A Year 2 Blog on the pH of Weak Acids and Weak Bases: 22nd September 2019

(I am revising what I have written for the pH of Weak Acids and Bases 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.*)

I am going to divide this analysis into two Sections viz.
A) the pH following the reaction of an Acid or a Base **with WATER**, and
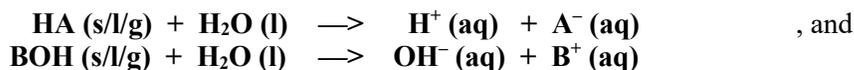B) the pH following the reactions of an Acid **with a BASE**.
(NB An "alkali" is a base that can dissolve in Water i.e. it is a "soluble" Base.)

- The pH of X is "–$\log_{10}$the Hydrogen ion concentration of X" = –$\log_{10}[H^+]$ of X , therefore to obtain the pH of any Acid or any Base all that you need to do is to find out $[H^+]$ for it and take the "$\log_{10}$" of it. (However, please remember that for a Base, what you get initially is the pOH and then you have to use the equation   **pH of a Base = 14.0 – pOH .**)

- In essence, to obtain the pH of something, all that you have to do is to first calculate the $[H^+ \text{(aq)}]$ or the $[OH^- \text{(aq)}]$ of that thing, and then do the logs to get the pH.

A) Reaction of an Acid or a Base with Water

A1) The reaction of STRONG Acids and STRONG Bases with Water

- The generic formula of an Acid is **"HA"** and that of a Base is **"BOH"**, where when each is added to Water you get a reaction to completion viz.

$$\textbf{HA (s/l/g) + H}_2\textbf{O (l)} \quad \longrightarrow \quad \textbf{H}^+ \textbf{(aq) + A}^- \textbf{(aq)} \qquad \text{, and}$$
$$\textbf{BOH (s/l/g) + H}_2\textbf{O (l)} \quad \longrightarrow \quad \textbf{OH}^- \textbf{(aq) + B}^+ \textbf{(aq)}$$

where A^- (aq) and B^+ (aq) are just spectator ions. (They do not figure in the Maths at all.)

- For aqueous solutions of Strong Acids and Strong Bases the Maths is very simple because Strong Acids/Bases go to completion, therefore the
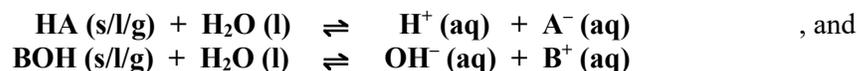$$\textbf{[H}^+ \textbf{(aq)] of a Strong Acid} \quad = \quad \textbf{[HA (s/l/g)]}$$

and the pH for a Strong Base is given by the fact that
$$\textbf{pH of a Strong Base} \quad = \quad \textbf{14.0 – pOH of the Strong Base} \qquad \text{, and the}$$
$$\textbf{pOH of a Strong Base} \quad = \quad \textbf{–}\log_{10}\textbf{[OH}^-\textbf{] of the Strong Base at completion}$$
$$\textbf{[OH}^- \textbf{(aq)] of a Strong Base} \quad = \quad \textbf{[BOH (s/l/g)]}$$

- For Strong Acids and Strong Bases therefore the Maths is very simple.

- The calculations for Weak Acid and Weak Bases is just a bit more complicated.

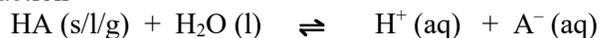## A2) __The reaction of WEAK Acids and WEAK Bases with Water__

- By definition, Weak Acids/Bases do not go to completion and instead reach a point of dynamic equilibrium that is very far to the left. Most of them dissociate only to 1×10^{-5}, and some of them dissociate only to 1×10^{-10} (or even less).

