

[A Second Year blog on the Equilibrium Acid Dissociation Constant \(for the week following Saturday the 15th of September 2019\)](#)

Please remember that K_a and K_b are applicable only for WEAK Acids/Weak Bases.

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

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

$$K_c = \frac{\text{The product of the concentrations of the Products to their stoichiometric ratios}}{\text{The product of the concentrations of the Reactants to their stoichiometric ratios}}$$

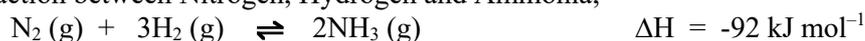
- The Equilibrium Concentration Constant

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

- 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).
- Hydrochloric Acid/Sulphuric Acid/and Nitric Acid are some of the strong acids. 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 perfectly 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.*
- **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.**

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).

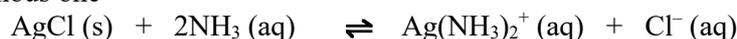
- The reversible reaction could be any reversible reaction. Last year we talked in great detail about the reversible reaction between Nitrogen, Hydrogen and Ammonia,



(and the reaction in the reverse direction would be an endothermic reaction). Another popular reversible reaction with examiners has been



- Both of the above reactions are homogenous reactions, but the next reversible reaction is an heterogenous one



and so is the next one



- OK, let us now talk about the dissociation of Weak Acids and Weak Bases, “K_a” and “K_b”.**

- I shall talk solely about Water as the solvent. *There are other reference solvents e.g. DMSO (Dimethyl Sulphoxide), but I shall not discuss other reference solvents.*

- If the reversible reaction is that for a Weak Acid (HA) dissolved in Water, then at the position of dynamic equilibrium



for a Weak Acid (ignoring the state symbols)

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

and since the concentration of Water molecules is just a number/a constant

$$K_c (\text{a constant}) \times [\text{H}_2\text{O}] (\text{another constant}) = K_a (\text{yet another constant})$$

the Equilibrium Dissociation Constant for a Weak Acid in Water (K_a) can be expressed as

$$K_a = \frac{[\text{H}^+] \cdot [\text{A}^-]}{[\text{HA}]}$$

and the K_a values for different substances have been determined by experimentation and are freely available from **many** different reference sources.

- This statement thus represents the fundamental equation in the determination of the Equilibrium Dissociation Constant for a Weak Acid in Water**

$$K_a = \frac{[\text{H}^+] \cdot [\text{A}^-]}{[\text{HA}]}$$

- A similar logic can be used for the determination of K_b (but I do not think that the 'A' Level Syllabus of any UK Examination Board as yet requires a detailed knowledge of K_b). However, in Chapter 5A I shall show you how to derive a K_b .
- The statements on the next page sum up everything to do with K_a and K_b .

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 herein.

This is a table published by UCLA, Santa Barbara. ("CLAS" stands for Santa Barbara's "Campus Learning Assistance Services").

