour of Universal Indicator in water as being green. Most people have heard of the very common indicator known as litmus. This indicator can either be found impregnated into paper or as a solution. This is one rare example of an indicator that has essentially one colour in acidic solution (red) and another colour in alkali (blue).

In this topic, explanations will be given which should lead you to understand why the above statements are false.

Indicators are Weak Acids

Indicators are molecules that partially dissociate to yield a proton and therefore are weak acids. We can represent an indicator using the general formula $HIn_{(aq)}$. Indicators must also have a Ka (so pKa)

$$\boxed{HIn_{(aq)} + H_2O_{(aq)} \rightleftharpoons H_3O^+_{(aq)} + In^-_{(aq)}}$$

Now let's imagine that HIn exhibits colour 1 and In^- exhibits colour 2. We can now write;

$$\boxed{\underset{\text{colour 1}}{HIn_{(aq)}} \rightleftharpoons H^+_{(aq)} + \underset{\text{colour 2}}{In^-_{(aq)}}}$$

and;

$$\boxed{K_a = \frac{[H^+][In^-]}{[HIn]}}$$

n.b. It is common to write Ka for an indicator as K_{In}
Putting this in the form of the Henderson-Hasselbalch equation gives;

$$\boxed{pH = pK_{In} + \log_{10}\left(\frac{[In^-]}{[HIn]}\right)}$$

both of these factors are controlled by relatively large volume of solution into which the indicator is placed and **not by the dissociation of the indicator**!

If a **small amount of these molecules** (just enough to see the colour) are added to a solution, the colour that is observed will depend upon the ratio:

$HIn : In^-$

It has been consistently shown that, to the human eye, if the ratio of any pairs of colours is roughly 10:1 or greater, we see one colour with no hint of the other. In this example we would see red. If the ratio shifted the other way to 1:10 then only blue would be observed. Of course, a ratio of 1:1 would be seen as purple.

If a small amount of indicator molecules are added to a large amount of solution then the pH will be controlled by the solution into which the molecules have been placed. The small amount of indicator (a weak acid **solution!) will have only a tiny effect on the pH of the solution. We could consider the pH of the solution to control the ratio of** $HIn:In^-$**. It will not be the indicator's dissociation that affects the pH!**

Looking at the equation above, for an indicator with a **pKa of 4.7** can you predict the pH of the solution that would cause the indicator to exhibit the colour purple? (Hint: This is the point when the weak acid and conjugate base are in equal proportions.)

pH=____

How large would the **smallest change in pH** need to be to alter the purple appearance to red?

change in pH=____

From the pH that causes the indicator to exhibit the purple colour, how large would the **smallest change in pH** need to be to alter the purple appearance to blue?

change in pH=____

Given these two pHs, over a range of how many pH units will an indicator change its colour from red to blue?

____pH units.

So, we can now see that most indicators exhibit two colours and that the change in colour occurs over a narrow pH range. Furthermore, this range is rarely in the region of pH7.

The **mid-point colour** exhibited by any indicator (purple in our example) occurs when:

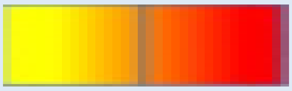
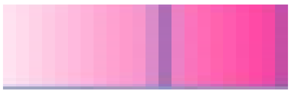
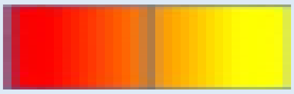
$$pH = pKa \qquad (\text{or } pK_{In})$$

Some typical Indicators

Two very common acid/base indicators are **methyl orange** and **phenolphthalein**.

- METHYL ORANGE has a *p*Ka of 3.7 so the range over which it changes colour is typically quoted as 3.0-4.3
- PHENOLPHTHALEIN has a *p*Ka of 9.3 so the range over which it changes colour is typically quoted as 8.6-10.0

Some other indicators are given below:

Indicator	pKa	pH range and colour change		
Alizarin yellow	11.2	10.1		12.0
Phenolphthalein	9.3	8.3		10.0
Bromothymol blue	7.3	6.0		7.6
Litmus	6.5	5.0		8.0
Bromocresol green	4.7	3.8		5.4
Methyl orange	3.7	3.1		4.4
Thymol blue	1.7	1.2		2.8

We can see that some indicators (with pKa less than 6) can actually exhibit both colours in acid conditions and many others (with pKa greater than 8) can exhibit both colours in alkaline conditions. Litmus has a pKa of 6.5 which essentially means that it is blue in all alkaline conditions and red in acidic conditions.

