

## Second Year blog on Ionic Product of Water Constant: 25<sup>th</sup> May 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 two books.)

**The Acid Dissociation Constant is  $K_a$ , and the Base Dissociation Constant is  $K_b$ .  $K_w = K_a \times K_b$  .**

- In Chapter 5A, I showed you the detailed calculations that you would need to perform to calculate the changing value of a pH during a titration of
  - a Strong Acid against a Strong Base
  - a Weak Acid against a Strong Base
  - a Strong Acid against a Weak Base, and
  - a Weak Acid against a Weak Base

Please make sure that you have mastered the calculations involved, and I remind you on the next page of the rules/the signposts involved in doing such calculations. Here we will discuss the last of the Equilibrium Constants that you are required to know for 'A' Level purposes viz. The Equilibrium Ionic Product of Water Constant ( $K_w$ ) for the reversible reaction  $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$  when it is at a position of dynamic equilibrium. For the reversible reaction (for a temperature of 298K/25°C)  $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$  at a position of dynamic equilibrium, these are the equations that you need to memorise.

•  $K_w = 1 \times 10^{-14}$  **Equation 1** and by taking the log of each side

$-\log_{10}(K_w) = -\log_{10}(1 \times 10^{-14}) = 14.0$  **Equation 2**

•  $K_a \times K_b = K_w = 1 \times 10^{-14}$  **Equation 3** and  $K_a = \frac{1 \times 10^{-14}}{K_b}$  and  $K_b = \frac{1 \times 10^{-14}}{K_a}$

• From  $\text{H}_2\text{O}(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq})$  it follows that  $K_c = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$  and therefore  $K_c \cdot [\text{H}_2\text{O}] = K_w = [\text{H}^+][\text{OH}^-]$  and since the mole reaction ratio is 1 : 1 : 1,  $[\text{H}^+] = [\text{OH}^-]$

$K_w = [\text{H}^+]^2 = [\text{OH}^-]^2 = 1 \times 10^{-14}$  **Equation 4** therefore

•  $[\text{H}^+] = \sqrt{(1 \times 10^{-14})} = 1 \times 10^{-7}$  **Equation 5**

The above tells you that the concentration of  $\text{H}^+$  ions in pure Water at 298K is "1 x 10<sup>-7</sup>", and since  $[\text{H}^+] = [\text{OH}^-]$ , then it must also be true that  $[\text{OH}^-] = "1 \times 10^{-7}"$ . From this it follows that

•  $-\log_{10}([\text{H}^+]) = \text{pH} = 7.0$  **Equation 6** and since  $[\text{H}^+] = [\text{OH}^-]$

•  $-\log_{10}([\text{OH}^-]) = \text{pOH} = 7.0$  **Equation 7**

which is why we are able to say that the pH of pure Water is "7.0" at 298K, and pure Water is "neutral" because there are exactly as many  $\text{H}^+$  ions in it as there are  $\text{OH}^-$  ions in it.

•  $\text{pH} + \text{pOH} = 14.0$  **Equation 8.**

Equation 8 can be derived more simply by saying that  $K_w = [\text{H}^+][\text{OH}^-]$ , therefore if we take the log of both sides of the equation, then we get  $-\log_{10}(K_w) = -\log_{10}([\text{H}^+] + -\log_{10}([\text{OH}^-])$  and since  $-\log_{10}(K_w) = -\log_{10}(1 \times 10^{-14}) = 14.0$ , this is equivalent to saying  $\text{p}K_w = \text{pH} + \text{pOH} = 14.0$ .

• **Please MEMORISE these equations.**

• **In an exam you do NOT want to waste time trying to remember them.**

### These are the rules/'signposts' that you need when dealing with Weak Acids and Weak Bases

- 1) The p of X =  $-\log_{10}(\text{the concentration of X})$ , therefore the **pH of a solution =  $-\log_{10}([\text{H}^+])$** , but
- 2) for a base please remember you will need to calculate the pOH first and then use the equation **pH = 14.0 - pOH**.
- 3) Concentration = Number of moles  $\div$  Volume of the solution, or **C = N  $\div$  V in dm<sup>3</sup>**
- 4) If you are dealing with a Weak Acid or a Weak Base, then you **MUST** use an ICE/RICE table. (*I prefer to call them RICE tables where the "R" stand for Reaction Equation, but the accepted name is an "ICE" table.*)
- 5) For reversible reactions that are at dynamic equilibrium at a given temperature,  $K_a$  and  $K_b$  are all about concentrations (raised to the power of their stoichiometric ratios). You must therefore construct an ICE/RICE table for **concentrations** (or for moles which you must then divide by volumes). **Your answer will therefore be wrong if you forget to put your Water in the reversible reaction equation** (because you must divide the moles by the same number of volumes on each side of the reversible reaction equation).
- 6) Please remember that in an ICE/RICE table you **ignore the change** in  $[\text{H}_2\text{O}]$ .  $[\text{H}_2\text{O}]$  is very small ( $K_w = 1 \times 10^{-14}$ ) and you can thus ignore  $\Delta[\text{H}_2\text{O}]$ . **However, we are not ignoring the "[H<sub>2</sub>O] = 1.0"**. We **cannot** ignore the "1.0" because then we would have two lots of the volume as the DIVISOR on one side of an equation and only one lot of volume on the other side – and then ALL the calculations thereafter would be wrong.  $K_a$  and  $K_b$  are about **concentrations**, and **C = N  $\div$  V**.
- 7) Therefore, in a titration, keep track of the number of moles of the Titrant that you are adding to the Analyte, **and** keep track of your volumes (because  $K_a$  and  $K_b$  are all about **concentrations**).
- 8) If the unknown variable in an ICE/RICE table is designated as "z", then you **can** resolve the value of "z" by using a *quadratic equation* – but that will involve you in a fair amount of number crunching and (usually) it will **not** make much difference to the value of the pH that eventually emerges. In the **vast** majority of cases, when solving for the value of "z<sup>2</sup>" you can ignore any numbers that involve "-z" or "+z", **but you cannot ignore any numbers that involve "times z" and " $\div$  z"**. Not using a quadratic equation makes the arithmetic much easier, and doing so makes no difference to the final value of the pH (which is normally given to just ONE decimal place anyway).
- 9)  **$K_a \cdot K_b = K_w = 1 \times 10^{-14}$** , and taking the log of both sides of the equation,  **$\text{p}K_a + \text{p}K_b = 14.0$** .
- 10) It is also true that **pH + pOH = 14.0**.
- 11) A titration curve is 'S-shaped' and it has three parts to it
  - one third is where either the acid or the base is being neutralised (i.e. if it is an acid/base titration)
  - a central point where the two reacting substances (the titrant and the analyte) have exactly reacted with each other, and this point is called the Equivalence Point, and
  - the last bit, where the **concentration** of the Titrant (which is being dripped from the burette into the conical flask), *as measured in the conical flask* is getting larger and larger.
- 12) When dealing with either a Weak Acid or a Weak Base, then by the very definition of "weakness" you are involved in reactions that reach a position of dynamic equilibrium when only a small proportion of their "acidity" or their "basicity" has been released and, to calculate your pH values, you must then use the Henderson-Hasselbalch equation (cf. Chapter 9 of the Year 2 Inorganic book) which for a Weak Acid "HA  $\rightleftharpoons$  H<sup>+</sup> + A<sup>-</sup>" says

$$\text{pH} = \text{p}K_a + \log_{10} \left\{ \frac{[\text{A}^-(\text{aq})]}{[\text{HA}(\text{aq})]} \right\} \frac{\text{Concentration of the SALT}}{\text{Concentration of the ACID}}$$

