Second Year blog on Equilibrium Constants: 25th 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.)

- In the Second Year blog of the 30th March 2019, 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.

- In this short Blog I remind you of some of the equations that you are required to know for the Equilibrium Ionic Product of Water Constant (K_w).

- For the reversible reaction $H_2O \rightleftharpoons H^+ + OH^-$ at a position of dynamic equilibrium, these are the equations (for a temperature of 298K/25°C) 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 $K_a = \dfrac{1 \times 10^{-14}}{K_b}$ and $K_b = \dfrac{1 \times 10^{-14}}{K_a}$

  - From $H_2O\ (aq) \rightleftharpoons H^+ (aq) + OH^- (aq)$ it follows that $K_c = \dfrac{[H^+].[OH^-]}{[H_2O]}$ and therefore

    $K_c . [H_2O] = K_w = [H^+].[OH^-]$ and since the mole reaction ration is $1:1:1$, $[H^+] = [OH^-]$

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

  - $[H^+] = \sqrt{(1 \times 10^{-14})} = 1 \times 10^{-7}$ **Equation 5**
    The above tells you that the concentration of H^+ ions in pure Water at 298K is "1×10^{-7}", and since $[H^+] = [OH^-]$, then it must also be true that $[OH^-] = $ "1×10^{-7}" . From this it follows that

  - $-\log_{10}([H^+]) = pH = 7.0$ **Equation 6** and since $[H^+] = [OH^-]$
  - $-\log_{10}([OH^-]) = pOH = 7.0$ **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 H^+ ions in it as there are OH^- ions in it.

  - $pH + pOH = 14.0$ **Equation 8**.

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

- **Please MEMORISE these equations.**

- **In an exam you do <u>NOT</u> 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 $= -\log_{10}$(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 ÷ Volume of the solution, or **C = N ÷ V in dm³**
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 $[H_2O]$. $[H_2O]$ is very small ($K_w = 1 \times 10^{-14}$) and you can thus ignore $\Delta[H_2O]$. **However, we are not ignoring the "$[H_2O] = 1.0$".** 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 ÷ 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

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

13) **Whenever you add a Weak Acid to Water you get H⁺ 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.