

## A Second Year blog on Acids and Bases: Part 1, 23rd March 2019

(This is a **revision** blog. It is merely a *summary* of some of the things that you need to know. *Everything in this blog can be found in the relevant Chapters of the Book.*)

Generally speaking, an acid can be defined according to three different descriptions

- The Arrhenius description  
where an Acid reacts with a Base to generate Water and a spectator salt
- the Brønsted–Lowry description  
where an Acid is a proton donor, and a Base is a proton acceptor
- the Lewis description  
where an Acid is a lone pair acceptor and a Base is a lone pair donor.

**Please could you remember that a proton ( $H^+$ ) **cannot exist on its own in Water.** It has such a huge charge density that it grabs hold of the nearest molecule of Water and *temporarily* bonds to it via one of the two lone or unbonded pairs of electrons on the O atom in the Water molecule viz. in Water, an  $H^+$  (aq) species is always piggy-backed on a molecule of Water surrounded by other molecules of Water viz.  $H_3O^+$ (aq) – and in modern Chemistry in Britain we depict this situation as  $H^+$ (aq). An  $H_3O^+$ (aq) species is called an “**hydronium**” ion (and it used to be called the “hydroxonium” ion).**

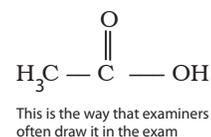
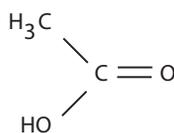
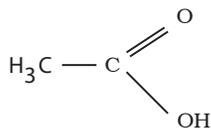
An Acid can thus be described as something that

- dissociates protons ( $H^+$  species)
- often reacts with a base to form WATER and ionic salts ( $H^+ + OH^- \rightarrow H_2O$ ), but
- **any** proton donor is an acid and **any** proton acceptor is a base (some acid/base reactions do not form water therefore the formation of water is not an *essential* component of an acid-base reaction)
- a compound/a substance that is an acid (and the generic form of an acid is written as “HA”) will have a cationic species that consists of a dissociable  $H^+$ , and also an anionic species ( $A^-$ ) that can accept a proton
- a *dilute* acid is one that has been diluted with water and this should not be confused with
- a **weak acid** which when it dissociates its protons reaches a position of dynamic equilibrium when only a relatively small proportion of its protons have been dissociated, whereas
- a **strong acid** is one which when it dissociates its protons reaches a position of dynamic equilibrium when all or very nearly all of its protons have been dissociated – and a *very strong* acid is one where the dissociation goes to completion and there are no or virtually no non-dissociated protons left and where the reaction cannot be reversed (because the ions are fully separated by/surrounded by water molecules)
- a strong acid will often be associated with a weak conjugate base and a weak acid will often be associated with a strong conjugate base, and
- it does not matter whether an acid is strong or weak, so long as there is something that is absorbing/reacting with the protons that are being dissociated, then the acidic substance will keep on dissociating its protons **until there are no more protons left to dissociate**, and finally
- in its most general sense, a base can be considered to be a lone pair donor (this being the contribution of the great Gilbert Lewis), and thus **in Organic Chemistry a nucleophile is a Lewis base.**

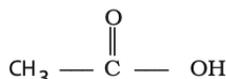
Equally, when a Carboxylic Acid is dissolved in Water it will dissociate a proton onto a water molecule to form  $H_3O^+$ (aq) or  $H^+$ (aq) (just as an Inorganic acid does), and this will react

- with some metals to produce  $H_2$ (g)
  - with  $CaCO_3$ (s) to produce  $CO_2$ (g) and  $H_2O$ (l), and
  - with an Hydroxide to produce Water plus a salt
- etc.

A Carboxylic Acid fits neatly with all these descriptions, where the “Carboxylic” bit means that the acids are Carbon based species. There are many ways to draw a Carboxylic Acid, and here are three ways for drawing Ethanoic Acid.