- 13) **Whenever you add a Weak Acid to Water you get H<sup>+</sup> ions, and when you add a Weak Base to Water you get OH<sup>-</sup> ions.**

- Incidentally, at half the volume of the volume at the equivalence point, the pH of a Weak Acid is equal to its  $pK_a$ . This stems from an analysis of the mid-point of the Henderson-Hasselbalch equation.
- When we talk about the strength of an acid we refer to how much of its dissociable protons the acid has dissociated at equilibrium at a given temperature viz. we are concerned with the concentration of hydrogen ions in the aqueous solution of the acid at equilibrium at a given temperature. We also saw that the value of  $K_a$  for acids can range from very large numbers to **very** small ones and that (i) this range of numbers cannot be accommodated easily in an ordinary *arithmetic* range and a log range is more appropriate, and (ii) that although a numerical value for  $K_a$  can be calculated for acids that dissociate almost all of their Hydrogen ions, nevertheless such a numerical number has no worth because  $K_a$  **is NOT constant for fully dissociated strong acids** and  $[H^+]$  alters with the concentration of the acid (whereas  $K_a$  is a constant for Weak Acids).
- As we saw in Chapter 5, the pH of any fully dissociable acid will be negative once its concentration is larger than  $1 \text{ mol dm}^{-3}$ , and this is precisely why the pH of an acid is not a *perfect* measure of its strength. **The measure of the strength of an acid should NOT vary according to its concentration** and unfortunately the value of a pH does vary according to the concentration involved. Even so, the invention of the pH index by Sørensen was a hugely important one because the pH index (despite its one minor fault) is a massively *convenient* one. **What Sørensen invented was not so much the pH of an acid, but an index of the concentration of  $H^+$  ions in a solution irrespective of what the acid is.** In this Chapter we will talk about the pH of pure Water.

### The pH of pure water

- We have seen in previous Chapters that pure Water dissociates a tiny proportion of its water molecules into  $H^+$  ions and  $OH^-$  ions<sup>1</sup>, and from an inspection of the Periodic Table we can calculate that
 

1 mole of Water	has a mass of	18.0g, therefore	
X moles	.....	1000.0g	(cf. footnote <sup>2</sup> )
where $X = (1 \text{ mol} \times 1000.0 \text{ g}) \div 18.0 \text{ g} = 55.5555\dots$ recurring = $55.\dot{5}$ moles.			
- By experimentation, scientists have established that at a temperature of 298K,  $1 \text{ dm}^3$  of pure water contains almost exactly  $1 \times 10^{-7}$  moles of  $H^+$  ions and since the stoichiometric ratio of
 
$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$
 is 1 : 1 : 1, there are therefore also  $1 \times 10^{-7}$  moles of  $OH^-$  ions in  $1 \text{ dm}^3$  of water at 298K.
- $(1 \times 10^{-7}) \times 100 \% \approx 1.8 \times 10^{-7} \% = 0.000,000,18 \%$ , of pure Water is thus ionised into  $H^+$  and  $OH^-$  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<sup>3</sup>, and “neutral” Water has a pH value of 7 at 298K.

<sup>1</sup> ... and in this sense Water can thus be thought of as an acid.

<sup>2</sup> The RMM of  $H_2O \approx (2 \times 1.00) + 16.0 = 18.0 \text{ g mol}^{-1}$ , but if we use Carbon-12 as the yardstick for the measurement of Mass, then the more accurate isotopic RAM of Hydrogen is 1.00794 atomic mass units, and the RAM for Oxygen would be 15.9994 amu and the RMM for Water would be 18.01528 amu (but I am not interested in such refinements for the moment), and I am happy to use here  $18.0 \text{ g mol}^{-1}$  for the RMM of Water instead of  $18.01528 \text{ g mol}^{-1}$ .

<sup>3</sup> An alkali is a soluble base that releases  $OH^-$  ions when dissolved in water..

- Pure Water is defined as being “neutral”, even though it has both  $1 \times 10^{-7}$  moles of  $H^+$  ions and  $1 \times 10^{-7}$  moles of  $OH^-$  ions in it at 298K, and it is “neutral” because the number of  $H^+$  ions is exactly equal to the number of  $OH^-$  ions and the effect of these ions is to cancel out each other out. As the temperature of pure Water changes, the position of its dynamic equilibrium alters, and Water thus has different pH values at different temperatures e.g.

at 0°C      pH  $\approx$  7.47 therefore at 273K water is neutral at a pH of 7.47, and  
 at 18°C     pH  $\approx$  7.11 therefore at 291K water is neutral at a pH of 7.11, and  
 at 25°C     pH  $\approx$  7.00 therefore at 298K water is neutral at a pH of 7.0, and  
 at 50°C     pH  $\approx$  6.61 therefore at 323K water is neutral at a pH of 6.61, and  
 at 100°C    pH  $\approx$  6.12 therefore at 373K water is neutral at a pH of 6.12.

- OK, at this point if you do not know the meaning of the word “nuance”, then please go and look it up, because this next bit of text is a rather “nuanced” bit of ‘A’ Level Chemistry.

- Pure Water<sup>4</sup> that has pH value of 7.0 at RTP (25°C/298K) is said to be “neutral”.
- “Neutral” here means that there are just as many  $H^+$  ions as there are  $OH^-$  ions in 1 dm<sup>3</sup> of Pure Water.
- The reversible reaction  $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$  is an endothermic reaction, therefore (using Le Chatelier’s principle) at a higher temperature the position of dynamic equilibrium of the reaction will shift to the right<sup>5</sup>, therefore
- more Water molecules will break down into  $H^+$  and  $OH^-$  ions, therefore
- **the concentration of  $H^+$  ions will increase**, and as a result of this
- **the pH of the Pure Water will become smaller.**

- In normal circumstances you would think that the Pure Water has become more acidic (and that this is being signalled by the reduction in its pH value), but **THIS IS NOT THE CASE**. The pH of Pure Water has gone down, but the Pure Water is now **NOT more acidic**, because the concentration of  $OH^-$  ions has increased by exactly the same amount, and the acidic effect of all the  $H^+$  ions is being cancelled out by the alkaline effect of exactly the same number of  $OH^-$  ions. **THE WATER IS STILL NEUTRAL**. It is just the case that because of the definitions involved, it looks as though the Water has become more acidic at a higher temperature. (*By the way, did you look up the meaning of “nuance” as I asked you to?*)

- **As the temperature increases, pure Water is NOT becoming more and more acidic! It remains NEUTRAL at all these temperatures because there are an equal number of  $H^+$  ions and  $OH^-$  ions in the water. It is merely the position of dynamic equilibrium that is changing, and therefore the concentration of the  $H^+$  and  $OH^-$  ions that is changing.**

- Here is a nice very simple rule
- If  $[H^+] < [OH^-]$  then the solution is **basic**
- If  $[H^+] = [OH^-]$  then the solution is **neutral**
- If  $[H^+] > [OH^-]$  then the solution is **acidic**.

- Thermodynamically a Strong Acid is unstable and when added to Water is anxious to convert to a more stable thermodynamic species. Equally, a Strong Base is thermodynamically unstable and when added to Water is anxious to convert to a more thermodynamically stable species. Weak Acids and Weak Bases are thermodynamically stable and have only a small tendency to react with Water.