Choice of Indicator

As long as the indicator's range (pKa ±1 pH unit) falls on the very steep (nearly vertical) part of a titration curve, then the indicator will be suitable. This means that, upon the addition of one drop of solution just before the end-point (the smallest addition) the **equivalence point** and the **colour change** (which we use to indicate the end-point) will both coincide.

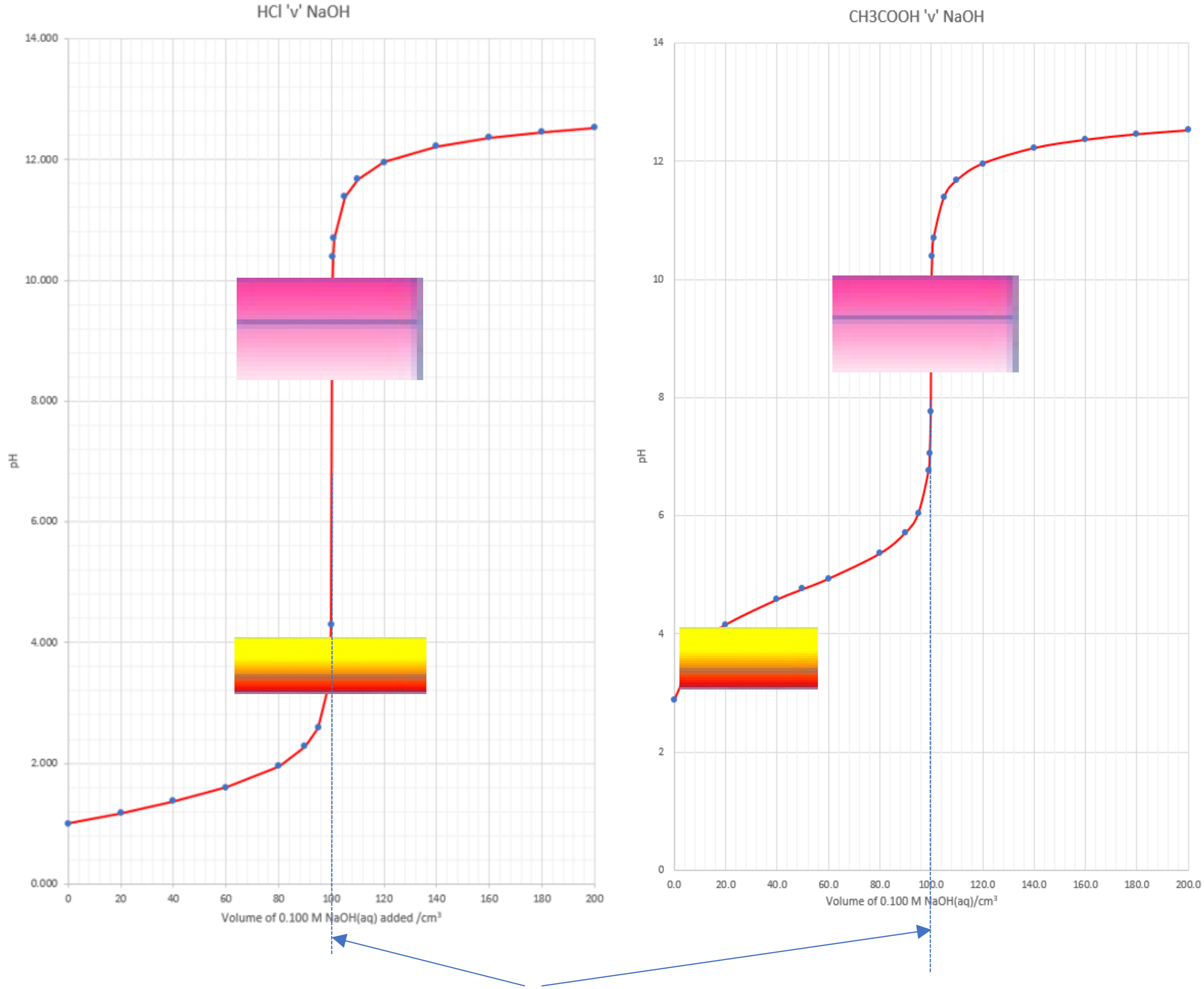
For a STRONG ACID 'v' STRONG BASE, both **methyl orange** and **phenolphthalein** are suitable.

