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

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

So little dissociation that we use the original value,
i.e. pre-equilibrium concentration of HA

Approximates closely **only for acids where** Ka < 10^{-4}
This is when the extent of dissociation is less than 5%

All the other Acids

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, $HF_{(aq)}$** $K_a = 1.6 \times 10^{-4}$

'Strong' Acids

$$pH = -log_{10}[H^+]$$

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.

$$\begin{array}{llll} x^2 & + K_a x & + (-K_a[HA]) & = 0 \\ ax + & bx + & c & = 0 \\ a=1 & b=Ka & c=-K_a[HA] & \end{array}$$

Solving for ethanoic acid

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

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

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

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.

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

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

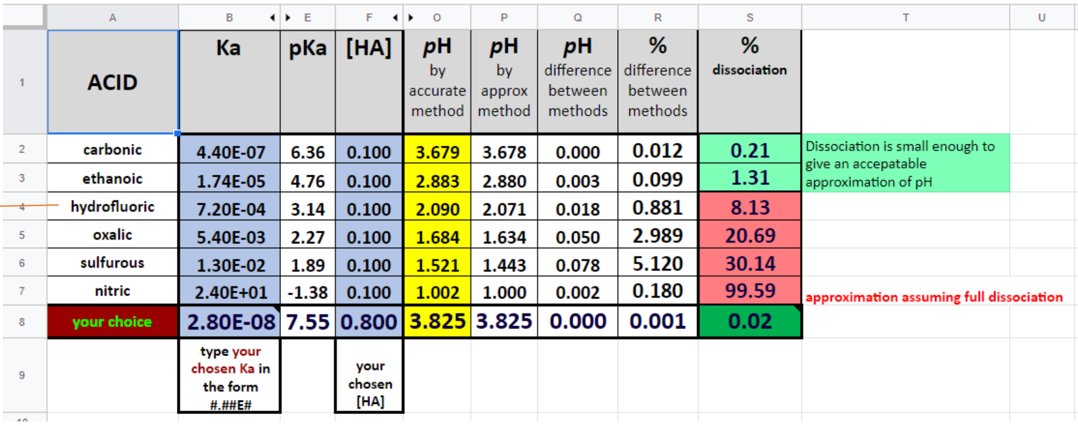
$-\log(8.133 \times 10^{-3}) =$ pH = 2.090

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



ACID	Ka	pKa	[HA]	**pH** by accurate method	**pH** by approx method	**pH** difference between methods	**%** difference between methods	**%** dissociation	
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
ethanoic	1.74E-05	4.76	0.100	2.883	2.880	0.003	0.099	1.31	
hydrofluoric	7.20E-04	3.14	0.100	2.090	2.071	0.018	0.881	8.13	
oxalic	5.40E-03	2.27	0.100	1.684	1.634	0.050	2.989	20.69	
sulfurous	1.30E-02	1.89	0.100	1.521	1.443	0.078	5.120	30.14	
nitric	2.40E+01	-1.38	0.100	1.002	1.000	0.002	0.180	99.59	approximation assuming full dissociation
your choice	2.80E-08	7.55	0.800	3.825	3.825	0.000	0.001	0.02	
	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!