A Second Year blog on Acids and Bases: 18th September 2019

(I am revising what I have written for K_w in the book, and here are a couple of points that you might like to consider. *Everything in this blog can be found in the relevant Chapters of the Book.*)

The concepts of K_a and K_b do **not** apply to Strong Acids and to Strong Bases. **They apply only to Weak Acids and Weak Bases in solution.**

It does not matter at all how much the *concentrations* of the substances in a reaction equation change, provided that the temperature does not change, then the K_a and K_b for Weak Acids and Weak Bases will **not** alter! At any given temperature the values for K_a and K_b will remain constant irrespective of any changes that take place in the concentrations of the solute and the solvent.
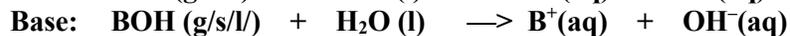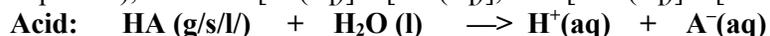
The responses described by Le Chatelier's Principle see to that.

Unsurprisingly, K_a and K_b are called "Constants" because (provided that the temperature does not change) **the values for K_a and K_b for Weak Acids and Weak Bases do not and will not alter.** Change the Concentrations as much as you like, then (provided that the temperature is kept the same) K_a and K_b **WILL NOT ALTER!**

"[H^+(aq)]" represents the *concentration* of Protons in Water when a given substance is dissolved in Water. Solvents (sometimes referred to as substrates) other than Water e.g. Dimethyl Sulphur Dioxide (DMSO) are also used, but I shall not consider such solvents.

Strong Acids/Strong Bases

A Strong Acid and a Strong Base are ones that when added to Water dissociate to completion (or almost to completion), therefore [H^+(aq)] = [HA(aq)], and [OH^-(aq)] = [BOH(aq)].

    Acid: **HA (g/s/l/) + H_2O (l)   —> H^+(aq) + A^-(aq)**

    Base: **BOH (g/s/l/) + H_2O (l)   —> B^+(aq) + OH^-(aq)**

    As a result, for Strong Acids   **pH   = $-\log_{10}[H^+]$ = $-\log_{10}[HA]$**

    and for Strong Bases   **pH   = 14.0 − pOH   = 14.0 − {$-\log_{10}[OH^-]$}**
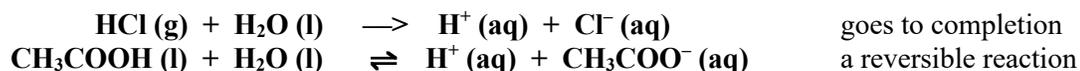
NB These equations are <u>EXTREMELY</u> important.

Weak Acids/Weak Bases

Weak Acids and Weak Bases are those that do **NOT** dissociate to completion. Instead, Weak Acids/Weak Bases reach a position of dynamic equilibrium when (normally) only a *very small amount* of dissociation has occurred.

The accurate way to calculate the pH of Weak Acids/Weak Bases is to use an **ICE table** and the relevant **"K_a" or "K_b" value** and a quadratic equation (cf. Chapter 5A). However, normally there is no need to use a quadratic equation because K_a/K_b tables give values that are generally rounded to (at most) two decimal places therefore the errors created by rounding are larger than the errors involved in the method of calculating the pH values.

NB Hydrochloric Acid/Sulphuric Acid/and Nitric Acid are some of the strong acids that go
to completion when in aqueous solution. Hydrobromic Acid and Hydroiodic Acid (HI) go even
more strongly to completion – but even so there could still be some molecules of undissociated HI
at room temperature. *It is therefore legitimate to claim that no reaction ever goes totally to
Completion because there may always be one or two molecules (out of 10^n molecules) of the
reactants that have not reacted.* **Even so, we still talk about reactions that <u>go to completion</u> in
contrast to reaction that <u>reach a position of dynamic equilibrium</u> when only a very small
proportion of the reactant molecules have reacted e.g.**

$$HCl\ (g)\ +\ H_2O\ (l)\quad \longrightarrow\quad H^+\ (aq)\ +\ Cl^-\ (aq)\qquad \text{goes to completion}$$
$$CH_3COOH\ (l)\ +\ H_2O\ (l)\quad \rightleftharpoons\quad H^+\ (aq)\ +\ CH_3COO^-\ (aq)\qquad \text{a reversible reaction}$$