- **The calculation of the pH values for Weak Acids/Bases requires the use of an ICE table.**

- The equations that govern the reactions are still the same, but for Weak Acids/Bases the reactions are reversible ones rather than reactions to completion (as on page 1).

$$\textbf{HA (s/l/g)} + \textbf{H}_2\textbf{O (l)} \quad \rightleftharpoons \quad \textbf{H}^+ \textbf{(aq)} + \textbf{A}^- \textbf{(aq)} \qquad \text{, and}$$
$$\textbf{BOH (s/l/g)} + \textbf{H}_2\textbf{O (l)} \quad \rightleftharpoons \quad \textbf{OH}^- \textbf{(aq)} + \textbf{B}^+ \textbf{(aq)}$$

- An ICE table should really be called a RICE table (because the calculations should start with the Reaction Equation that sets out the stoichiometric ratios concerned), but the accepted convention is to call it an ICE table.

A2.1) __The reaction of a WEAK Acid with Water__

- For the reversible reaction
$$HA \text{ (s/l/g)} + H_2O \text{ (l)} \quad \rightleftharpoons \quad H^+ \text{ (aq)} + A^- \text{ (aq)}$$

$$K_c = \frac{[H^+ \text{ (aq)}] \cdot [A^- \text{ (aq)}]}{[HA \text{ (s/l/g)}] \cdot [H_2O \text{ (l)}]} \quad,$$

and since K_c and $[H_2O \text{ (l)}]$ are constants, then $K_c \times [H_2O \text{ (l)}] = $ **K_a is also a constant,** and

$$K_a = \frac{[H^+ \text{ (aq)}] \cdot [A^- \text{ (aq)}]}{[HA \text{ (s/l/g)}]}$$

- ICE tables are used to determine the pH of Weak Acids (and Weak Bases) where the initials stand for
  - **I**nitial concentration (in mol dm^{-3}, or in an American textbook M for Molarity)
  - **C**hange in concentration (in mol dm^{-3}, or in an American textbook M for Molarity)
  - **E**quilibrium concentration (in mol dm^{-3}, or in an American textbook M for Molarity).

- This is what an ICE table looks like irrespective of the identity of the Weak Acid, but let us say that we are dealing with Benzoic Acid where we have been given the Concentration of the Benzoic Acid as being "n" mol dm^{-3}, then since " $C_6H_5.COOH \text{ (aq)} \rightleftharpoons H^+ \text{ (aq)} + C_6H_5.COO^- \text{ (aq)}$"

$$\text{the } K_a \text{ for Benzoic Acid} = \frac{[H^+ \text{ (aq)}] \cdot [C_6H_5.COO^- \text{ (aq)}]}{[C_6H_5.COOH \text{ (aq)}]}$$

- If we designate the change in concentration of Hydrogen ions as "x", then we know from the stoichiometric ratios of the reaction equation (i.e. 1 : 1 : 1) that the change in concentration of the $C_6H_5.COO^-$ ions was also "+x" and the change in concentration of the $C_6H_5.COOH$ was "–x" i.e. **MINUS** x.

Substances	$[C_6H_5.COOH$ (aq)$]$	$[H^+]$ (aq)	$[C_6H_5.COO^-$ (aq)$]$
Initial Conc. in mol dm^{-3}	n	0	0
Δ in Conc. in mol dm^{-3}	–x	+x	+x
Equilibrium Conc. in mol dm^{-3}	n – x	x	x

and since

$$[H^+] = [C_6H_5.COO^-] = x$$

then
the K_a for Benzoic Acid $= \dfrac{x \cdot x}{n - x} = \dfrac{x^2}{n - x}$

therefore
$$K_a \cdot (n–x) = x^2$$

and therefore
$$x^2 + K_a.x – nK_a = 0$$

and this is now a quadratic equation in x, the resolution of which is complicated but not difficult.

- However, there are two reasons why you do not need to go down the quadratic equation route
  - the examiners know that quite a few 'A' Level Chemistry students do not do 'A' Level Maths, and *more importantly*
  - the K_a values in most published tables are rounded to one or at best two decimal places therefore the simplification (based on the 5% assumption) that is widely accepted is that "**n–x ≈ n**".