For a WEAK ACID 'v' STRONG BASE, only **phenolphthalein** is suitable.

For a STRONG ACID 'v' WEAK BASE, only **methyl orange** is suitable.

For a WEAK ACID 'v' WEAK BASE, no indicator is suitable.

If we consider methyl orange and phenolphthalein:



volume of 0.100 mol dm^{-3} NaOH required to fully neutralise the acid (the equivalence point)
This is what **a titration is attempting to find by the indicator colour change.**

Going Further: Calculating pH for All Acids

You have learned how to calculate the pH of strong acids and weak acids. But, in reality, both of these calculations that you have learned lead to **approximate answers**.

In the case of strong monoprotic acids such as hydrochloric acid, we assume that this acid is FULLY DISSOCIATED. Well, that can't be entirely accurate as there are acids that are stronger still, *e.g.* hydrobromic acid. If hydrochloric acid was 100% strong then it would have an infinite value for the Ka. It actually has a finite value of 1.3×10^6 mol dm^{-3}

But, **as long as the solution of acid is dilute** (ideally 0.100 mol dm^{-3} or less) it is **so extensively dissociated** that we assume 100% and then we can use the $-\log_{10}[H^+]$. The difference between the **true value** and the **approximate** value would be almost impossible to detect using instrumentation like a pH meter. You must appreciate though that it is still an **approximation**!

At the other extreme, you have learned to calculate the pH of weak acids such as ethanoic acid. To do this, you have used the equation

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

Using the correct chemical assumption that $[H^+]=[A^-]$ in a simple dilute solution of the acid and that there is a minute extent of dissociation, we can use this form of the equation to estimate the pH

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

So….

$$\boxed{\sqrt{(K_a \times [HA])} = [H^+]}$$

When we do this for 0.100 mol dm^{-3} ethanoic acid with a Ka of 1.7×10^{-5} we get a pH of 2.88

So, we can calculate **approximate pHs** of acids that we assume to be strong but are not actually 100% dissociated! And, we can calculate **approximate pHs** of acids that we assume to not dissociate at all because it makes it convenient in our calculations.

You could consider your knowledge of acid pH calculations to be summarised as follows:

'Weak' Acids	All the other Acids	'Strong' Acids
$Ka = \frac{[H^+]^2}{[HA]}$ So little dissociation that we use the original value, i.e. pre-equilibrium concentration of HA	These acids are too strong to be 'weak acids' but too weak to be classified as 'strong acids. **Too strong** for the assumption that the equilibrium concentration of HA is the same as the original concentration that was instantaneously produced when the acid was dissolved in water (the concentration on the label) *i.e.* no dissociation of HA. **Too weak** for the assumption that the acid fully dissociates. **These are the majority of acids**! And you can't even calculate, approximately, the pHs for these. Even worse is the fact that you can't do anything but approximate for the others! Let's see how we can do this for <u>ALL ACIDS</u> and <u>ACCURATELY</u> For example, **hydrofluoric acid, $HF_{(aq)}$** K_a= 1.6×10^{-4}	$pH=-log_{10}[H^+]$
Approximates closely **only for acids where** $Ka < 10^{-4}$ This is when the extent of dissociation is less than 5%		Approximates closely only when solutions are dilute and ONLY when the Ka>1

Calculating the pH of acids the accurate way:

We are **not going to ignore the dissociation for HA, however small or large**.
We are going to use:

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

But the true concentration of HA at equilibrium will be represented as

$[HA]_{\rightleftharpoons} = ([HA] - x)$ -where x is the amount of HA that has been dissociated into H^+ and A^-