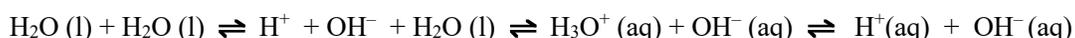
<sup>4</sup> “Pure” here means that there are no other ions present in the water other than  $H^+$  and  $OH^-$  ions.

<sup>5</sup> If you need to revise Le Chatelier’s laws, then please go back and read Chapter 3 of last year’s book on Thermodynamics.

- *If you are confused, then do not worry because you are in good company.* Can you remember that in “Chapter 1: Acids and Bases”, I told you that Svante Arrhenius’ Doctoral Thesis was actually about Electrolysis and not that much about Acids and Bases, and that his supervisors did not much like his Doctoral Thesis and (I believe) gave him the lowest recognition ever awarded for such a thesis by Uppsala University – but that *eventually* the value of Arrhenius’ work was recognised by everybody and **he was awarded the Nobel Prize in 1903**.<sup>6</sup> Now are you beginning to see why his supervisors were confused? I used to be very confused when I was doing my ‘A’ Levels, but I hope that **you** will very quickly get the hang of all of this as you work through it.

### **The Equilibrium Ionic Product of Water Constant, $K_w$**

- The reaction equation for the dissociation of pure water is



therefore the  $K_c$  for pure Water at a given temperature is

$$K_c = \frac{[\text{H}^+(\text{aq})] \cdot [\text{OH}^-(\text{aq})]}{[\text{H}_2\text{O}(\text{l})]}$$

and just as with  $K_a$ , since  $[\text{H}_2\text{O}(\text{l})]$  is just a number (which at 298K is 55.5), the Equilibrium Ionic Product of Water Constant,  $K_w$ , at equilibrium at a given temperature can be and is defined as

$$K_c \cdot [\text{H}_2\text{O}(\text{l})] = K_w = [\text{H}^+(\text{aq})] \cdot [\text{OH}^-(\text{aq})]$$

- The  $K_c$  for pure water at 298K is almost exactly  $1.8 \times 10^{-16}$  therefore (ignoring the units)

$$K_w = K_c \cdot 55.5 \approx 1.8 \times 10^{-16} \times 55.5 \approx 1 \times 10^{-14} \quad \text{at 298K}$$

and, since the stoichiometric ratio of  $\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq})$  is 1 : 1 : 1,  $[\text{H}^+] = [\text{OH}^-]$  then  $[\text{H}^+(\text{aq})] = 1 \times 10^{-7} \text{ mol dm}^{-3}$ , and  $[\text{OH}^-(\text{aq})] = 1 \times 10^{-7} \text{ mol dm}^{-3}$ , therefore

$$K_w = 1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6} = [\text{H}^+(\text{aq})] \cdot [\text{OH}^-(\text{aq})] \approx (1 \times 10^{-7} \text{ mol dm}^{-3}) \cdot (1 \times 10^{-7} \text{ mol dm}^{-3})$$

$$\begin{aligned} \text{or} \quad [\text{H}^+]^2 &= [\text{OH}^-]^2 = 1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}, \\ \text{and} \quad [\text{H}^+] &= [\text{OH}^-] = 1 \times 10^{-7} \text{ mol dm}^{-3} \end{aligned}$$

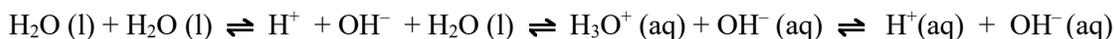
- The pH of X is the  $-\log_{10}(X)$ , therefore

$$\text{the pH of pure Water at 298K} = -\log_{10}(1 \times 10^{-7}) = 7.0$$

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<sup>6</sup> I recently bought Fowler and Hoyle’s 1964 ground-breaking paper explaining the conditions for the formation of Carbon-12 in stars, and all that I can understand in the *whole paper* is the spelling of the author’s names (and in fact even though Fowler is the first author on the paper, the idea was actually Hoyle’s). Hoyle was one of the great unrecognised geniuses of the last century, and men are so petty, that he was never given a Nobel Prize because he did not care how many people he upset (and he did upset quite a few people). Mind you, this sort of thing happens all the time in Science. When Geoff Palmer (now Professor Sir Godfrey Henry Oliver Palmer), the first **black** Professor in Scotland, was applying for a Doctoral post in the UK, he was apparently told by Sir Keith Joseph to ‘go back to the West Indies and grow bananas’. Can you believe that? **Can you believe that!** The strange thing is that Keith Joseph was actually a nice man (I had lunch with him in 1974) and a very clever man, but he was clearly “somewhat”, to say the least, **colour-prejudiced**. Mind you, that was the time of Enoch Powell (an extremely clever but totally colour-prejudiced man) in this country – and the “Establishment” in this country (both Conservative **and** Labour) was at that time **VERY** racially prejudiced.

- **At the Equivalence Point for the titration of a Strong Acid against a Strong Base, the H<sup>+</sup> ions from the acid and the OH<sup>-</sup> ions have exactly neutralised each other, and the pH of the solution is therefore just that of the dissociated H<sup>+</sup> ions from pure Water = 7.0 .**
- These are all very important relationships so please take the time to make sure that you can reconstruct them from first principles for yourself. Start with



and then work out every line in the logic on the previous page until you get to

$$[\text{H}^+]^2 = [\text{OH}^-]^2 = 1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}, \quad \text{and} \quad [\text{H}^+] = [\text{OH}^-] = 1 \times 10^{-7} \text{ mol dm}^{-3}$$

- Keep doing it until you get it right three times out of three attempts. Please remember that you can read something and think that you have understood it – until you have to do it for yourself, and then you may find that you cannot do it (*and the worst place to find out that you cannot do it is in the exams*). You do **not** have to memorise the K<sub>c</sub> for water, but

**you must know the value of K<sub>w</sub> at 298K = 1 x 10<sup>-14</sup> mol<sup>2</sup> dm<sup>-6</sup>.**

**The useful consequence of the relationship  $K_w = [\text{H}^+(\text{aq})] \cdot [\text{OH}^-(\text{aq})] = 1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$**

- A very useful consequence flows from the fact that  $K_w = [\text{H}^+(\text{aq})] \cdot [\text{OH}^-(\text{aq})] = 1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ .

- Since
 

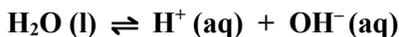
log of (X . Y)	=	log of (X times Y)	=	log X + log Y
then if we take the log of the equation	$K_w$	=	$[\text{H}^+(\text{aq})] \cdot [\text{OH}^-(\text{aq})]$	
we would get	$\log_{10} K_w$	=	$\log_{10} [\text{H}^+] + \log_{10} [\text{OH}^-]$	
and ∴	$-\log_{10} K_w$	=	$-\log_{10} [\text{H}^+] + \{-\log_{10} [\text{OH}^-]\}$	
therefore	$\text{p}K_w$	=	$\text{pH} + \text{pOH} = -\log_{10} (1 \times 10^{-14}) = 14.0$	

or  **$\text{pH} + \text{pOH} = 14.0$**

and this is an extremely useful relationship because it provides us with a very easy way to calculate the pH of a strong base (i.e. the “**acidity**” of a strong base).

