Physical Chemistry – crib sheet
Acids and Dissociation theory

Basic definition

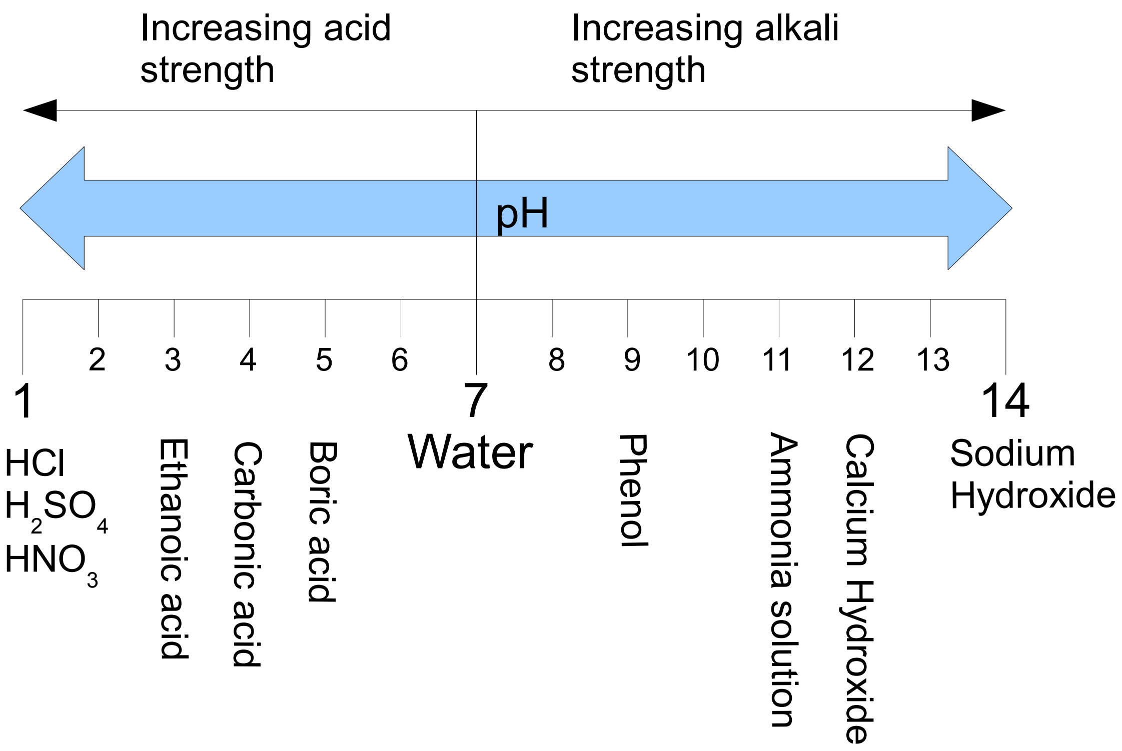
An acid is a compound with a dissociatable (removable) hydrogen.

A strong acid is an acid where the hydrogen can be easily removed. Mineral acids (*such as hydrochloric acid [HCl], nitric acid [*HNO_3*], phosphoric acid [*H_3PO_4*] and sulfuric acid [*H_2SO_4*]*) are examples of strong acids.

A weak acid is an acid where the hydrogen is not very easily removed. Organic acids (*such as methanoic [CHOOH], ethanoic [*CH_3COOH*] and propanoic [*CH_3CH_2COOH*]*) are examples of weak acids.

pH scale

The pH scale is a scale based on the strength of the acids and bases. It goes from 0 to 14 with pure water being 7. The scale has no units.



Calculating the pH of an acid.