Technically speaking, in bond line diagrams, the methyl/ethyl/propyl/etc species should be *drawn* with the **Carbon atom next to the bond line** – but many scientists do not do so, and they (legitimately) draw the bond line diagram as follows. **(NB The “–COOH” bit is the characteristic of a Carboxylic Acid.)**



or this could be written as “**R–COOH**”.

Functionally a Carboxylic Acid is the same as a non-Carboxylic Acid. The main difference between a non-Carboxylic Acid and a Carboxylic Acid is that **most** Carboxylic Acids are weak acids. Let us therefore look at this aspect of Carboxylic Acids.

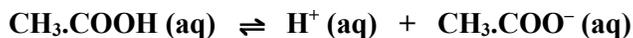
There may be some of you who are not doing ‘A’ Level Maths, and there may be others who are doing ‘A’ Level Maths but who are (as yet) not comfortable with the Maths in ‘A’ Level Chemistry. To talk about Acids, I need **ALL of you** to be at the same starting point – therefore I am going to remind you of a number of things.

### The strength of an Acid

In Brønsted–Lowry terms an acid is a species that dissociates protons, and a strong acid is one that dissociates all or virtually all of its protons (viz. Hydrochloric Acid, Nitric Acid, Sulfuric Acid, Hydrobromic Acid, Hydroiodic Acid, Perchloric Acid, and Chloric Acid) so much so that the reaction with water can be written as a **reaction to completion** e.g.



whereas a weak acid is one that is formed as a result of a reversible reaction where the position of dynamic equilibrium lies very far to the left (viz. dynamic equilibrium is reached when only a very small proportion of the available protons has been dissociated) and it is written e.g.

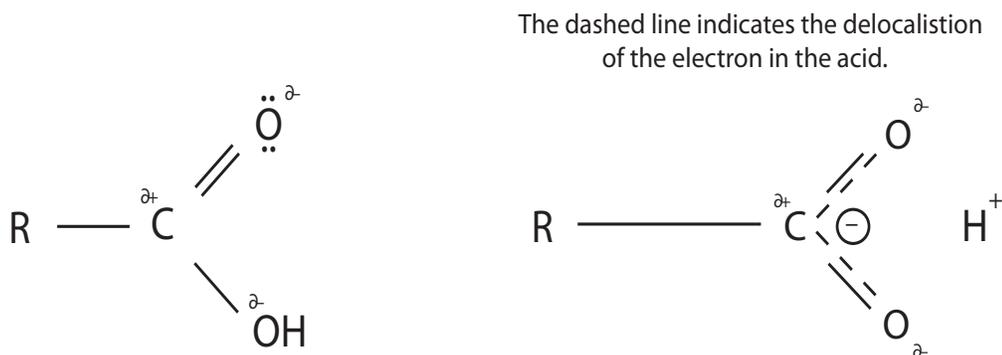


The way that your understanding of this will be tested in the exams is to ask you about relative strengths of acids.

- i) You could be given the  $\text{pK}_a$  value of different acids, and then asked why they have  $\text{pK}_a$  values of that *relative* magnitude, or
- ii) you could be asked to list some acids that you have been given in the order of the strength of the acids

and the answer that the examiners are looking for is almost always in terms of the **increase** in electron density or the **reduction** in electron density that is created in the “ $-\text{CO}^{\delta-}-\text{O}^{\delta-}$ ” bit of the acids involved (the area enclosed by the dashed lines in the right hand diagram below).

## Two of the Resonance forms of a Carboxylic Acid



The greater the electron density that there is in the “ $-\text{CO}^{\delta-}-\text{O}^{\delta-}$ ” area, then the more tightly will the  $\text{H}^+$  be held, **and the harder will it then be for the  $\text{H}^+$  proton to be dissociated.**

The most common species that **PUSHES** electron density onto another species is the **Alkyl Group** (i.e.  $-\text{C}_n\text{H}_{2n+1}$ ), whereas there are many species that ‘suck’ electron density off other species – and this is nearly always determined by a differential in electronegativity. **A more electronegative species will always PULL electron density off a less electronegative species** (that being the definition of electronegativity).

