

Second Year blog on Equilibrium Constants: 18th 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.)

- A number of you are extremely good at Maths and are doing ‘A’ Level Maths. However, some of you are numerate and (especially if you want to get into Med School) you need to be able to manipulate numbers competently (otherwise you could very easily kill a patient), therefore let me do some (revision) Maths for you about K_c , K_a , and K_w .

The dissociation of Water

- **Please could you remember that a proton (H^+) cannot exist on its own in Water.** It has such a huge charge density that it grabs hold of the nearest molecule of Water and *temporarily* bonds to it via one of the two lone (or unbonded) pairs of electrons on the O atom in the Water molecule through a dative bond viz. in Water, an H^+ species is always piggy-backed on a molecule of Water surrounded by other molecules of Water viz. $H_3O^+(aq)$ – and in modern Chemistry in Britain we depict this situation as $H^+(aq)$. An $H_3O^+(aq)$ or $H^+(aq)$ species is called an “**hydronium**” ion (and it used to be called the “hydroxonium” ion). The Americans tend to use the label $H_3O^+(aq)$, whereas we in Great Britain tend to use the label $H^+(aq)$.
- **18g** of Water constitute **1 mole** of Water (cf. footnote¹), therefore **1000g** of Water or 1 dm^3 of Water have/has ($1\text{ mole} \times 1000\text{g} \div 18\text{g} =$) **55.555555 or 55.5 moles** of H_2O molecules in it.
- By experimentation, scientists have established that at a temperature of 298K, 1 dm^3 of pure Water contains 1×10^{-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 1×10^{-7} moles of OH^- ions in 1 dm^3 of Water at 298K.
- $[(1 \times 10^{-7}) \div 55.5] \times 100\% = 0.000,000,18\%$ of Water is thus ionised into H^+ and OH^- ions – therefore only a truly **TINY** amount of Water is ever ionised. We define **acidic** substances as those having a pH value of less than 7.0 at 298K, and those with pH values of more than 7.0 at 298K are called **bases**, and “neutral” Water has a pH value of 7.0 at 298K.
- Pure Water is defined as “neutral”, even though it has both 1×10^{-7} moles of H^+ ions and 1×10^{-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 these ions cancel out the effect of each other. **At a different temperature there would be a different number of H^+ and OH^- ions in one mole of Water, and Water would thus have a different pH value at a different temperature.**

¹ RMM of $H_2O \approx (2 \times 1) + 16 = 18\text{ g mol}^{-1}$.

K_c / K_a / pK_a

- For any reversible reaction that is in a position of dynamic equilibrium at a given temperature (and all of these conditions are vital)



then there will always be a constant, “K” (but not to be confused with the symbol for temperature in Kelvins), such that if liquids are involved (gases tend to be talked of in terms of “partial pressure” rather than “concentration”)

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

- As we have already seen, literally a miniscule amount of Water molecules dissociate before a position of dynamic equilibrium is reached, and the concentration of Water molecules in Water i.e. $[H_2O] = 55.5$.
- Therefore for the dissociation of some tiny amount of Water molecules in (let us say) one litre of Water molecules



it must be the case that

$$K_c = \frac{[H^+] \cdot [H_2O]}{[H_2O] \cdot [H_2O]} \quad \text{or} \quad K_c = \frac{[H^+]}{[H_2O]}$$

therefore $K_c \cdot [H_2O] = [H^+]$

but $K_c \cdot [H_2O] = K_a$, and $[H_2O] = 55.5$

therefore $K_a = 55.5$ and $pK_a = -\log_{10}(55.5) = -1.745 \approx -1.74$.

Strong Acids

- The technical definition of a Strong Acid is one that has a pK_a that is less than that of the Hydroxonium or Hydronium ion, therefore if any acid has a pK_a value of less than -1.74 **then it is a Strong Acid.**

Weak Acids

- A Weak Acid is one that has a pK_a value anywhere between that of the Hydronium ion and that of a molecule of pure Water, therefore all that we need to do now is calculate the pK_a of pure Water and we will have numbers that establish the pK_a boundaries of a Weak Acid (and the calculation is usually done for a temperature of 298K).
- At a position of dynamic equilibrium, a truly tiny proportion of Water molecules will have dissociated into H^+ ions and OH^- ions viz.



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

but since $K_a = K_c \cdot [H_2O]$ and $[H_2O] = 55.5$ and $K_w = [H^+].[OH^-] = 1 \times 10^{-14}$

then
$$K_a = \frac{K_w}{55.5} = \frac{1 \times 10^{-14}}{55.5} = 1.8 \times 10^{-16}$$

therefore $pK_a = 15.745 \approx 15.74$.

- **There you have it. Any acid that has a pK_a value $-1.74 < pK_a < 15.74$ is a Weak Acid.**
- I hope that that has reminded you a bit about the calculations involved in $K_c / K_a / pK_a /$ and K_w , and I hope that you are doing question after question from past exam papers until you are even doing them in your sleep. You need to be so familiar with answering past exam papers that you can finish them with a good 10 minutes to spare.

Not long to go now. Good luck.