So, it follows that the $[H^+] = x$ and also $[A^-] = x$

Therefore we can write $K_a = \dfrac{x \times x}{([HA] - x)} = \dfrac{x^2}{([HA] - x)}$

Rearranged, this becomes $K_a([HA] - x) = x^2$

$$x^2 + K_a x - K_a[HA] = 0$$

You may recognize this as a quadratic equation.

$$x^2 + K_a x + (-K_a[HA]) = 0$$

$$ax + bx + c = 0$$

$a=1$ $b=Ka$ $c= -K_a[HA]$

Solving for ethanoic acid

$a=1$ $b=1.7 \times 10^{-5}$ $c= -1.7 \times 10^{-6}$

$$\boxed{x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}}$$

$$x = \frac{-1.7 \times 10^{-5} \pm \sqrt{(1.7 \times 10^{-5})^2 - (4 \times 1 \times -1.7 \times 10^{-6})}}{2 \times 1} = 1.295 \times 10^{-3} \quad \text{or} \quad -1.313 \times 10^{-3}$$

And $x = [H^+]$

We can ignore the solution that suggests $x = [H^+] = -1.313 \times 10^{-3}$ mol dm^{-3} as it has no physical meaning!

Thus, the solution that suggests $[H^+] = 1.295 \times 10^{-3}$ mol dm^{-3} must be the correct solution.

$\text{pH} = -\log_{10} 2.593 \times 10^{-3} = 2.89$

Now, when you compare this to the value for 0.100 M ethanoic acid using the approximation, you get a pH of 2.88 which is almost identical; probably, within the error incurred in its measurement.

Let's try this for hydrofluoric acid. This has a $K_a > 10^{-4}$ which is too high for the approximation method. It dissociates more than 5%!

For HF $K_a = 7.20 \times 10^{-4}$ mol dm^{-3}

So, for a 0.100 mol dm^{-3} HF

$$x = \frac{-7.20 \times 10^{-4} \pm \sqrt{(7.20 \times 10^{-4})^2 - (4 \times 1 \times -7.20 \times 10^{-5})}}{2 \times 1} = 8.133 \times 10^{-3} \text{ or } -8.853 \times 10^{-3}$$

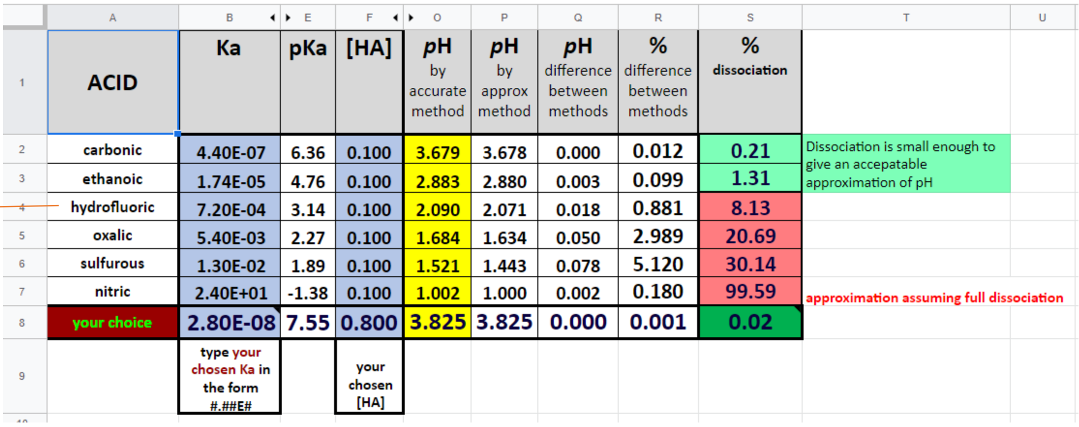
$-\log(8.133 \times 10^{-3}) =$ pH = 2.090

by approximation we would obtain pH = 2.071

Below is a table containing a selection of acids that increase in strength. It is easy to see how the percentage difference between the **value obtained by approximation** and the **value obtained via this correct method** becomes increasingly large. This coincides with the level of dissociation that I have placed alongside.