The factors that will affect the pushing or the pulling of electron density will thus be (i) the Inductive effect (based on electronegativity), and (ii) the M effect. In the 12<sup>th</sup> of January blog I told you about species that push electron density onto another species and species that pull electron density off other species – therefore **please read that blog again.**

A **strong** acid is one that dissociates all or nearly all of its protons, and anything that increases the electron density in the “ $-\text{COOH}$ ” part of a Carboxylic Acid **will cause the  $\text{H}^+$  proton in “ $-\text{COOH}$ ” to be held more tightly** and this will reduce the tendency of the acid to dissociate its protons and it will thus become a **weaker** acid.

In contrast, anything that reduces the electron density in the “ $-\text{COOH}$ ” part of a Carboxylic Acid will cause the  $\text{H}^+$  proton in “ $-\text{COOH}$ ” to be held less tightly, and this will increase the tendency of the acid to dissociate its protons and it will thus become a stronger acid.

**The more the electron density in the “ $-\text{COOH}$ ” bit, the more tightly will the  $\text{H}^+$  proton be held!**

**By definition, the MORE protons that an acid dissociates, the STRONGER it is as an acid and the lower will its pH value be. (At ‘A’ Level it is good enough to say that a strong acid will have a pH of 0-3, and if it is a highly concentrated acid then its pH value could even be *negative*.)**

## Dissociation of Pure Water to give a pH of 7

The RMM or  $M_r$  of Water is  $[(2 \times 1) + (1 \times 16.0) = ] 18 \text{ gmol}^{-1}$ , therefore  
18g of Water make up 1 mole of Water (cf. footnote<sup>1</sup>), therefore  
1000g of Water or **1dm<sup>3</sup> of Water** has  $(1 \text{ mole} \times 1000\text{g} \div 18\text{g}) = 55.55555$  moles of H<sub>2</sub>O molecules in it.

By experimentation, scientists have established that at a temperature of 298K, 1 dm<sup>3</sup> of pure Water contains  $1 \times 10^{-7}$  moles of H<sup>+</sup> ions and (since the stoichiometric ratio of H<sub>2</sub>O (l)  $\rightleftharpoons$  H<sup>+</sup> (aq) + OH<sup>-</sup> (aq) is 1 : 1 : 1) there are therefore also  $1 \times 10^{-7}$  moles of OH<sup>-</sup> ions in 1 dm<sup>3</sup> of Water at 298K.

If at 298K there are  **$1 \times 10^{-7}$  moles of H<sup>+</sup> ions in 1dm<sup>3</sup> of pure Water**, then  $[\text{H}^+] = 1 \times 10^{-7}$ , and since  $\text{pH} = -\log_{10}([\text{H}^+])$ , then the pH of pure Water =  $-\log_{10}(1 \times 10^{-7}) = 7.0$ , but remember that this is true **only** at 298K. As the temperature rises, Le Chatelier's Law says that the dynamic equilibrium will shift to the RIGHT therefore there will be **more** protons in the mixture, therefore the  $K_a$  will **get larger** and the **pH will decrease** but the Water still remains neutral because there are just as many OH<sup>-</sup> ions in the Water as there are H<sup>+</sup> ions.

If you see the above expressed in  $K_w$  rather than  $K_a$ , then do not be put off by that. At 298K, you might see it given as  
just remember that  $K_w = 1.008 \times 10^{-14}$  instead of  $[\text{H}^+] = 1 \times 10^{-7}$ , but  
 $K_w = [\text{H}^+].[\text{OH}^-]$  and  $[\text{H}^+] = [\text{OH}^-]$  therefore  $[\text{H}^+] = \sqrt{K_w}$

therefore to get  $[\text{H}^+]$  take the square root of  $K_w$  and then to get the pH take  $-\log_{10}([\text{H}^+])$ .