- If we want to know the strength of an acid then all we need to do is to calculate the negative log to the base 10 of the hydrogen ion concentration of the aqueous solution of that acid. That is very simple and straightforward – **but how would we calculate the strength of a base**, because for the strength of a base we want to know NOT the concentration of the Hydrogen ions, but **the concentration of the Hydroxide ions, i.e. we want to know the pOH**.
- Well as it happens, the relationship  $\text{p}K_w = \text{pH} + \text{pOH} = 14.0$  simplifies the process because arithmetically  $\text{pOH} = 14.0 - \text{pH}$ , and all that we have to do now to get the pOH of a solution is to find out the pH of the solution and then subtract that number from “14.0”, and that will be the answer! We will do some worked examples in a few moments’ time, and then you will see how the Maths works in practice.
- At this stage you should say to me *“I am awfully sorry Sir, but I am still rather confused as to how we are going to use K<sub>w</sub>”* – and when I was learning ‘A’ Level Chemistry, I shared your confusion. Let us therefore retrace our steps and go back to the basics.

- The fundamental reaction in all this stuff about  $K_w$  is summarised in the equation



and we know that this reversible reaction **at dynamic equilibrium** lies **VERY** far to the left viz. only a **tiny** amount of water molecules ever break down at any one time into  $\text{H}^+$  and  $\text{OH}^-$  ions.

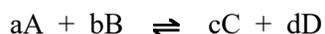
- We have been through the detailed algebra to show that for the above reaction, when it is in dynamic equilibrium, we can derive a constant**

$$K_w = [\text{H}^+(\text{aq})] \cdot [\text{OH}^-(\text{aq})] = 1 \times 10^{-14}$$

therefore  $[\text{H}^+] = \frac{1 \times 10^{-14}}{[\text{OH}^-]}$  and  $[\text{OH}^-] = \frac{1 \times 10^{-14}}{[\text{H}^+]}$

- Now, according to Le Chatelier's principle, **if we were to add more  $\text{H}^+$  ions** (via an acid) to the pure Water in this reaction, then the  $\text{H}^+$  ions that we have added would react with the existing  $\text{OH}^-$  ions to form Water and the position of dynamic equilibrium would move to the left because  $\text{OH}^-$  ions have been used up and Water would have been formed. The concentration of  $\text{OH}^-$  ions has thus been reduced and this change will be governed directly by the  $K_c$  involved, and we have shown above that  $K_c \times [\text{H}_2\text{O(l)}] = K_w = 1 \times 10^{-14}$ .
- We have also shown that  $\text{pH} + \text{pOH} = 14.0$ , therefore if we know the pH of the reaction at its new position of dynamic equilibrium, then we can do the Arithmetic and get the value of the pOH (which will be given by  $\text{pOH} = 14.0 - \text{pH}$ ).
- Equally, **if we were to add  $\text{OH}^-$  ions** (via an alkali) to the pure water in this reaction, then they would react with the existing  $\text{H}^+$  ions and form Water and the position of dynamic equilibrium would again move to the left – but this time it is the concentration of  $\text{H}^+$  ions that will have reduced and this movement will be governed directly by the  $K_c$  involved, and we have shown above that  $K_c \times [\text{H}_2\text{O(l)}] = K_w = 1 \times 10^{-14}$ .
- If therefore we know the pOH of the reaction at its new position of dynamic equilibrium, then we can do the arithmetic and get the value of the pH (which will be given by  $\text{pH} = 14.0 - \text{pOH}$ ).
- Now can you see how important are the algebraic equations that we have derived.
- It is interesting and useful to note that if  $K_w = [\text{H}^+(\text{aq})] \cdot [\text{OH}^-(\text{aq})] = 1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$  at 298K, then with regard to acidity and basicity, the larger that  $[\text{H}^+(\text{aq})]$  is, the smaller that  $[\text{OH}^-(\text{aq})]$  must be and *vice versa* i.e. the more acidic a solution is the less basic it will be, and the more basic a solution is the less acidic it will be.
- The concentration of  $\text{H}^+$  ions and  $\text{OH}^-$  ions relative to each other determines whether a solution is acidic or basic.**
- If you look at the 30<sup>th</sup> March 2019, Second Year Blog on my website, then you will see the details for the calculation of the pH values during the titration of Strong Acids against Strong Bases/Weak Acids against Strong Bases/Weak Bases against Strong Acids/etc. All that I am now going to do here is to do some simple calculations for you.

- If we were to dissolve an acidic or a basic substance in pure Water, then if it were an acid (irrespective of whether the acid were strong or weak) we would change the  $[H^+]$  of the Water, and if it were a base (irrespective of whether the base were strong or weak) then we would change the  $[OH^-]$ . Let us therefore play around with the four possibilities (strong and weak acids, and strong and weak bases), and then we can get a feel of what is going on.
- On page 10 I have created a little table showing the concentrations of all the ions that are relevant to the acidity/basicity of a solution when I add acids and bases to 1 dm<sup>3</sup> of pure Water to get (totally arbitrarily) 0.2 mol dm<sup>-3</sup> of
  - i) a Strong Acid (I have arbitrarily used HCl)
  - ii) a Strong Base (I have arbitrarily used NaOH)
  - iii) a Weak Acid, (I have arbitrarily used Ethanoic Acid) and
  - iv) a Weak Base (I have arbitrarily used “Phenylamine”, C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>, or “Aniline” as it is also called). C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>(aq) has hardly any tendency to attract a proton/to be a lone pair donor<sup>7</sup> (because the lone pair on the “N” atom gets pulled very close to the N atom by the Mesomeric effect that we talked about in Organic Chemistry (Chapter 3, Second Year Organic Chemistry).
- You will notice that when I add HCl (g) (a strong acid) to the water (to get HCl (aq)), I ignore the anionic Cl<sup>-</sup> (aq) ions because they are irrelevant to the definition of acidity/basicity. *They are merely spectator ions.*
- This is **not** the case with CH<sub>3</sub>COO<sup>-</sup> (aq) basic ions and C<sub>6</sub>H<sub>5</sub>NH<sub>3</sub><sup>+</sup> (aq) acidic ions . CH<sub>3</sub>COO<sup>-</sup> (aq) is **not** a spectator ion. It is the conjugate base of the Weak Acid CH<sub>3</sub>.COOH (aq), and equally C<sub>6</sub>H<sub>5</sub>NH<sub>3</sub><sup>+</sup> (aq) is the conjugate acid of the Weak Base C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub> (aq).
- The volume of the solution that I am going to use for my demonstration of the Maths involved is 1 dm<sup>3</sup>, and the ‘amounts’ are in moles, therefore the units are “ mol dm<sup>-3</sup>”. North Americans tend to denote this as “M” or “moles per litre”. We in Europe talk about moles per cubic decimetre. *However, the two units represent exactly the same dimension.*
- A strong acid such as HCl dissociates almost completely, therefore in effect its  $[H^+]$  at Equilibrium is the same as the Initial concentration of the acid.
- However, Ethanoic Acid/Acetic Acid is a weak acid with a K<sub>a</sub> of 1.76 x 10<sup>-5</sup>, therefore (using an ICE table) the  $[H^+]$  caused by the dissociation of e.g. 0.2 mol dm<sup>-3</sup> Ethanoic Acid  $\approx \sqrt{(0.2 \times 1.76 \times 10^{-5})} \approx 1.88 \times 10^{-3} \text{ mol dm}^{-3}$ , and the approximate pH of CH<sub>3</sub>.COOH is 2.73, and the more accurate figure using a quadratic equation is still 2.73 (cf. working on page 17). I have done all the arithmetic for you in the Appendix. When you get to the Appendix, please could you check my working (and you **must** use an ICE table) to see whether or not I have made a mistake in my arithmetic.
- Please do the calculations for yourself before looking at my workings in the Appendix, and please remember that
 
$$CH_3COOH(l) + H_2O(l) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$
 The molar ratios in the equation above are 1 : 1 : 1 : 1 , and in the table that you construct the Initial Concentration of CH<sub>3</sub>COOH is 0.2 mol dm<sup>-3</sup>. **It is not the Equilibrium Concentration.**
- You do not need to know about K<sub>b</sub> for ‘A’ Level purposes but K<sub>b</sub> is merely the counterpart of K<sub>a</sub>. For any reversible reaction