carbonic acid and ethanoic acid are less than 5% dissociated and the difference in pH by the two methods is for these acids is tiny. The pH for HF is around 1% out and it is dissociated by >5%.

hydrofluoric acid example given above



	A	B	E	F	O	P	Q	R	S	T	U
1	**ACID**	**Ka**	**pKa**	**[HA]**	**pH** by accurate method	**pH** by approx method	**pH** difference between methods	**%** difference between methods	**%** **dissociation**		
2	carbonic	4.40E-07	6.36	0.100	3.679	3.678	0.000	0.012	0.21	Dissociation is small enough to give an accepatable approximation of pH	
3	ethanoic	1.74E-05	4.76	0.100	2.883	2.880	0.003	0.099	1.31		
4	hydrofluoric	7.20E-04	3.14	0.100	2.090	2.071	0.018	0.881	8.13		
5	oxalic	5.40E-03	2.27	0.100	1.684	1.634	0.050	2.989	20.69		
6	sulfurous	1.30E-02	1.89	0.100	1.521	1.443	0.078	5.120	30.14		
7	nitric	2.40E+01	-1.38	0.100	1.002	1.000	0.002	0.180	99.59	approximation assuming full dissociation	
8	your choice	2.80E-08	7.55	0.800	3.825	3.825	0.000	0.001	0.02		
9		type your chosen Ka in the form #.##E#		your chosen [HA]							

In general, we can write:

$$\boxed{x = \frac{-Ka \pm\sqrt{\{Ka^2 - (4 \times -Ka \times [HA])\}}}{2}}$$

pH calculator

You can find a Google Sheet on *CramNow* that will allow you to select **any acid** and it will calculate the pH correctly if you know the **Ka** of the acid and its concentration. Download a copy and have a play! You can also open the hidden columns to see how this spreadsheet works!

Going further; Something to think about.

When we calculate the pH of solution of acid or base, the concentrations are typically so high that we can ignore the naturally occurring $[H^+]$ and $[OH^-]$ produced by natural dissociation of water.
The added H^+ and OH^- ions from added acid or base are relatively so numerous that the contribution to the pH made by the naturally occurring is insignificant.
However, if we continue to dilute an acid or alkali repeatedly, the pH must be ultimately be limited to 7 because it will eventually be so dilute, it will be effectively just water.

For example, if we repeatedly dilute a 0.100 mol dm^{-3} solution of $HCl_{(aq)}$ by ten times, each dilution, the $[H^+]$ will become 0.01 (pH2), 0.001 (pH3), 0.0001 (pH4) etc. It would lead to a ridiculous outcome, *i.e.* an extremely dilute acid would have a pH of 13. This is clearly chemically wrong. This is because we are not considering the naturally occurring H^+ from water's autoionization.

The table below helps to illustrate why the naturally occurring H^+ become more significant as the solution of acid becomes more diluted.
Please be aware that this is still a bit of an approximation. This is because I am assuming here that the natural contribution from the autoionization of water is always going to be 10^{-7} mol dm^{-3}, whatever else is added. This can't be correct as this is an equilibrium and other added H^+ affect the 'natural equilibrium' that gave a figure of 10^{-7} mol dm^{-3} H^+ ions. I'll show you how to calculate the correct pH after dilution below the table*. An understanding of this is not necessary in order to understand acids and bases!

Dilution	$[HCl_{(aq)}]$ These are added protons	pH if we don't consider those occurring naturally H^+	Naturally occurring H^+ that contribute to the pH	Total $[H^+]$	pH
0	0.1	1	insignificant	extremely close to 0.1	extremely close to 1
1	0.01	2	insignificant	very, very close to 0.01	very, very close to 2
2	0.001	3	insignificant	very close to 0.001	very close to 3
3	0.0001	4	insignificant	effectively 0.0001	effectively 4
4	0.00001	5	Approx. 0.0000001	0.0000101	4.996
5	0.000001	6	Approx. 0.0000001	0.0000011	5.959
6	0.0000001*	7	Approx. 0.0000001*	0.0000002*	6.699*
7	0.00000001	8	Approx. 0.0000001	0.00000011	6.959
8	0.000000001	9	Approx. 0.0000001	0.000000101	6.996
12	0.00000000000001	13			Extremely close to 7