Strong acids are simple to calculate the pH of. A strong acid will completely dissociate when in solution, so the H^+ concentration (*this can be written as [*H^+*]*) is the concentration of the acid.

$$[HCl]_{(aq)} \rightarrow [H^+]_{(aq)}\ [Cl^-]_{(aq)}$$

If the strong acid has more than one hydrogen (such as in sulfuric or phosphoric acid), then the concentration of the acid should be multiplied by the number of hydrogens

The formula used to calculate the pH of an acid from the $[H^+]$ is

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

pH values are normally expressed to one decimal place

Example

Find the pH of 0.3 mol dm^{-3} hydrochloric acid (HCl)

HCl is a monoprotic acid (*it has one H*), so $[H^+] = 0.3$. The pH is therefore $-\log_{10} [0.3] = 0.5$

Find the pH of 0.4 mol dm^{-3} sulfuric acid (H_2SO_4)

Sulfuric acid is a diprotic acid (*it has two H*), $[H^+] = 0.4 \times 2 = 0.8$. The pH is 0.1

For a weak acid, calculating the pH is different.

In solution, a weak acid will not completely dissociate – only a very small amount of H^+ is produced for every mole of acid (sometimes it is less than 1%). Calculating the pH of a weak acid depends on the amount of H^+ produced by the small amount of dissociation.

$$[CH_3COOH]_{(aq)} \rightleftharpoons [CH_3COO^-]_{(aq)} + [H^+]_{(aq)}$$

Example

Find the pH of 0.1 mol dm^{-3} ethanoic acid given that only 1.3% dissociation occurs

The concentration of the acid at the start of the reaction is 0.1 mol dm^{-3}. 1.3% dissociation means that in every mole of acid, 1.3% of a mole of acid will form H^+ in solution. In this example, there is 0.1 mol dm^{-3}, therefore there will be 0.1 x 1.3% H^+ = 1.3×10^{-3} mol dm^{-3}.

This value can then be placed in the $pH = -\log_{10} [H^+]$ formula.

$pH = -\log_{10} [1.3 \times 10^{-3}] = 2.9$

<u>Finding the $[H^+]$ from pH</u>

To find the $[H^+]$ from pH is fairly simple.

Example

Acid raid has a pH of 3.4. What is the $[H^+]$?

Start by using the equation for finding pH from $[H^+]$

pH = -log10 [H^+] and substitute in the values known.

3.4 = -log10 [H+].

Change the sign for the pH and log value

-3.4 = log[H^+]

Re-arrange to leave [H^+] by itself

log – 3.4 = [H^+]

Simple enough. However this cannot be done on a calculator. On a calculator the "anti-log" needs to be taken. This is usually found by pressing "shift" then "log". It is sometimes written as 10^x.

When using the calculator, remember to use "–" before the pH value

shift	log	-	3.4	=	3.39×10^{-4} mol dm^{-3}.

Dissociation

To dissociate means to break apart.

When the acid goes into solution, it forms two ions; H^+ and the anionic part (usually just called A^- for ease). Depending on the strength of the acid, the acid will have a greater or lesser amount of dissociation. As the acid has these two ions, it is commonly written as just [HA]. This is an accepted shortened way of writing any form of acid.

Dissociation constant

This is a number which shows how much an acid dissociates by. The larger the number, the greater the amount the acid breaks apart (this is known as the degree of dissociation). The dissociation constant has a symbol – Ka

Strong acids completely dissociate. The likes of HCl and HNO_3 have Ka values of 1.3×10^6 and 2.4×10^1 respectively; in other words [H^+] = [HA].

For weak acids, Ka values are of more use.

Ka is normally seen written as $\mathrm{Ka} = \frac{[\mathrm{H}^+][\mathrm{A}^-]}{[\mathrm{HA}]}$ and has the units mol dm^{-3}.

Take the reaction when ethanoic acid (CH_3COOH) is dissolved in water. An equilibrium forms very quickly:

$$[CH_3COOH]_{(aq)} \rightleftharpoons [CH_3COO^-]_{(aq)} + [H^+]_{(aq)}$$

The equilibrium is over towards the starting materials rather than dissociated products.