<u>SUMMARY</u>

- When a reversible reaction $\qquad aA\ +\ bB\ \rightleftharpoons\ cC\ +\ dD$

  reaches a position of dynamic equilibrium **at a given temperature**[1], then there is a number /
  a Constant (called the Equilibrium Constant) **"K_c"** that expresses the following ratio

  K_c = <u>The product of the concentrations of the Products to their stoichiometric ratios</u>
  The product of the concentrations of the Reactants to their stoichiometric ratios

- The Equilibrium Concentration Constant

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

- There are many different derivations of the general equilibrium constant, "K", e.g.
  K_c stands for the Equilibrium **Concentration** Constant for liquids and aquated/aqueous solutions
  K_p stands for the Equilibrium **Pressure** Constant for gases
  K_a stands for the Equilibrium **Acid Dissociation** Constant (for Weak Acids)
  K_b stands for the Equilibrium **Base Dissociation** Constant (for Weak Bases)
  K_w stands for the Equilibrium **Ionic Product of Water** Constant,
  and so on.

- Please note that EVERYTHING in Chemical Equilibria applies only to **REVERSIBLE REACTIONS** that have reached dynamic equilibrium at a given temperature. You CANNOT apply the different Equilibrium Constants (K_c / K_p / K_a / K_w / etc) to anything else.

- I am sure that now that you have read the preceding statement, you will never make the mistake of applying any of the "K"s to a reaction that goes to completion (i.e. to reactions involving strong acids or strong bases).

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[1] .... and please remember that the reaction MUST have reached dynamic equilibrium, and that some reactions do this very quickly while other reactions may take a long time (a day/a week/a month/a year/whatever) to reach this point (but that they can be speeded up by the use of catalysts).

- **The concept of "K" does not apply to Strong Acids and Strong Bases. It applies only to Weak Acids and Weak Bases where "K" remains unchanged when the concentrations involved are altered.**