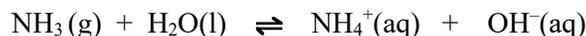


<sup>7</sup> Jim Clark of “chemguide” gives the K<sub>b</sub> of Phenylamine as “4.17 x 10<sup>-9</sup>” and the pK<sub>b</sub> as “9.38”.

that is in dynamic equilibrium at a given temperature, there is a constant  $K_c$  such that

$$K_c = \frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b}$$

therefore for a base such as Ammonia,



$$K_c = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3][\text{H}_2\text{O}]} \quad \text{and since } [\text{H}_2\text{O}] \text{ is a constant that } = 55.5, \text{ then}$$

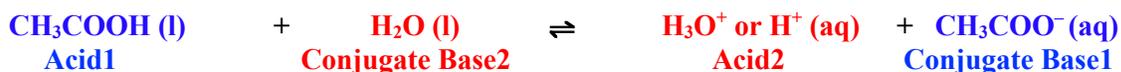
$$K_c[\text{H}_2\text{O}] = K_b \text{ for Ammonia} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

and since the stoichiometric ratios are 1 : 1 : 1 : 1,  $[\text{NH}_4^+] = [\text{OH}^-]$ .

- Now if I tell you that the  $K_b$  for Ammonia is  $1.75 \times 10^{-5}$ , and that the  $\text{p}K_b$  for  $\text{NH}_3 = 4.75$ , could you please work out what  $[\text{NH}_3]$  is. Please do try to do it (and make sure that you understand any assumptions that you make), because it WILL thereby consolidate your understanding of  $K_w$ .
- By coincidence, the **ACID** Dissociation Equilibrium Constant,  $K_a$  for  $\text{CH}_3\text{COOH}$  ( $1.76 \times 10^{-5}$ ) is almost exactly the same number arithmetically as the **BASE** Dissociation Equilibrium Constant,  $K_b$  for  $\text{NH}_3$  ( $1.75 \times 10^{-5}$ ), therefore the numbers that you get for Ammonia will be almost exactly the same as the numbers that we got for Ethanoic Acid. However, the numbers that you arrive at will be the  $\text{pOH}$  for Ammonia and to get the  $\text{pH}$  for Ammonia we will need to use the relationship  
 **$\text{pH for a base} = 14.0 - \text{pOH for that particular base.}$**

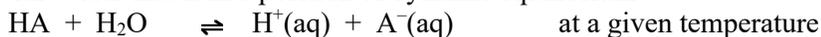
$$\underline{K_w = K_a \times K_b}$$

- In our first year together we talked about “Conjugation”, but we have not talked about it much this year – but now we need to do so in order to understand one of the relationships involved in  $K_w$ , the Equilibrium Constant for the Ionic Product of Water.
- Let us look at the reaction of a Weak Acid such as Ethanoic Acid (or Acetic Acid as it is also known) with Water, and highlight the relationships involved viz.



- **An acid is a proton DONOR**  
 $\text{CH}_3\text{COOH}$  donates a proton to  $\text{H}_2\text{O}$ , and  $\text{H}_3\text{O}^+ \text{ or } \text{H}^+(\text{aq})$  donates a proton to  $\text{CH}_3\text{COO}^-(\text{aq})$ .  
Acid1 Acid2
- **A base is a proton ACCEPTOR**  
 $\text{H}_2\text{O}$  accepts a proton from  $\text{CH}_3\text{COOH}$ , and  $\text{CH}_3\text{COO}^-$  accepts a proton from  $\text{H}^+$ .  
Conjugate Base2 Conjugate Base1

- You will remember that from our considerations of the Equilibrium Acid Constant  $K_a$  (Chapter 5), for any reversible acid reaction with Water that is in a position of dynamic equilibrium

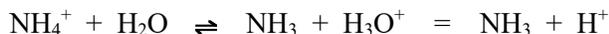


there is a Constant  $K_a$  such that

$$K_a = \frac{[\text{H}^+] \cdot [\text{A}^-]}{[\text{HA}]} \quad \text{where } K_a = K_c \times [\text{H}_2\text{O}]$$

therefore

**a) for the ACID reaction of AMMONIUM with Water (where a proton is being donated)**

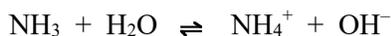


we can say that

$$K_a = \frac{[\text{H}^+] \cdot [\text{NH}_3]}{[\text{NH}_4^+]}$$

and

**b) for the BASE reaction of AMMONIA with Water (where a proton is being received)**



we can say that

$$K_b = \frac{[\text{NH}_4^+] \cdot [\text{OH}^-]}{[\text{NH}_3]}$$

and if we now multiply  $K_a$  by  $K_b$  and cancel the common terms we get

$$K_a \times K_b = \frac{[\text{H}^+] \cdot [\text{NH}_3]}{[\text{NH}_4^+]} \times \frac{[\text{NH}_4^+] \cdot [\text{OH}^-]}{[\text{NH}_3]} = [\text{H}^+] \cdot [\text{OH}^-]$$