* I am now going to show you why the **intuitive feeling is not correct**, *i.e.* it is not correct to assume that the total concentration of H^+ ions must simply be the sum of those from the original hydrochloric acid (1 x 10^{-7}mol dm^{-3}) plus 1 x 10^{-7}mol dm^{-3} from those that we there originally from the water. If this were the case, the pH would be:

$$pH = -\log_{10} [(1 \times 10^{-7} \text{mol dm}^{-3}) + (1 \times 10^{-7} \text{mol dm}^{-3})] = -\log_{10} [(2 \times 10^{-7} \text{mol dm}^{-3}) = 6.70$$

Here is the solution:

Let's recall the equation for the ionic product of water.

$$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-7} \times 1.00 \times 10^{-7} = 1.00 \times 10^{-14}\ \text{mol}^2\ \text{dm}^{-6}$$

This is the case in pure water (@25°C).

But, we have a greater concentration of H^+ ions than 1 x 10^{-7}mol dm^{-3}!

Let's imagine a situation where we suddenly added sufficient H^+ ions to this water so that the $[H^+]$ ions was instantaneously raised to 2 x 10^{-7}mol dm^{-3}.

This is would mean that in that instant, $[H^+][OH^-] > 1.00 \times 10^{-14} = Kw$

So, the system is **out of equilibrium** and the equilibrium position must shift to the right to restore the value of Kw

$$H^+ + OH^- \rightleftharpoons H_2O$$

Some H^+ needs to be used up and its concentration go down. This decrease could be described as **x mol dm^{-3}**.
For the decrease of x mol dm^{-3} of H^+, there must be a decrease of **x mol dm^{-3}** of OH^- (to make H_2O)
Once this happens, the value of Kw will be restored to **1.00 x 10^{-14} mol² dm⁻⁶**

We can express this mathematically as: $Kw = ([H^+]-x)([OH^-]-x)$

$$Kw = [H^+][OH^-] - [H^+]x - [OH^-]x + x^2$$

This is a quadratic equation so can be solved to give x.

Solving this equation gives 2 values for x. 0.382 x 10^{-7} mol dm^{-3} (and a chemically impossible value).

Remember what **x represents**. It is the **reduction in $[H^+]$needed to restore the value of Kw**.

New equilibrium $[H^+]$ = 2.00 x 10^{-7}- 0.383 x 10^{-7}= **1.617 x 10^{-7}** mol dm^{-3}

New pH = $-\log_{10}[H^+]$ = $-\log_{10}$1.617 x 10^{-7} mol dm^{-3} = 6.79

The intuitive and wrong answer for the pH was = 6.70

Going Further: Calculating the *p*H of Bases including Conjugate Bases of Weak Acids (Salts)

Introduction

So far, we have concentrated almost entirely on acids and the way in which they dissociate in water by their reaction with it. Although we have defined bases (in a Lowry-Brønsted context), there has been no quantitative discussion regarding **bases**. Ignoring bases is rather like ignoring the fact that a coin has a tails side when discussing the statistics of coin tossing.

So, here is a brief explanation of the base chemistry side of things.

Bases and their reaction in water

Let's consider a base B. How will B behave when placed in water?

We can represent this reaction as follows:

$$B_{(aq)} + H_2O_{(aq)} \rightleftharpoons BH^+_{(aq)} + OH^-_{(aq)}$$

BASE ACID CONJ. ACID CONJ. BASE

The **stronger the base**, the further the equilibrium lies **to the right**. If the reaction went to completion, it would be equivalent to adding the same number of moles of NaOH to water.

- Write an expression for K_b. This is the base equivalent of K_a.

K_b = ____________

Remember the 'trick' with $[H_2O]$ that we did when writing K_a (the **$[H_2O]$ is so large it is effectively a constant**!)

The larger the K_b the farther to the right the equilibrium lies.

Let's look at an example. We'll use the example of **ammonia**.