$$\sqrt{K_w} = \sqrt{(1.008 \times 10^{-14})} \approx 1 \times 10^{-7} \quad \text{and} \quad -\log_{10}(1 \times 10^{-7}) = 7.0$$

NB  $[(1 \times 10^{-7}) \div 55.6] \times 100 \% = 0.000,000,18\%$  of **Water** is thus ionised into H<sup>+</sup> and OH<sup>-</sup> ions – therefore a truly **TINY** amount of Water is ever ionised. We define acidic substances as those having a pH value of less than 7 at 298K, and those with pH values of more than 7 at 298K are called bases, and “neutral” Water has a pH value of 7 at 298K (**and only at 298K**). **As Water gets hotter, its pH value declines but it still remains neutral.**

Pure Water is defined as “neutral”, even though it has both  $1 \times 10^{-7}$  moles of H<sup>+</sup> ions and  $1 \times 10^{-7}$  moles of OH<sup>-</sup> ions in it at 298K, and it is “neutral” because the number of H<sup>+</sup> ions is exactly equal to the number of OH<sup>-</sup> ions, and these ions cancel out the effect of each other. **At a different temperature there would be a different number of H<sup>+</sup> and OH<sup>-</sup> ions in one mole of Water, and Water would thus have a different pH value at a different temperature – but it would still be neutral. At 100°C the pH of Water is 6.14 but it is still NEUTRAL because  $[\text{H}^+] = [\text{OH}^-]$ .**

## **Amphoteric species**

A species that can either dissociate a proton or accept a proton is called “amphoteric” (or “amphiprotic”). Examples of amphoteric species are

- a) **Water**, where  $\text{H}_2\text{O} + \text{H}^+ \longrightarrow \text{H}^+(\text{aq})$  or  $\text{H}_2\text{O} \longrightarrow \text{H}^+ + \text{OH}^-$   
b) **Dihydrogen phosphate**  $\text{H}_2\text{PO}_4^- \longrightarrow \text{H}^+ + \text{HPO}_4^{2-}$  or  $\text{H}_2\text{PO}_4^- + \text{H}^+ \longrightarrow \text{H}_3\text{PO}_4$   
and you can make up many examples for yourself.

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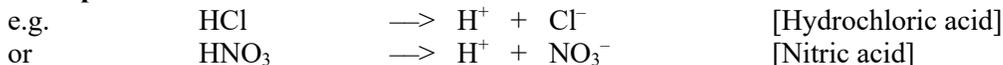
<sup>1</sup> RMM of H<sub>2</sub>O  $\approx (2 \times 1) + 16 = 18 \text{ gmol}^{-1}$ .

## Classifications of Acids

### **Mono- / di- / and triprotic Acids**

An acid may dissociate some or all of its protons. If it dissociates one proton it is called monobasic or monoprotic, if it dissociates two protons it is called dibasic or diprotic, if it dissociates three protons it is called tribasic or triprotic, ....., and so on. (However, I prefer the term “....protic” rather than “.....basic”.) We thus get

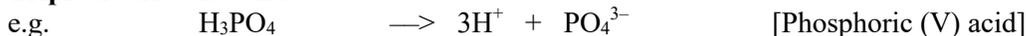
#### **Monoprotic/monobasic acids**



#### **Diprotic/dibasic acids**



#### **Triprotic/tribasic acids**



### **Anionic/neutral/and cationic acids**

You do not often see the following nomenclature, but just in case you come across it, here it is: a Brønsted–Lowry acid is anything that dissociates a proton therefore you can classify acids as