but, on page 4 we saw that

$$K_w = [\text{H}^+] \cdot [\text{OH}^-]$$

therefore we now know that

$$K_w = K_a \times K_b \quad (\text{and } K_w = 1 \times 10^{-14}).$$

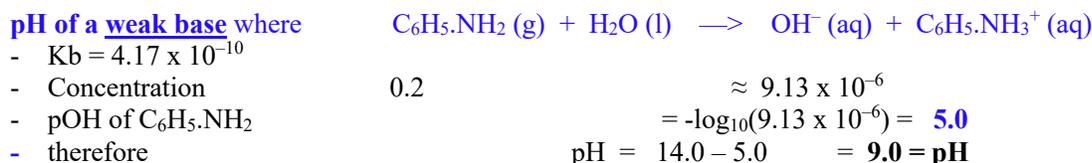
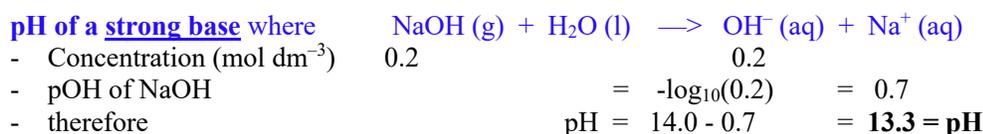
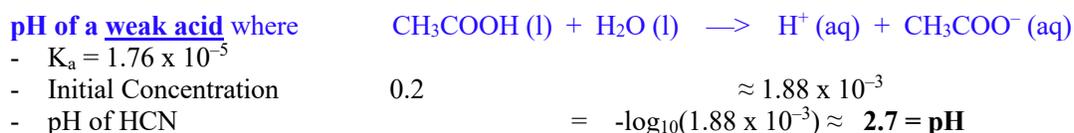
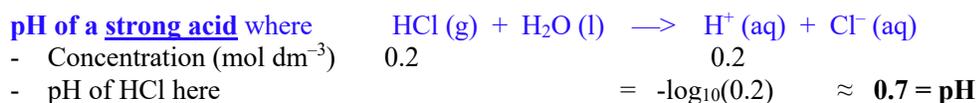
- Therefore if you are ever given  $K_a$  in the exam and asked to work out  $K_b$  (or vice versa), then you now know what to do because  $K_w$  at 298K =  $1 \times 10^{-14}$ .
- OK, let me now construct a table (that I mentioned on page 8) that results when acids and bases are added to 1 dm<sup>3</sup> of pure water to get 0.2 mol dm<sup>-3</sup> of
  - a Strong Acid (I have arbitrarily used HCl)
  - a Strong Base (I have arbitrarily used NaOH)
  - a Weak Acid, (I have arbitrarily used CH<sub>3</sub>COOH)and
  - a Weak Base (I have arbitrarily used “Phenylamine”, C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub> (aq), or “Aniline” as it is also called).
- Please note that in Chapter 5A, I have written out in great detail the instructions for calculating the changing pH values in the titration of a
  - a Strong Acid against a Strong Base
  - a Weak Acid against a Strong Base
  - a Weak Base against a Strong Acid, and
  - a Weak Base against a Weak Acid.

- Please do read that Chapter again. It will give you a very clear idea of how to calculate pH values and how to use the equation  $\text{pH} + \text{pOH} = 14.0$ .

**NB To get  $K_a$  for an acid, write the reaction equation for the acid with water and then write  $K_a$ .  
To get  $K_b$  for a base, write the reaction equation for the base with water and then write  $K_b$ .**

- Lastly, from page 4 we know that  $\text{p}K_w = \text{pH} + \text{pOH} = -\log_{10}(1 \times 10^{-14}) = 14.0$ , therefore we can now calculate all the pHs and the pOHs that we want.

Everything in this table (arbitrarily) has an initial concentration of  $0.2 \text{ mol dm}^{-3}$ . For the calculation of the pH and the pOH values of the Weak Acids/Weak Bases please re-read the “rules/signposts” on page 6. **NB I have not used the refinement of a quadratic equation for the calculations in this table.**



To 1 dm <sup>3</sup> of Water Add	[H <sup>+</sup> ions] from the acid/base	[H <sup>+</sup> ions] from the water at the start	pH	[OH <sup>-</sup> ions] from the acid/base	[OH <sup>-</sup> ions] from the water at the start	pOH	Spectator ion <b>NOT a spectator ion</b>
0.2 mol of HCl (g)	0.2	$1 \times 10^{-7}$	<b>0.7</b>	none	$1 \times 10^{-7}$	13.3	<b>Cl<sup>-</sup></b>
0.2 mol of CH <sub>3</sub> .COOH (l)	0.002	$1 \times 10^{-7}$	<b>2.7</b>	none	$1 \times 10^{-7}$	11.3	<b>CH<sub>3</sub>.COO<sup>-</sup></b>
0.2 mol of NaOH (s)	none	$1 \times 10^{-7}$	<b>13.3</b>	0.2	$1 \times 10^{-7}$	<b>0.7</b>	<b>Na<sup>+</sup></b>
0.2 mol of NH <sub>3</sub> (g/l)	none	$1 \times 10^{-7}$	<b>9.0</b>	$9.13 \times 10^{-6}$	$1 \times 10^{-7}$	<b>5.0</b>	<b>NH<sub>4</sub><sup>+</sup></b>

- Did you get the same answers as I did? NB Teachers can and DO make mistakes therefore please check my calculations on pages 17 and 18!

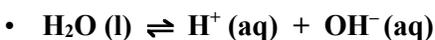
**CH<sub>3</sub>.COO<sup>-</sup> species are NOT spectator ions. They accept protons from Water molecules!**

**NH<sub>4</sub><sup>+</sup> species are NOT spectator ions. They donate protons to Water molecules!**

### But what about the [H<sup>+</sup>] of Water itself

- $1 \times 10^{-7}$  is small enough to be insignificant in relation to the other numbers in the table. If you calculate the pH values both with and without the concentration of H<sup>+</sup> ions from the Water you will see what I mean. It will make no difference to the answer for the number of decimal places that we are using.

**This is a collection of just some of the most useful equations/statements in this Chapter.**



therefore the  $K_c$  for pure Water at a given temperature is

$$K_c = \frac{[\text{H}^+ \text{(aq)}] [\text{OH}^- \text{(aq)}]}{[\text{H}_2\text{O (l)}]}$$

and just as with  $K_a$ , since  $[\text{H}_2\text{O (l)}]$  is just a number (which at 298K is 55.5), the Equilibrium Ionic Product of Water Constant,  $K_w$ , at a given temperature can be and is defined as

$$K_c \cdot [\text{H}_2\text{O (l)}] = K_w = [\text{H}^+ \text{(aq)}] \cdot [\text{OH}^- \text{(aq)}] = 1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$$

$$\text{pH} + \text{pOH} = 14.0$$

therefore  $\text{pOH} = 14.0 - \text{pH}$

“pOH” is an index of the Hydroxide (OH<sup>-</sup>) ion concentration, [OH<sup>-</sup>], in a given solution.

From the above it can be shown that  $[\text{H}^+] = \frac{1 \times 10^{-14}}{[\text{OH}^-]}$

and  $[\text{OH}^-] = \frac{1 \times 10^{-14}}{[\text{H}^+]}$

$$K_w = [\text{H}^+ \text{(aq)}] \cdot [\text{OH}^- \text{(aq)}] \approx (1 \times 10^{-7} \text{ mol dm}^{-3}) \cdot (1 \times 10^{-7} \text{ mol dm}^{-3})$$

but from the stoichiometric ratios involved in  $\text{H}_2\text{O (l)} \rightleftharpoons \text{H}^+ \text{(aq)} + \text{OH}^- \text{(aq)}$ , then

$$[\text{H}^+]^2 = [\text{OH}^-]^2 = 1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}, \quad \text{and} \quad [\text{H}^+] = [\text{OH}^-] = 1 \times 10^{-7} \text{ mol dm}^{-3}$$

- **Pure Water**<sup>1</sup> that has pH value of 7 at RTP (25°C/298K) is said to be “**neutral**”.
  - If  $[\text{H}^+] < [\text{OH}^-]$  then the solution is **basic**
  - If  $[\text{H}^+] = [\text{OH}^-]$  then the solution is **neutral**
  - If  $[\text{H}^+] > [\text{OH}^-]$  then the solution is **acidic**.

$$K_w = K_a \times K_b$$

- OK, let us do some worked examples (and I will do a few of them so that you get the hang of what to do).

### Example 1

- What is the pH of an aqueous solution that has an Hydrogen ion concentration of  $7.50 \times 10^{-10} \text{ mol dm}^{-3}$  at 298K?

#### Answer 1

- $\text{p}[\text{H}^+] = -\log_{10}(7.50 \times 10^{-10}) \approx \mathbf{9.12}$  – which makes it a moderately **weak basic** solution. You omit the units when you are doing the maths for the logs, and please use the correct number of significant figures.