Table of Acids with Ka and pKa Values*   **CLAS**

Acid	HA	A⁻	Ka	pKa	Acid Strength	Conjugate Base Strength
Hydroiodic	HI	I⁻				
Hydrobromic	HBr	Br⁻				
Perchloric	$HClO_4$	ClO_4^-	Strong acids completely dissociate in aq solution $(K_a > 1, pK_a < 1)$. Conjugate bases of strong acids are ineffective bases.			
Hydrochloric	HCl	Cl⁻				
Chloric	$HClO_3$	ClO_3^-				
Sulfuric (1)	H_2SO_4	HSO_4^-				
Nitric	HNO_3	NO_3^-				
Hydronium ion	H_3O^+	H_2O	1	0.0		
Iodic	HIO_3	IO_3^-	1.6×10^{-1}	0.80		
Oxalic (1)	$H_2C_2O_4$	$HC_2O_4^-$	5.9×10^{-2}	1.23		
Sulfurous (1)	H_2SO_3	HSO_3^-	1.54×10^{-2}	1.81		
Sulfuric (2)	HSO_4^-	SO_4^{2-}	1.2×10^{-2}	1.92		
Chlorous	$HClO_2$	ClO_2^-	1.1×10^{-2}	1.96		
Phosphoric (1)	H_3PO_4	$H_2PO_4^-$	7.52×10^{-3}	2.12		
Arsenic (1)	H_3AsO_4	$H_2AsO_4^-$	5.0×10^{-3}	2.30		
Chloroacetic	$CH_2ClCOOH$	CH_2ClCOO^-	1.4×10^{-3}	2.85		
Citric (1)	$H_3C_6H_5O_7$	$H_2C_6H_5O_7^-$	8.4×10^{-4}	3.08		
Hydrofluoric	HF	F⁻	7.2×10^{-4}	3.14		
Nitrous	HNO_2	NO_2^-	4.0×10^{-4}	3.39		
Formic	HCOOH	HCOO⁻	1.77×10^{-4}	3.75		
Lactic	$HCH_3H_5O_3$	$CH_3H_5O_3^-$	1.38×10^{-4}	3.86		
Ascorbic (1)	$H_2C_6H_6O_6$	$HC_6H_6O_6^-$	7.9×10^{-5}	4.10		
Benzoic	C_6H_5COOH	$C_6H_5COO^-$	6.46×10^{-5}	4.19		
Oxalic (2)	$HC_2O_4^-$	$C_2O_4^{2-}$	6.4×10^{-5}	4.19		
Hydrazoic	HN_3	N_3^-	1.9×10^{-5}	4.72		
Citric (2)	$H_2C_6H_5O_7^-$	$HC_6H_5O_7^{2-}$	1.8×10^{-5}	4.74		
Acetic	CH_3COOH	CH_3COO^-	1.76×10^{-5}	4.75		
Propionic	CH_3CH_2COOH	$CH_3CH_2COO^-$	1.34×10^{-5}	4.87		
Pyridinium ion	$C_5H_4NH^+$	C_5H_4N	5.6×10^{-6}	5.25		
Citric (3)	$HC_6H_5O_7^{2-}$	$C_6H_5O_7^{3-}$	4.0×10^{-6}	5.40		
Carbonic (1)	H_2CO_3	HCO_3^-	4.3×10^{-7}	6.37		
Sulfurous (2)	HSO_4^-	SO_4^{2-}	1.02×10^{-7}	6.91		
Arsenic (2)	$H_2AsO_4^-$	$HAsO_4^{2-}$	$8/9.3 \times 10^{-8}$	7.10/7.03		
Hydrosulfuric	H_2S	HS^-	$1.0 \times 10^{-7}/9.1 \times 10^{-8}$	7/7.04		
Phosphoric (2)	$H_2PO_4^-$	HPO_4^{2-}	6.23×10^{-8}	7.21		
Hypochlorous	HClO	ClO⁻	$3.5/3.0 \times 10^{-8}$	7.46/7.53		
Hypobromous	HBrO	BrO⁻	2×10^{-9}	8.70		
Hydrocyanic	HCN	CN⁻	6.17×10^{-10}	9.21		
Boric (1)	H_3BO_3	$H_2BO_3^-$	5.8×10^{-10}	9.23		
Ammonium ion	NH_4^+	NH_3	5.6×10^{-10}	9.25		
Phenol	C_6H_5OH	$C_6H_5O^-$	1.6×10^{-10}	9.80		
Carbonic (2)	HCO_3^-	CO_3^{2-}	4.8×10^{-11}	10.32		
Hypoiodous	HIO	IO⁻	2×10^{-11}	10.70		
Arsenic (3)	$HAsO_4^{2-}$	AsO_4^{3-}	$6.0 \times 10^{-10}/3.0 \times 10^{-12}$	9.22/11.53		
Hydrogen peroxide	H_2O_2	HO_2^-	2.4×10^{-12}	11.62		
Ascorbic (2)	$HC_6H_6O_6^-$	$C_6H_6O_6^{2-}$	1.6×10^{-12}	11.80		
Phosphoric (3)	HPO_4^{2-}	PO_4^{3-}	$4.8/2.2 \times 10^{-13}$	12.32/12.66		
Water	H_2O	OH^-	1.0×10^{-14}	14.0		
Group I metal hydroxides (LiOH, NaOH, etc.)			Strong bases completely dissociate in aq solution $(K_b > 1, pK_b < 1)$. Conjugate acids (cations) of strong bases are ineffective bases.			
Group II metal hydroxides (Mg(OH)₂, Ba(OH)₂, etc.)						

* Compiled from Appendix 5 Chem 1A, B, C Lab Manual and Zumdahl 6th Ed. The pKa values for organic acids can be found in Appendix II of Bruice 5th Ed.

Source: University of California Santa Barbara

A Bit of background

- The answer to the question "How Far does this reaction go?" has been the subject of much work, but the research into this question was probably started in the 1860s when Berthelot and St Gilles published some work on the reversible reaction of the formation and breakdown of Esters (which we looked at in modest detail in "Chains & Rings" last year). Scientists have subsequently done a massive amount of work on dynamic equilibria (especially for industrial applications)[2], and we will talk about a tiny part of the fruits of their work in the next few weeks.