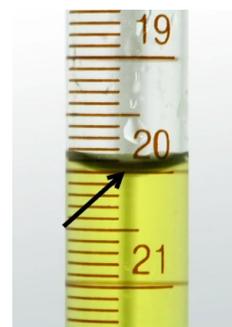
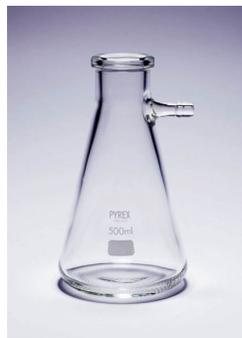
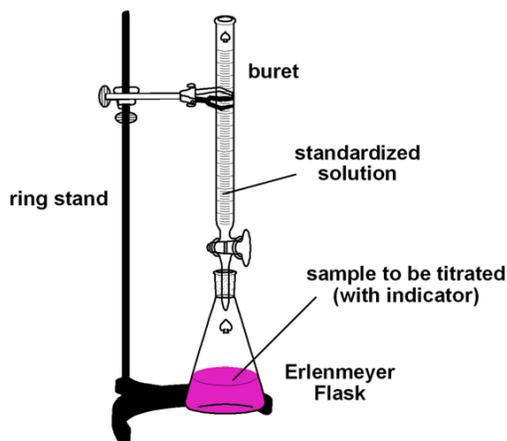
- An **anionic** acid: one that has a negative charge (such as HSO<sub>4</sub><sup>-</sup>) and dissociates a proton.
- A **neutral** acid: one that has no charge (most acids and even Water) and dissociates a proton.
- A **cationic** acid: one that has a positive charge (e.g. NH<sub>4</sub><sup>+</sup>) and dissociates a proton.

If you were to titrate ammonia solution (a weak base) with hydrochloric acid (a strong acid), ammonium chloride would be formed. The ammonium (NH<sub>4</sub><sup>+</sup>) ion is slightly acidic (it has a proton that it can dissociate in the right circumstances), and so pure ammonium chloride has a pH of slightly less than 7.

Equally, if you were to titrate Sodium Hydroxide solution (a strong base) with Ethanoic Acid, then at the Equivalence Point the pure Sodium Ethanoate (NaCH<sub>3</sub>COO) formed has a slightly alkaline pH (of > 7) because the lone pairs of electrons in the Oxygen atoms in the COO<sup>-</sup> species in the Ethanoate ion make it slightly basic (it has a small tendency to donate lone pairs of electrons and/or accept protons onto those lone pairs of electrons). **NB You cannot donate any of the Hs in the “CH<sub>3</sub>–” bit. If you did, then that would stop the molecule being Ethanoic Acid or Sodium Ethanoate. The proton (*singular*) from the acid CH<sub>3</sub>COOH molecule must come from the “–COOH” bit. It is the “–COOH” bit that is the acid part of CH<sub>3</sub>COOH, and it is the lone pairs of electrons in the NaCH<sub>3</sub>COO that make it a base.**

However, in the UK you will not see acids classified in this manner very often.

Let me remind you of the set-up of for a burette/conical flask/clamp/etc. (The diagram below is from Sachi's Acids and Bases.) In England a burette is spelt differently from that below.



