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 ***pKa***.
- ***pKa***= -log Ka (just like we did with *p*H!)
- the **smaller** the value of ***pKa***, 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 $[H^+]$.

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

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

Taking the square root of both sides:

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

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

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

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

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, HCl. 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!

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

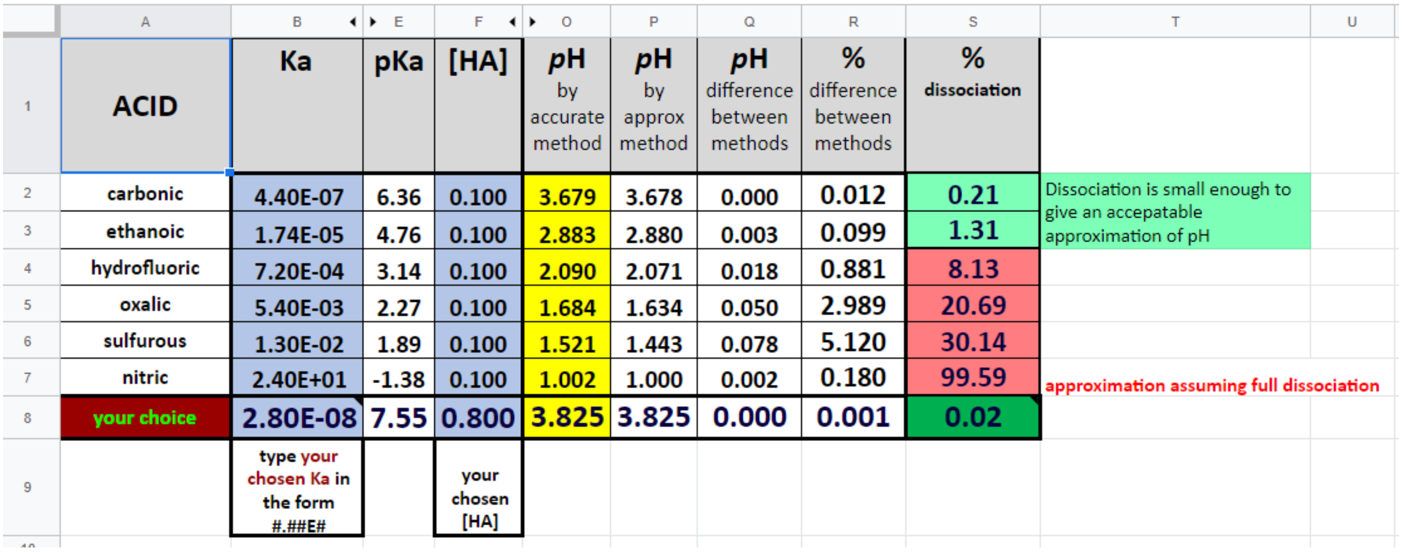
BUT you must be aware of its limitations. In my experience, students often try using this equation when it is the wrong equation to use. You must remember that this only works when you are trying to calculate the pH of a **simple solution of a** weak acid**. If there has been anything done to the acid, 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*