- All the differing Equilibrium Constants for a reversible reaction in dynamic equilibrium derive from the question "**How Far does this reaction go?**". Some reactions do not reach dynamic equilibrium until almost all the reactants have reacted and only a tiny proportion of them are left in the reaction (and here we say that the position of dynamic equilibrium lies very far to the right), whereas other reactions reach dynamic equilibrium when only a small proportion of the reactants has been used up) and in this instance we say that the position of equilibrium lies very far to the left). The position of dynamic equilibrium for most Carboxylic Acids lies very much to the left (and this is another way of saying that Carboxylic Acids dissociate only a very small proportion of their dissociable protons), and in Organic Chemistry we discussed this in much greater detail and we also learnt about the Mesomeric and Inductive forces that are involved.

NB Since K_c is a constant, and $[H_2O]$ is a constant, then $K_c.[H_2O] = K_a$ **IS ALSO A CONSTANT**.

- In the table on the previous page, almost at the bottom of the table is the K_a of Water at "1×10^{-14}" (and that gives a pK_a of "14", and a pH of "7.0" can also be derived from this). In contrast, almost at the top of the table is the K_a for H^+ (aq) at a value of "1.0" (which gives pK_a of "0.0").

- **Anything that has a K_a and thus also a pK_a that is greater than that of the Hydronium ion H_3O^+ (aq) = H^+ (aq) (8th one down in the table on page 2) is be considered to be a STRONG Acid.**

By definition any species that has a pK_a less than that of the Hydronium ion (<0.0) **is a STRONG ACID.**

- All through these lessons on Chemical Equilibria, I would like you to remember that the relevant Equilibrium Constant (K) is just a number, and that that number will not alter for a given reaction in a closed system at a given temperature. For example, no matter how much we alter the Concentrations of the Reactants and/or the Products in a specified reaction, the Equilibrium Concentration Constant **K_c will not and cannot alter**. When the reaction has been allowed to reach dynamic equilibrium after a change in Concentration, i.e. when all the Le Chatelier changes have taken place, the Equilibrium Concentration Constant will still be the same. **K_c will be UNALTERED.** This may sound a fairly trivial thing – but in reality this principle has massively important theoretical consequences, and in Chemical Engineering it is of enormous practical and financial importance!

- When talking about the dissociation of pure Water, please remember that
$$H_2O \ (l) \ + \ H^+ \ = \ H_3O^+ \ (aq) \ or \ H^+(aq)$$

- **H_3O^+ (aq)   or H^+(aq)   is the Hydronium ion.**

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[2] If you want to become a Chemical Engineer, then please take careful note of this.

- The reaction equation for the dissociation of pure Water is

$$H_2O \text{ (l)} + H_2O \text{ (l)} \rightleftharpoons H_2O \text{ (l)} + H^+ + OH^- \rightleftharpoons H_3O^+ \text{ (aq)} + OH^- \text{ (aq)} \quad \text{or} \quad H^+\text{(aq)} + OH^- \text{(aq)}$$
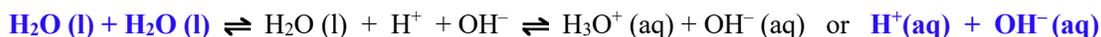
therefore at a position of dynamic equilibrium, the K_c for pure Water at a given temperature is

$$K_c = \frac{[H^+\text{(aq)}] \,.\, [OH^-\text{(aq)}]}{[H_2O \text{ (l)}] \,.\, [H_2O \text{ (l)}]}$$

and just as with K_a, since $[H_2O \text{ (l)}]$ is just a number, then the Equilibrium Ionic Product of Water Constant, K_w , at equilibrium at a given temperature can be and is defined as $\quad K_w = K_c \text{ x a constant}$

therefore $\qquad\qquad\qquad K_w = [H^+\text{(aq)}] \,.\, [OH^-\text{(aq)}]$

and since we know from experimentation that

$$K_w = 1 \text{ x } 10^{-14} \quad \text{at 298K}$$

and, since the stoichiometric ratio of $H_2O \text{ (l)} \rightleftharpoons H^+ \text{ (aq)} + OH^- \text{(aq)}$ is 1 : 1 : 1,
then $[H^+] = [OH^-]$
and $[H^+\text{(aq)}] = 1 \text{ x } 10^{-7} \text{ mol dm}^{-3}$, and $[OH^-\text{(aq)}] = 1 \text{ x } 10^{-7} \text{ mol dm}^{-3}$, therefore

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

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

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

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

- At a different temperature the pH of pure Water has a different value, but we will come to that.