  therefore the above equation can be simplified from

  $$(n–x) . K_a = x^2 \qquad \text{to} \qquad nK_a = x^2$$

  and since the value of "n" is usually given, and the value of K_a is known, then

  $$x = \sqrt{(nK_a)}$$

- The K_a for Ethanoic Acid is 1.76×10^{-5} mol dm^{-3}, and the pH of 0.100 mol dm^{-3} of Ethanoic Acid would be given by

  $$[H^+] = [CH_3.COO^-] = x$$

then
the K_a for Ethanoic Acid $= \dfrac{x^2}{0.100 - x}$

and since
$$0.100 – x \approx 0.100$$

then
the K_a for Ethanoic Acid $= \dfrac{x^2}{0.100} = 1.76 \times 10^{-5}$
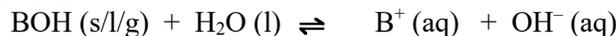
therefore
$x^2 = 1.76 \times 10^{-6}$

and
$x = 1.33 \times 10^{-3} = [H^+]$

therefore
$$\mathbf{pH = –log_{10}(1.33 \times 10^{-3}) \approx 2.88 \text{ or } 2.9}$$

A2.2)   The reaction of a WEAK Base with Water

- For the reversible reaction

  $$BOH (s/l/g) + H_2O (l) \rightleftharpoons B^+ (aq) + OH^- (aq)$$

  $$K_c = \dfrac{[B^+ (aq)] . [OH^- (aq)]}{[BOH (s/l/g)] . [H_2O (l)]} \qquad ,$$

and since K_c and [H_2O (l)] are constants, then K_c x [H_2O (l)] = **K_b is also a constant,** and

$$K_b \quad = \quad \frac{[B^+ \text{ (aq)}] \cdot [OH^- \text{ (aq)}]}{[BOH \text{ (s/l/g)}]}$$

- Just as we did for the K_a of a Weak Acid, we can use an ICE/RICE table to calculate the K_b for a Weak Base. Let us say that we are considering the addition of 0.2 mol dm^{-3} Phenylamine/Aniline (with a $K_b = 4.17$ x 10^{-10}) to Water. The ICE table would be

Substances	[$C_6H_5.NH_2$ (aq)]	[OH^- (aq)]	[$C_6H_5.NH_3^+$ (aq)]
Initial Conc. in mol dm^{-3}	0.2	0	0
Δ in Conc. in mol dm^{-3}	$-x$	$+x$	$+x$
Equilibrium Conc. in mol dm^{-3}	$0.2 - x$	x	x

where $\quad$ **[OH$^-$ (aq)]$_{Equilibrium}$ = [C$_6$H$_5$.NH$_3^+$ (aq)]$_{Equilibrium}$ = x**

and, just as with a Weak Acid, we can make the assumption that $(0.2 - x) \approx 0.2$

therefore $\qquad K_b = \dfrac{x^2}{0.2} = 4.17$ x 10^{-10} $\quad$ therefore $\quad x^2 = 8.34$ x 10^{-11}, and

therefore $\qquad$ x $= 9.1232$ x $10^{-6} = $ [OH$^-$ (aq)]

therefore $\qquad$ pOH $= -\log_{10}(9.1232$ x $10^{-6}) = 5.04$

therefore $\qquad$ **pH $= 14.0 - 5.04 = 8.96 \approx 9.0$.**

B) <u>The pH following the reactions of an Acid with a BASE</u>

The calculations involved in the reactions of Acids with Bases can be found in my 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", so please refer to that Blog – but do remember that, for the moment, no UK 'A' Level Examination Board has as yet included in its Syllabus the calculations required for a **Weak** Base with an Acid.

Please note that the calculation of the Initial pH of a Weak Acid does not require the use of the Henderson-Hasselbalch Equation, but once you start adding the Base to it (whether the Base be Strong or Weak) you will need to use the Henderson-Hasselbalch Equation to calculate the pH, and the H–H Equation states that

$$\textcolor{blue}{\mathbf{pH \quad = \quad pK_a \quad + \quad log_{10} \left\{ \dfrac{[A^- \text{ (aq)}]_{Equilibrium}}{[HA \text{ (aq)}]_{Equilibrium}} \right\}}} \qquad \textcolor{blue}{\underline{\textbf{Concentration of the SALT}}}$$
$$\textcolor{blue}{\textbf{Concentration of the ACID}}$$

You may also need to use the fact that $\quad$ pKa + pKb = 14.0.