The Ka for this reaction will be

$$Ka = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

From the original reaction, it can be seen that for every mole of acid, 1 mole of CH_3COO^- and 1 mole of H^+ are produced. There are two reasonable assumptions which can be made from the Ka and equilibrium equations

1. The concentration of $[A^-]$ = the concentration of $[H^+]$. This can simplify the equation for Ka to be just $Ka = \frac{[H^+]^2}{[HA]}$.

2. The concentration of $[H^+]$ will be greatly less than that of the undissociated acid.

<u>Using the Ka value to find a pH</u>

The pH of an acid cannot be directly found from a Ka value as to find a pH, the [H+] must be known. To find this is very simple.

Typically, a Ka value will be given (though this may not always be the case) and the concentration of the acid. Remember, the concentration of the acid will **<u>NOT</u>** be the concentration of $[H^+]$ - do not get the two confused!!!!

Example

A weak acid, HA (0.1 mol dm^{-3}, Ka = 3.1 x 10^{-3} mol dm^{-3}) is dissolved in water. What is the pH of the solution?

First write the equation for Ka

$$Ka = \frac{[H^+][A^-]}{[HA]} \text{ or } Ka = \frac{[H^+]^2}{[HA]}$$

Substitute in the numbers given in the question

$$3.1 \times 10^{-3} = \frac{[H^+]^2}{0.1}$$

The final step is to re-arrange the equation to leave just $[H^+]$. Remember, to remove a square, take the square root

$$\sqrt{3.1 \times 10^{-3} \times 0.1} = [H^+]$$
$$[H^+] = 0.0176 \text{ mol dm}^{-3}$$

As a quick check, remember that $[H^+]$ will be less than [HA], which can be seen here (it is roughly 1/10th the concentration)

Next, convert $[H^+]$ to pH using pH = $-\log_{10}[H^+]$

$$pH = -\log_{10} [0.0176] = 1.8$$

The value of using Ka over pH

As has been seen, pH is a scale which relies purely on the amount of $[H^+]$ present. If a strong acid has a low enough concentration, it will have a pH much higher than expected (e.g. a solution of 0.001 mol dm^{-3} HCl has a pH of 3 instead of pH 1 for 0.1 mol dm^{-3}). A weak acid with a high enough concentration will have a much lower pH than expected (e.g. a solution of 1 mol dm^{-3} CH_3COOH has a pH of 2, roughly that of phosphoric acid).

This can be confusing as it gives no indication of the strength of the acid.

Ka uses all of the components of the equilibrium. As the concentration of acid changes, the concentration of $[H^+]$ and $[A^-]$ will change by the same amount. The value for Ka always remains the same so is an excellent way of telling how strong an acid is.

pKa

It can be hard to tell how weak an acid is by looking just at the Ka values. Phenol, for example, is a very weak acid ($Ka = 1.2882 \times 10^{-10}$). On the pH scale, it is about 9.4 (which would make it alkaline). The problem is that the weaker the acid, the bigger the $x10^{-x}$ number becomes and unfortunately, after a certain point the brain cannot understand such tiny numbers.

To get around this problem, the pKa scale is used. This goes between 2 and 12 and is much simpler to understand (the weaker the acid, the closer to 12 it is – phenol has a pKa value of 9.89).

Relationship between pKa and Ka

The relationship between the two is given by

$$pKa = -\log_{10} Ka$$

It is quite usual for books and websites to give dissociation values for weak acids in terms of pKa as they are much easier to understand and give an instant idea of how weak the acid is.

As with finding the $[H^+]$ value from a pH, a Ka value can be found from a pKa in exactly the same way by using the antilog of the negative pKa

Example

2-chlorophenol has a pKa of 8.49. What is it's Ka?