- The above is possibly the best point from which to start any understanding of the concepts of K_w and pH.

- Pure Water is defined as being "neutral", even though it has both $1 \text{ x } 10^{-7}$ moles of H^+ ions and $1 \text{ x } 10^{-7}$ 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 opposing ions is to cancel each other out.

- The dissociation of pure Water is an **endothermic reaction**, therefore **the Product is favoured by an increase in the temperature.**

- If the Product is favoured, then as the temperature of the reaction increases, K_c / K_a / and K_w will rise. 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 ≈ 7.47 therefore at 273K Water is neutral at a pH of 7.47, and
at 18°C   pH ≈ 7.11 therefore at 291K Water is neutral at a pH of 7.11, and
at 25°C   pH ≈ 7.00 therefore at 298K Water is neutral at a pH of 7.0, and
at 50°C   pH ≈ 6.61 therefore at 323K Water is neutral at a pH of 6.61, and
at 100°C   pH ≈ 6.12 therefore at 373K Water is neutral at a pH of 6.12.

- Since the dissociation of pure Water into H^+ and OH^- ions is an **endothermic reaction**, as the temperature of the Water rises
  - the position of dynamic equilibrium moves to the right, and therefore from

$$K_c = \frac{[H^+].[OH^-]}{[H_2O]}$$

  - we can see that the Concentration of Hydrogen ions rises, and
  - because pH = the **negative** of the log to the Base 10 of the Concentration of Hydrogen ions, **the pH DECLINES**.

- I will say that again.
  - **Pure** Water[3] 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^3 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[4], 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**.

- 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.

- 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 **THAT 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 as the concentration of H^+ ions, 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**.

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[3] "Pure" here means that there are no other ions present in the Water other than H^+ and OH^- ions.
[4] If you need to revise Le Chatelier's laws, then please go back and read Chapter 3 of last year's book on Thermodynamics.

- **Thermodynamically a Strong Acid is unstable** and when added to Water it 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.

- If you are given the **initial concentrations** of an aqueous substance X (i.e. [X]) and the values of K_a (for a Weak Acid) or K_b (for a Weak Base), then **from K_w you can calculate the pH of that substance**. Let me now construct the table that results when Acids and Bases are added (in gaseous/liquid/or solid form) to 1 dm^3 of pure Water to get 0.2 mol dm^{-3} of
  i)   a Strong Acid *(I have arbitrarily used HCl (g))*
  ii)   a Strong Base *(I have arbitrarily used NaOH (s))*
  iii) a Weak Acid *(I have arbitrarily used CH_3COOH (l))*, and
  iv) a Weak Base *(I have arbitrarily used "Phenylamine", $C_6H_5NH_2$ (l), 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 **pH + pOH = 14.0 .**

NB To get K_a for an Acid, write the reaction equation for the Acid with Water, and then write out the resulting equation for K_a.
   To get K_b for a Base, write the reaction equation for the Base with Water, and then write out the equation for K_b.

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

Everything in this next table (arbitrarily) has an initial concentration of 0.2 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 8. NB I have **not** used the refinement of a quadratic equation for the calculations in this next table.

pH of a <u>Strong Acid</u> where $HCl\,(g) + H_2O\,(l) \longrightarrow H^+\,(aq) + Cl^-\,(aq)$
- Concentration (mol dm^{-3})   0.2   0.2
- pH of HCl here $= -log_{10}(0.2) \approx \mathbf{0.7 = pH}$
NB A Strong Acid, when added to Water, dissociates to completion (or almost to completion).