### Example 2

- What is the Hydrogen ion concentration of an aqueous solution that has a pH of 5.65 at 298K?

#### Answer 2

- $\text{p}[\text{H}^+] = -\log_{10}[\text{H}^+] = 5.65$ , therefore  $[\text{H}^+] = 10^{-5.65} = 2.24 \times 10^{-6}$ , therefore  $[\text{H}^+] = 2.24 \times 10^{-6}$  which makes it a moderately **weak acidic** solution.

Once you get the hang of these calculations, they are just so easy!

### Example 3

- What is the pH of  $0.00500 \text{ mol dm}^{-3}$  Sulphuric Acid at 298K?

#### Answer 3

- The trick here is that they want you to see that (i) Sulphuric Acid ( $\text{H}_2\text{SO}_4$ ) dissociates TWO protons, and (ii) they want you to appreciate that Sulphuric is a very strong acid that dissociates almost to completion!<sup>8</sup>



Therefore 1 mole of Sulphuric Acid will dissociate TWO moles of Hydrogen ions.

- Concentration of  $\text{H}_2\text{SO}_4 (\text{aq}) = 0.00500 \text{ mol dm}^{-3}$  therefore  $[\text{H}^+] = 2 \times 0.00500 \text{ mol dm}^{-3}$  and  $\text{p}[\text{H}^+] = -\log_{10}(2 \times 0.00500) = 2.00 = \text{pH}$ .

Once you get the hang of these calculations they are just so easy, and you should now be able to see that if the pH of Sulphuric Acid had been 1.5 then  $-\log_{10} [\text{H}^+] = 1.5$  and  $\log_{10} [\text{H}^+] = -1.50$ , therefore  $[\text{H}^+] = 10^{-1.5} = 0.0316 \text{ mol dm}^{-3}$ , therefore the Concentration of the diprotic Sulphuric Acid would have been **HALF THAT AMOUNT =  $0.016 \text{ mol dm}^{-3}$** ?<sup>9</sup>

<sup>8</sup> ... and  $\text{H}_3\text{PO}_4$  would dissociate THREE protons.

<sup>9</sup> Did you notice the change in the number of significant figures? If the smallest number of significant figures in the question is two, then the answer must be given to **only** two significant figures.

#### Example 4

- What is the pH of pure water if its  $K_w$  is  $4.52 \times 10^{-15} \text{ mol}^2 \text{ dm}^{-6}$  at  $15^\circ\text{C}/288\text{K}$ ?

#### Answer 4

- $K_w = [\text{H}^+(\text{aq})] \cdot [\text{OH}^-(\text{aq})]$  , but since the mole ratio of the dissociation of pure water has a stoichiometric ratio of 1 : 1 : 1, then  $[\text{H}^+(\text{aq})] = [\text{OH}^-(\text{aq})]$  ,  
therefore  $K_w = [\text{H}^+(\text{aq})]^2 = 4.52 \times 10^{-15} \text{ mol}^2 \text{ dm}^{-6}$   
therefore  $[\text{H}^+(\text{aq})] = \sqrt{(4.52 \times 10^{-15})} \text{ mol dm}^{-3} = 6.723 \times 10^{-8} \text{ mol dm}^{-3}$   
therefore  $\text{pH} = -\log_{10}(6.723 \times 10^{-8}) = 7.17$ .

NB Pure water has a pH of 7 **only** at 298K.

- OK, let us now do an example where you calculate the strength of a strong base.

#### Example 5 : Calculate the pH of a STRONG Base

- What is the pH of  $0.100 \text{ mol dm}^{-3}$  Barium Hydroxide,  $\text{Ba}(\text{OH})_2$  solution at 298K where  $K_w = 1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ ?

I hope that you can see that they want you to notice that there are two hydroxy ions for every Barium ion!

#### Answer 5

- For each mole of Barium Hydroxide there are two moles of  $\text{OH}^-$  ions, therefore  $[\text{OH}^-] = 0.200 \text{ mol dm}^{-3}$ .
- $[\text{OH}^-] = 0.200 \text{ mol dm}^{-3}$  , therefore  $-\log_{10}(0.200) = \text{pOH} = 0.7$   
but  $\text{pH} = 14.0 - \text{pOH}$  , therefore  $\text{pH} = 13.3$  .
- **Could it be easier!** NB You can do some common sense stuff and think to yourself “Barium Hydroxide is a strong Base therefore its pH must be something like 12-14, therefore unless I have made a silly arithmetical error, then my answer must be correct.”

### Example 6 : Calculate the pH of a weak acid

- I have already shown you how to do ICE calculations in this Chapter and in Chapter 5A.
- The examiners are asking slightly 'unfair' questions therefore, even though calculations for bases is strictly speaking not in the Syllabus, even so an understanding of the relationships involved in  $K_w$  is in the syllabus, therefore let us do one where you are given a  $K_a$  and asked to calculate the pH of a base.

**Example 7 :** What is the pH of  $0.100 \text{ mol dm}^{-3}$  Ammonia solution if  $K_a$  for the Ammonium ion is  $5.62 \times 10^{-10}$ , and  $K_w$  is  $1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ ?

In order to calculate the pH of something you need to know the concentration of Hydrogen ions in that thing. Here you asked for the pH of Ammonia and Ammonia is a base, and not an acid. The information provided concerns **Water** and **Ammonium** and not (Ammonia). So how are you going to set about answering the question. Think about it *before* you start your answer, and clearly the fact that you have been given the  $K_w$  of Water is a hint by the examiners as to what they think you might want to do.

Some of the things that we have learnt are that

a)  $K_a \times K_b = K_w$  so we could use that information, and another thing that we have learnt is that

b) the pH of a base =  $14.0 - \text{pOH}$ , so we may be able to use that, and we have also learnt that

c)  $K_w = [\text{H}^+(\text{aq})] \cdot [\text{OH}^-(\text{aq})] = 1 \times 10^{-14}$

We also know (from our knowledge of Chemistry) that

d) **Ammonia is a weakish base**, therefore its pH will be around the 9-11, and that

e) an acid is something that when reacted with Water **releases  $\text{H}^+$  ions**, and a

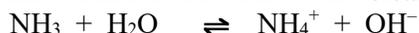
f) a base is something that when reacted with Water **releases  $\text{OH}^-$  ions**.

NB Ammonium is a weak acid, and this is confirmed by the fact that its  $K_a$  is so small ( $5.62 \times 10^{-10}$ ).

### Solution

- $\text{NH}_3$  is a base, therefore let us use this fact.