First write the relationship equation

$pKa = -\log_{10} Ka$

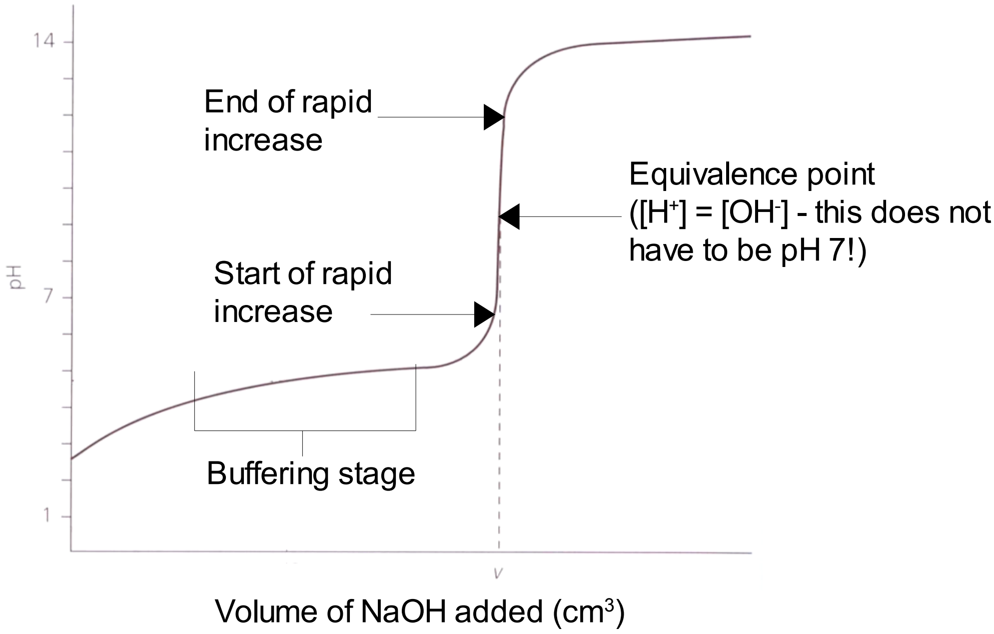
On the calculator

shift	log	-	8.49	=

3.2359×10^{-9} mol dm^{-3} = Ka.

<u>Finding the pKa from a graph</u>

A pKa can be found from most acid/base reactions. In a reaction between HCl and NaOH (a strong acid and strong base), as more NaOH is added to the HCl, the more the pH changes. When plotted, it looks like this

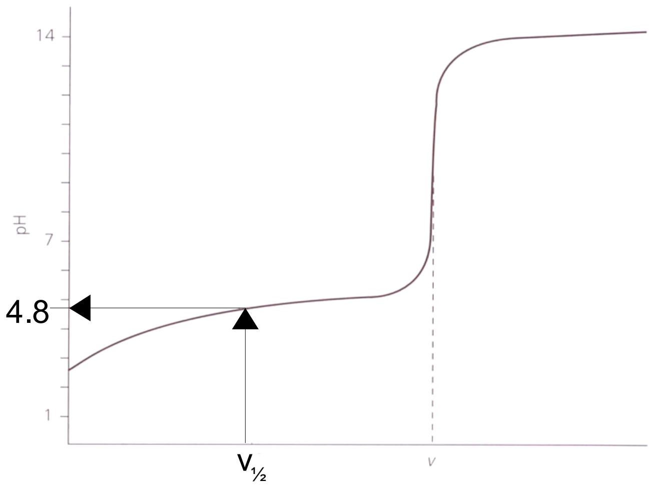


At the start, there is 100% acid. As more base is added, the pH increases slowly (the buffering stage) before rapidly increasing.

If the point at which the rapid increase starts and finishes is measured and the mid-point found (the equivalence point), it is possible to find the volume of base required by dropping a line down to the x axis. This is called “v”.

The next stage is to divide v by 2 (known as $v_{½}$) and find that point on the x axis.

The final stage is to draw a line from $v_{½}$ to the line on the graph and over to the y axis. The pH value at that point is the pKa value.