Ammonia has a K_b value of **1.8 x 10^{-5}** mol dm^{-3}. We can write an equation for base dissociation.

$$NH_{3\,(aq)} + H_2O_{(aq)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-_{(aq)}$$

BASE ACID C. ACID C.BASE

From this equilibrium, we can see that the addition of ammonia (a base) to water increases the $[OH^-]$ so the pH rises.

Using assumptions that we have applied to weak acid calculations, we can arrive at the following expression:

$$K_b = \frac{[OH^-][NH_4^+]}{[NH_3]} \qquad \text{so,} \qquad K_b = \frac{[OH^-_{(aq)}]^2}{[NH_{3(aq)}]}$$

$$[OH^-] = \sqrt{(K_b \times [NH_3])}$$

$$[OH\text{-}] = \sqrt{(1.8 \times 10^{-5}\ \text{mol dm}^{-3} \times\ 0.100\ \text{mol dm}^{-3})}$$

$$= 0.00134\ \text{mol dm}^{-3}$$

Then we recall $K_w = [H^+][OH^-] = 10^{-14}$

$$[H^+] = \frac{K_w}{0.00134} = \frac{10^{-14}}{0.00134} = 7.5 \times 10^{-12}\ \text{mol dm}^{-3}$$

$$pH = -log_{10}\ 7.5 \times 10^{-12}\ \text{mol dm}^{-3} = \mathbf{11.1} = pH$$

The connection between K_b and K_a?

Let's consider the general example of HA . You are familiar with this.

$$HA_{(aq)} + H_2O_{(aq)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$$

conjugate base (**salt**)

-this can be quantified using K_a

The conjugate base (salt) $A^-_{(aq)}$ also forms an equilibrium with water:

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

-this can be quantified using K_b

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

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

$$K_a \times K_b = \frac{[H^+]\cancel{[A^-]}}{\cancel{[HA]}} \times \frac{\cancel{[HA]}[OH^-]}{\cancel{[A^-_{(aq)}]}} \qquad \text{(cancelling!)}$$

So . . . .

$$\boxed{K_a \times K_b = K_w = [H^+][OH^-] = 10^{-14}}$$

This means that we can find K_b of the conjugate base if we know K_a of the acid that produced it!

The K_b of the ethanoate ion must be $\frac{K_w}{K_a} = \frac{10^{-14}}{1.7 \times 10^{-5}} = 5.88 \times 10^{-10}$ mol dm^{-3}

Calculating the pH of a salt such as sodium ethanoate

$$K_a \times K_b = K_w = 10^{-14}$$

This is a **very useful relationship** as it will allow us to calculate the *p*H of a salt such as sodium ethanoate from knowledge of the K_a of its conjugate acid, i.e. ethanoic acid.

1. Calculate the pH of 0.100 mol dm^{-3} CH_3COONa (sodium ethanoate **salt**)

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2. Calculate the pH of a 0.180 mol dm^{-3} methylamine solution.
   K_b for methylamine is 4.41 x 10^{-4} mol dm^{-3}

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3. Calculate the pH of the 'neutralised' ethanoic acid in the ethanoic acid 'v' sodium hydroxide titration. When you calculated pHs, the pH at 50cm^3 was deliberately avoided. Now calculate its pH?

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4. A final thought-provoking weak acids problem. Calculate the pH of the 0.100M solution of ethanoic acid when only 1 drop (0.05 cm^3 of 0.100) mol dm^{-3} $NaOH_{(aq)}$ has been added. You should get a very odd result. Can you explain it?
Hint:Think about assumptions that you have made.

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Answers

1. The K_b of the ethanoate ion must be $\frac{K_w}{K_a} = \frac{10^{-14}}{1.7 \times 10^{-5}} = 5.88 \times 10^{-10}$ mol dm^{-3}

$[OH^-] = \sqrt{(K_b \times [CH_3COO^-])} = \sqrt{5.88 \times 10^{-10} \times 0.100} = 7.67 \times 10^{-6}$ mol dm^{-3}

$$[H^+] = \frac{10^{-14}}{7.67 \times 10^{-6}} = 1.30 \times 10^{-9} \text{ mol dm}^{-3}$$

pH = $-log_{10}$ 1.30×10^{-9} = 8.89

2.