pH of a <u>weak Acid</u> where $CH_3COOH\,(l) + H_2O\,(l) \rightleftharpoons H^+\,(aq) + CH_3COO^-\,(aq)$
- $K_a = 1.76 \times 10^{-5}$
- Initial Concentration   0.2 $\approx 1.88 \times 10^{-3}$
- pH of $CH_3.COOH$ $= -log_{10}(1.88 \times 10^{-3}) \approx \mathbf{2.7 = pH}$
NB If this is a Weak Acid, then by definition, it dissociates to a position of dynamic equilibrium that lies very much to the left (i.e. it hardly dissociates at all).

pH of a <u>Strong Base</u> where   NaOH (s) + H_2O (l)   —> OH^- (aq) + Na^+ (aq)
Here NaOH is dissolving in Water and thus the Na^+ ions become surrounded by Water molecules,
and the OH^- ions become surrounded by Water molecules. *The H2O(l) molecules therefore act purely
as a solvent.* That is the only reaction that occurs between the NaOH(s) and the H_2O(l).
- Concentration (mol dm^{-3})   0.2   0.2
- pOH of NaOH   = $-log_{10}(0.2)$ =   0.7
- therefore   pH =   14.0 - 0.7   = **13.3 = pH**

**NB A Strong Base, when added to Water, dissociates to completion (or almost to completion). The
      pH of this NaOH is thus very close to "14.0" (near the top of the pH scale).**

pH of a <u>weak Base</u> where $C_6H_5.NH_2$ (l) + H_2O (l)   ⇌ OH^- (aq) + $C_6H_5.NH_3^+$ (aq)
Here the Base (from the Brønsted-Lowry viewpoint of a Base) has taken on a Proton.
- $K_b = 4.17 \times 10^{-10}$
- Concentration   0.2   ≈ 9.13×10^{-6}
- pOH of $C_6H_5.NH_2$ = $-log_{10}(9.13 \times 10^{-6})$ = **5.0**
- therefore   pH =   14.0 – 5.0   = **9.0 = pH**

NB The pH value of 9.0 confirms that it is a Weak Base.

To 1 dm^3 of Water Add	[H^+ ions] from the Acid/Base	[H^+ ions] from the Water at the start	pH	[OH^- ions] from the Acid/Base	[OH^- ions] from the Water at the start	pOH	Spectator ions In blue Red font indicates NOT a spectator ion
0.2 mol of HCl (g)	0.2	1×10^{-7}	**0.7**	none	1×10^{-7}	13.3	**Cl^-**
0.2 mol of $CH_3.COOH$ (l)	0.002	1×10^{-7}	**2.7**	none	1×10^{-7}	11.3	**$CH_3.COO^-$**
0.2 mol of NaOH (s)	none	1×10^{-7}	**13.3**	0.2	1×10^{-7}	**0.7**	Na^+
0.2 mol of NH_3 (g/l)	none	1×10^{-7}	**9.0**	9.13×10^{-6}	1×10^{-7}	**5.0**	**NH_4^+**

- **Did you get the same answers as I did?** *NB Teachers can and DO make mistakes therefore please
  check my calculations.*

$CH_3.COO^-$ species are <u>NOT</u> spectator ions because they accept a proton from Water molecules!

NH_4^+ species are <u>NOT</u> spectator ions because they donate protons to Water molecules!

- I would advise you as strongly as I possibly can to now read the Blog entitled "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". When you have done so, then you will have been given all the theory that
  you will need for any UK 'A' Level Chemistry exam.

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

1) The p of X $= -\log_{10}$(the concentration of X), therefore the **pH of a solution $= -\log_{10}([H^+])$** , 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^3**

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 [H$_2$O]. [H$_2$O] is very small ($K_w = 1 \times 10^{-14}$) and you can thus ignore Δ**[H$_2$O]**. **However, we are not ignoring the "[H$_2$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^2"** you can ignore any numbers that involve "–z" or "+z", but you **cannot** ignore any numbers that involve "times z" and "÷ 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) $K_a . K_b = K_w = 1 \times 10^{-14}$, and taking the log of both sides of the equation , **pK_a + pK_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$^+$ + A$^-$ " says

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

13) **Whenever you add a Weak Acid to Water you get H$^+$ ions, and when you add a Weak Base to Water you get OH$^-$ 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.