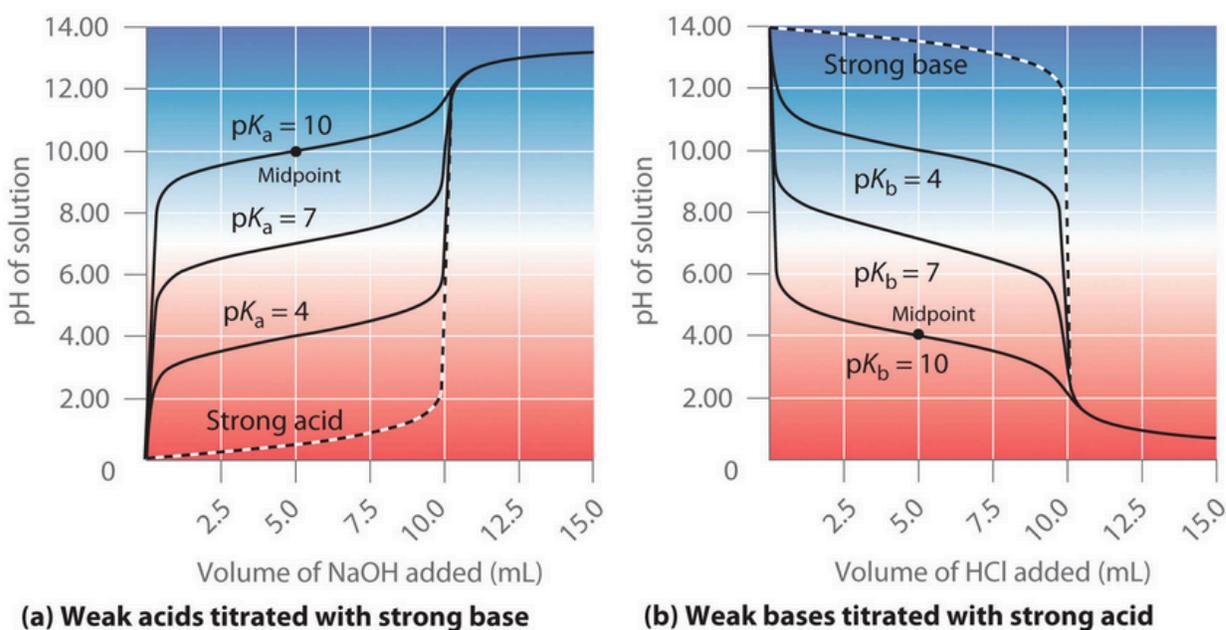
An “Erlenmeyer” flask is just a name for a conical flask.

If you see a conical flask with a tube in the neck of the flask, then it is one that can be used to create a vacuum in the flask to speed up *filtration*. It is called a **Büchner** flask/vacuum flask/filtration flask. **You should not use a vacuum flask for titration. You could break the little protruding tube at the neck of the flask when you are swirling the flask and then you will cut yourself.**

Please take your readings from the bottom of the meniscus (as in the right hand diagram above).

Let me make a point about the shapes of titration graphs. The *exact* location of the titration curve on a titration graph for a weak acid or a weak base will depend on its  $pK_a$  or its  $pK_b$  value. You can see that on the graphs overleaf. Just look at how the shape of the curve changes when the strength of the acid (described by its  $pK_a$  value) or base (described by its  $pK_b$  value) changes. In the graph on the left, you are starting with an acid into which you are adding a strong alkali/base (NaOH). If the acid is a strong one (e.g. HCl) then you get the dotted line, but with weak acid or weak bases you get different weak acid/weak base curves.

The volumes on the x-axis in the graphs here are for our purposes arbitrary because the volumes needed would change according to the concentrations of the NaOH used in (a) and the concentrations of the HCl used in (b).



Source: Chemistry LibreTexts 15.6: Acid-Base Titration Curves

The examiners do ask questions about the **shapes** of titration curves e.g. Question 12 from the Edexcel paper (6CH04\_01\_rms\_20160817) of 2016.

**We are now literally a few weeks away from the exams and, if you are not 100% confident about the calculations involved, it would pay you to read Year 2, Inorganic Chemistry over the Easter hols. (in fact revise everything over the Easter hols – and for all your subjects!)**

The best piece of advice that I can offer you is to dig a big hole in your garden, put your mobile phone in it, cover the hole in and do not get your phone out until all your exams are over. You are coming up to the first **MAJOR** exams in your life. **Work morning noon and night for the next few weeks.** Getting into the University of your (first) choice is fiercely competitive. You cannot walk into Oxford/Cambridge/Imperial/wherever. **Everybody wants to get into one of the best Universities. You are not the only person in the world who wants to get the best start in life. Remember, in this country we still have some of the best Universities in the WHOLE WORLD and you will be competing not just with other students from this country – but with other students from all over the world.** Remember also that an overseas student pays more than twice as much in fees than you do. If you were the admissions Tutor for a world-class University, whom would you be tempted to admit – someone who would pay £22,000 pa in fees, or someone who would pay £9,000 pa?

I shall talk about ICE tables next week.