Buffers

A buffer is something which **slows** the progress of a reaction.

Take the reaction of $NaOH_{(aq)}$ and $HCl_{(aq)}$.

At the start of the reaction, there is 100% HCl. HCl is a strong acid, so dissociates to form H^+ and Cl^-. 1cm^3 of NaOH is added. NaOH is a strong base, so dissociates completely to form Na^+ and OH^-.

The Na^+ reacts with Cl^- to form NaCl with the OH^- reacting with H^+ to form water. As NaCl is an ionic solid, it will break up again to form Na^+ and Cl^-. However, the water does not break up. The pH goes up slightly.

This breaking up and formation of H_2O carries on for a while with only small increases in the pH.

During this stage, buffering takes place. NaCl is formed – this is called the "salt of the acid".

After the buffering stage, the amount of OH^- produced by the dissociation of NaOH is greater than the amount of H^+ available from the dissociation of the acid and so the pH begins to rise rapidly.

Calculating the pH of a buffer

A buffer solution is made up of the acid and the salt of the acid (*for example, ethanoic acid and sodium ethanoate*). This will have a particular pH.

The salt of the acid will completely dissociate when in solution

$$[CH_3COONa]_{(aq)} \rightarrow [CH_3COO^-]_{(aq)}\ [Na^+]_{(aq)}$$

The concentration of the anionic part (CH_3COO^-) can be said to be the same as the concentration of the salt (*this is the same as for a strong acid, the $[H^+] = [HA]$*).

The weak acid will only partially dissociate in water

$$[CH_3COOH]_{(aq)} \rightleftharpoons [CH_3COO^-]_{(aq)} + [H^+]_{(aq)}$$

Here the $[H^+]$ will be much less than that of the undissociated acid. The weak acid will also have either a pKa or Ka value.

$$\mathrm{Ka} = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

As the buffer is a mixture of the salt and the acid, the $[CH_3COO^-]$ from the salt replaces that of the acid

$$\mathrm{Ka} = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

The $[H^+]$ can then be found by rearranging the formula. In effect, it will become

$$[H^+] = \mathrm{Ka} \times \frac{[\mathrm{acid}]}{[\mathrm{base}]}$$

From this, the pH can be found.

Example

Calculate the pH of a buffer solution made by dissolving 18.5g propanoic acid (C_2H_5COOH, pKa = 4.87) and 12g of sodium propanoate (C_2H_5COONa) in water and making up to a final volume of 250cm^3.

The formula for the buffer, $[H^+] = \mathrm{Ka} \times \frac{[\mathrm{acid}]}{[\mathrm{base}]}$ requires the acid and base concentrations rather than the masses. The first step is to convert the masses into number of moles.

C_2H_5COOH = 74g mol^{-1}, C_2H_5COONa = 96g mol^{-1}.

In 250cm^3, there will be $\frac{18.5}{74}$ moles of acid = 0.25 and $\frac{12}{96}$ moles of salt = 0.125

The question says that the final volume is 250cm^3. The standard unit for volume is the dm^3. As 250cm^3 is ¼ of a dm^3, multiply the answer by 4 to give the number of moles in a dm^3.

Acid = 0.25 mol in 250cm^3 = 0.25 x 4 = 1.0 mol dm^{-3}
Salt = 0.125 mol in 250cm^3 = 0.125 x 4 = 0.5 mol dm^{-3}

The pKa is known, so by taking the antilog the Ka can be found = 1.3490 x 10^{-5} mol dm^{-3}.

Put the numbers into the formula to find $[H^+]$

$$[H^+] = 1.3490 \times 10^{-5} \times \frac{1}{0.5} = 2.6980 \times 10^{-5}$$

Using the equation to find the pH from $[H^+]$, $pH = -\log_{10} [H^+]$,

$pH = -\log_{10} [2.6980 \times 10^{-5}] = 4.6$