A base is something that when reacted with Water **releases  $\text{OH}^-$  ions**



- therefore  $K_b = \frac{[\text{NH}_4^+] \cdot [\text{OH}^-]}{[\text{NH}_3]}$

- The reaction ratio is 1 : 1 : 1 : 1, therefore  $[\text{NH}_4^+] = [\text{OH}^-]$ , and we were given that  $[\text{NH}_3] = 0.1 \text{ mol dm}^{-3}$

$$\text{therefore} \quad K_b = \frac{[\text{OH}^-]^2}{[\text{NH}_3]} = \frac{[\text{OH}^-]^2}{0.1}$$

- but  $K_a \times K_b = K_w = 1 \times 10^{-14}$  therefore since  $K_a = (5.62 \times 10^{-10})$

$$(5.62 \times 10^{-10}) \times \frac{[\text{OH}^-]^2}{0.1} = 1 \times 10^{-14}$$

- therefore  $[\text{OH}^-]^2 = \frac{(1 \times 10^{-14}) \times (0.1)}{(5.62 \times 10^{-10})} = 1.7794 \times 10^{-6}$

therefore  $[\text{OH}^-] = 1.334 \times 10^{-3}$

and  $\text{pOH} = -\log_{10}[\text{OH}^-] = -\log_{10}(1.334 \times 10^{-3})$

therefore  $\text{pOH} = 2.9$

- therefore **pH of Ammonia = 14.0 – 2.9 = 11.1**
- The examiners should NOT give you a calculation such as the one that we have just done, but (as I have said) they do ask things that seem to stray from the syllabus but which when examined very closely do come under the remit of the syllabus – therefore in the first 6 chapters of Year Inorganic Chemistry and in my blogs I have now more prepared you for what you might just conceivably be asked.

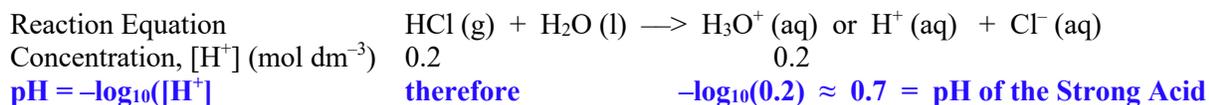
### **Example 8 : Calculate the pH of a weak BASE**

- You are not required to know how to do this at ‘A’ Level, but I have prepared you for it in my Second Year Blog “Calculation of pH values during a titration (a blog for Second Year 'A' Level students who are just about to sit their final exams), 30th March 2019” on page 20 and following.
- That wraps up the stuff that you need to know about the Equilibrium Constants  $K_c/K_p/K_a$  and  $K_w$  for ‘A’ Level work. Please could you do masses of questions from past exam papers so that you familiarise yourself with the calculations involved.
- Having covered the Equilibrium Constants for K ( $K_c / K_p / K_a / K_w$ ), I will in the next Chapters take you through the
  - Rate of Reaction constant “k”
  - Buffer Solutions, and
  - Henderson-Hasselbalch equations

and I know that those of you who want to get into Med School are anxious to get onto these last two topics.

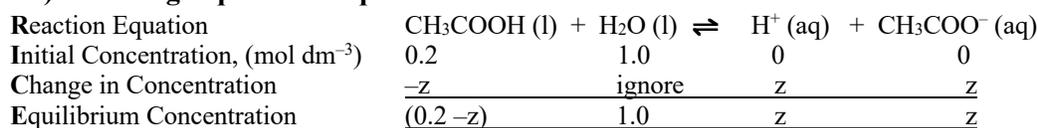
## APPENDIX: CALCULATIONS FOR THE TABLE ON PAGE 11

### A) The addition of a Strong Acid to Water (i.e. one that goes “to completion”)



### B) The addition of a Weak Acid to Water (i.e. one that does not go “to completion”) **YOU MUST USE AN ICE/A RICE TABLE FOR A WEAK ACID OR A WEAK BASE**

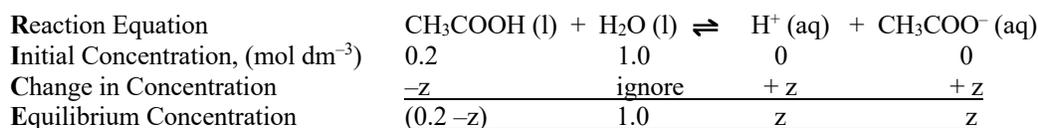
#### B1) Not using a quadratic equation



$$K_a = 1.76 \times 10^{-5} = \frac{z \cdot z}{(0.2 - z)}, \text{ therefore } z^2 = 3.52 \times 10^{-6}, \text{ therefore } z \approx 1.876 \times 10^{-3}$$

and  $-\log_{10}(z) = 2.7 = \text{the pH of the Weak Acid}$

#### B2) Using a quadratic equation (my guess is that it will no difference whatsoever to the value of the pH)



$$K_a = 1.76 \times 10^{-5} = \frac{z \cdot z}{(0.2 - z)}, \text{ therefore } z^2 = (3.52 \times 10^{-6}) - (1.76 \times 10^{-5}) \cdot z$$

therefore  $z^2 + (1.76 \times 10^{-5}) \cdot z - (3.52 \times 10^{-6}) = 0$  .

The values for the quadratic equation are therefore

$$a = 1$$

$$b = (1.76 \times 10^{-5})$$

$$c = -(3.52 \times 10^{-6})$$

and 
$$z = \frac{-(1.76 \times 10^{-5}) \pm \sqrt{\{(1.76 \times 10^{-5})^2 + 4 \cdot (3.52 \times 10^{-6})\}}}{2}$$

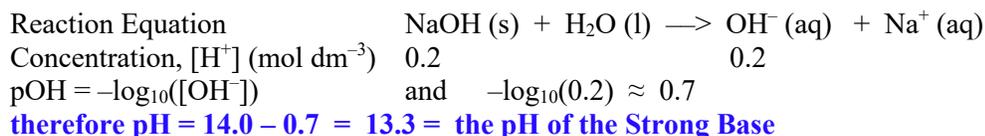
therefore 
$$z = \frac{-(1.76 \times 10^{-5}) \pm \sqrt{\{3.0976 \times 10^{-10} + 1.408 \times 10^{-5}\}}}{2}$$

therefore 
$$z = \frac{-(1.76 \times 10^{-5}) \pm (3.752374 \times 10^{-3})}{2} = \frac{3.735 \times 10^{-3}}{2} \approx 1.8674 \times 10^{-3}$$

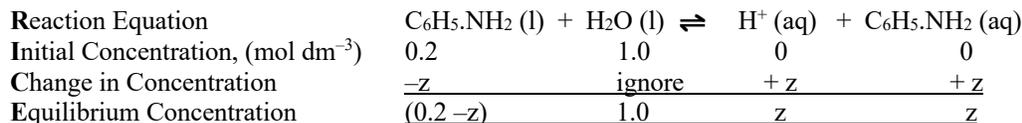
and  $-\log_{10}(z) = 2.7 = \text{the pH of the Weak Acid}$

NB As you can see, when  $K_a$  is a very small number, then using the sophistication of a quadratic solution is **totally unnecessary**. I shall therefore **not** use a quadratic solution when I do the pOH and pH of a Weak Base on page 18.

**C) The addition of a Strong Base to Water (i.e. one that goes “to completion”)**



**D) The addition of a Weak Acid to Base (i.e. one that does not go “to completion”)**  
**YOU MUST USE AN ICE/A RICE TABLE FOR A WEAK ACID OR A WEAK BASE**



$K_b = 4.17 \times 10^{-10} = \frac{\text{z} \cdot \text{z}}{(0.2 - \text{z})}$  , therefore  $z^2 = 8.34 \times 10^{-11}$  , therefore  $z \approx 9.1324 \times 10^{-6}$

and  $-\log_{10}(z) = 5.0 = \text{the pOH of the Weak Acid}$   
**therefore the pH of the Weak Acid = 14.0 – 5.0 = 9.0 .**

I have now taken you through the calculations for Weak Acids and Weak Bases in this note and in Chapter 5A.

I hope that you have picked up the techniques that are involved.