$[OH^-] = \sqrt{(K_b \times [methylamine])} = \sqrt{(4.41 \times 10^{-4} \times 0.180)} = 8.91 \times 10^{-3}$ mol dm^{-3}

$$[H^+] = \frac{10^{-14}}{8.91 \times 10^{-3}} = 1.12 \times 10^{-12} \text{ mol dm}^{-3}$$

pH = $-log_{10}$ 1.30×10^{-9} = 11.95

3. So, the pH of the 'neutralised' ethanoic acid, where 50 cm^3 of 0.100 mol dm^{-3} NaOH were added to 50cm^3 of 0.100 mol dm^{-3} must have a pH calculated as follows:

Remember that the salt concentration is half of the original acid concentration because the volume has been doubled!
So, as the acid was 0.100 mol dm^{-3}, the salt (ethanoate) will be 0.0500 mol dm^{-3}

$[OH^-] = \sqrt{(K_b \times [CH_3COO^-])} = \sqrt{(5.88 \times 10^{-10} \times 0.0500)} = 5.42 \times 10^{-6}$ mol dm^{-3}

$$[H^+] = \frac{10^{-14}}{5.42 \times 10^{-6}} = 1.85 \times 10^{-9} \text{ mol dm}^{-3}$$

pH = $-log_{10}$ 1.30×10^{-9} = 8.73

4. The pH at this point is

$$pH = pKa + \log n_{A-} / n_{HA}$$

$$pH = 4.77 + \log 5 \times 10^{-6} / 4.995 \times 10^{-3}$$

$$pH = 4.77 + \log 1.001 \times 10^{-3}$$

$$pH = 4.77 + (-3.00)$$

$$pH = 1.77$$

This is odd since this suggests that pH is more acidic after one drop of alkali has been added than when the acid has undergone no neutralisation whatsoever. This just can't be right!
This exposes the error that is made by **ignoring the slight natural dissociation.** When using the *Henderson-Hasselbach* equation, we are assuming that there is no dissociation, other than that which we force by adding strong base. It isn't a problem once some more NaOH has been added. **The error becomes insignificant.**

Important ACID-BASE Equations and when to use them.

Equation 1

$$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}\ \text{mol}^2\,\text{dm}^{-6}$$

K_w is known as the **ionic product of water** and it has a value of 10^{-14} $\text{mol}^2\,\text{dm}^{-6}$ (ONLY at 25 °C!)

Equation 2a

$$pH = -\log[H^+]$$

Equation 2b

$$[H^+] = \text{antilog}_{10}\ (-\,pH)$$

10^x button on most calculators!

Equation 3a

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

Equation 3b ⚠ Caution

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

Equation 3c ⚠ Caution

$$[H^+] = \sqrt{K_a \times [HA]}$$

Making the assumption that $[H^+] = [A^-]$ when HA has been dissolved in water!

Making the assumption that $[HA]$ at equilibrium is approx. equal to $[HA]$ before any dissociation.

⚠ Caution These equations (**3b and 3c**) <u>should only be used</u> when dealing with a simple solution of a weak acid that has been dissolved in water, i.e. no neutralisation has taken place!

Equation 4

$$pK_a = -\log_{10} K_a$$

Values of *Ka* vary so greatly that dissociation of molecules is often quoted on the p*Ka* scale. The **<u>more acidic</u>** a molecule, the **<u>greater the *Ka*</u>** and the **<u>smaller the p*Ka*</u>**

For situations when **some neutralisation has taken place**, we need to use the following equation.

Equation 5
'Henderson-Hasselbalch' eqn!

Salt concentration, which is also the conjugate base.

$$pH = pK_a + \log_{10}\left(\frac{[A^-]}{[HA]}\right) \quad \text{OR} \quad pH = pK_a + \log_{10}\left(\frac{n_{A^-}}{n_{HA}}\right)$$

ratio of concentrations

ratio of moles

Remember $[A^-]/[HA]$ has the **same value** as n_{A^-}/n_{HA}

This equation has its limitations. See earlier!