Table of Acids with Ka and pKa Values*
CLAS

Acid	HA	A ⁻	Ka	pKa	Acid Strength	Conjugate Base Strength
Hydroiodic	HI	I ⁻	Strong acids completely dissociate in aq solution (Ka > 1, pKa < 1). Conjugate bases of strong acids are ineffective bases.			
Hydrobromic	HBr	Br ⁻				
Perchloric	HClO ₄	ClO ₄ ⁻				
Hydrochloric	HCl	Cl ⁻				
Chloric	HClO ₃	ClO ₃ ⁻				
Sulfuric (1)	H ₂ SO ₄	HSO ₄ ⁻				
Nitric	HNO ₃	NO ₃ ⁻				
Hydronium ion	H ₃ O ⁺	H ₂ O	1	0.0		
Iodic	HIO ₃	IO ₃ ⁻	1.6 x 10 ⁻¹	0.80		
Oxalic (1)	H ₂ C ₂ O ₄	HC ₂ O ₄ ⁻	5.9 x 10 ⁻²	1.23		
Sulfurous (1)	H ₂ SO ₃	HSO ₃ ⁻	1.54 x 10 ⁻²	1.81		
Sulfuric (2)	HSO ₄ ⁻	SO ₄ ²⁻	1.2 x 10 ⁻²	1.92		
Chlorous	HClO ₂	ClO ₂ ⁻	1.1 x 10 ⁻²	1.96		
Phosphoric (1)	H ₃ PO ₄	H ₂ PO ₄ ⁻	7.52 x 10 ⁻³	2.12		
Arsenic (1)	H ₃ AsO ₄	H ₂ AsO ₄ ⁻	5.0 x 10 ⁻³	2.30		
Chloroacetic	CH ₂ ClCOOH	CH ₂ ClCOO ⁻	1.4 x 10 ⁻³	2.85		
Citric (1)	H ₃ C ₆ H ₅ O ₇	H ₂ C ₆ H ₅ O ₇ ⁻	8.4 x 10 ⁻⁴	3.08		
Hydrofluoric	HF	F ⁻	7.2 x 10 ⁻⁴	3.14		
Nitrous	HNO ₂	NO ₂ ⁻	4.0 x 10 ⁻⁴	3.39		
Formic	HCOOH	HCOO ⁻	1.77 x 10 ⁻⁴	3.75		
Lactic	HCH ₃ H ₅ O ₃	CH ₃ H ₅ O ₃ ⁻	1.38 x 10 ⁻⁴	3.86		
Ascorbic (1)	H ₂ C ₆ H ₆ O ₆	HC ₆ H ₆ O ₆ ⁻	7.9 x 10 ⁻⁵	4.10		
Benzoic	C ₆ H ₅ COOH	C ₆ H ₅ COO ⁻	6.46 x 10 ⁻⁵	4.19		
Oxalic (2)	HC ₂ O ₄ ⁻	C ₂ O ₄ ²⁻	6.4 x 10 ⁻⁵	4.19		
Hydrazoic	HN ₃	N ₃ ⁻	1.9 x 10 ⁻⁵	4.72		
Citric (2)	H ₂ C ₆ H ₅ O ₇ ⁻	HC ₆ H ₅ O ₇ ²⁻	1.8 x 10 ⁻⁵	4.74		
Acetic	CH ₃ COOH	CH ₃ COO ⁻	1.76 x 10 ⁻⁵	4.75		
Propionic	CH ₃ CH ₂ COOH	CH ₃ CH ₂ COO ⁻	1.34 x 10 ⁻⁵	4.87		
Pyridinium ion	C ₅ H ₄ NH ⁺	C ₅ H ₄ N	5.6 x 10 ⁻⁶	5.25		
Citric (3)	HC ₆ H ₅ O ₇ ²⁻	C ₆ H ₅ O ₇ ³⁻	4.0 x 10 ⁻⁶	5.40		
Carbonic (1)	H ₂ CO ₃	HCO ₃ ⁻	4.3 x 10 ⁻⁷	6.37		
Sulfurous (2)	HSO ₄ ⁻	SO ₄ ²⁻	1.02 x 10 ⁻⁷	6.91		
Arsenic (2)	H ₂ AsO ₄ ⁻	HAsO ₄ ²⁻	8/9.3 x 10 ⁻⁸	7.10/7.03		
Hydrosulfuric	H ₂ S	HS ⁻	1.0 x 10 ⁻⁷ /9.1 x 10 ⁻⁸	7/7.04		
Phosphoric (2)	H ₂ PO ₄ ⁻	HPO ₄ ²⁻	6.23 x 10 ⁻⁸	7.21		
Hypochlorous	HClO	ClO ⁻	3.5/3.0 x 10 ⁻⁸	7.46/7.53		
Hypobromous	HBrO	BrO ⁻	2 x 10 ⁻⁹	8.70		
Hydrocyanic	HCN	CN ⁻	6.17 x 10 ⁻¹⁰	9.21		
Boric (1)	H ₃ BO ₃	H ₂ BO ₃ ⁻	5.8 x 10 ⁻¹⁰	9.23		
Ammonium ion	NH ₄ ⁺	NH ₃	5.6 x 10 ⁻¹⁰	9.25		
Phenol	C ₆ H ₅ OH	C ₆ H ₅ O ⁻	1.6 x 10 ⁻¹⁰	9.80		
Carbonic (2)	HCO ₃ ⁻	CO ₃ ²⁻	4.8 x 10 ⁻¹¹	10.32		
Hypoiodous	HIO	IO ⁻	2 x 10 ⁻¹¹	10.70		
Arsenic (3)	HAsO ₄ ²⁻	AsO ₄ ³⁻	6.0 x 10 ⁻¹⁰ /3.0 x 10 ⁻¹²	9.22/11.53		
Hydrogen peroxide	H ₂ O ₂	HO ₂ ⁻	2.4 x 10 ⁻¹²	11.62		
Ascorbic (2)	HC ₆ H ₆ O ₆ ⁻	C ₆ H ₆ O ₆ ²⁻	1.6 x 10 ⁻¹²	11.80		
Phosphoric (3)	HPO ₄ ²⁻	PO ₄ ³⁻	4.8/2.2 x 10 ⁻¹³	12.32/12.66		
Water	H ₂ O	OH ⁻	1.0 x 10 ⁻¹⁴	14.0		
Group I metal hydroxides (LiOH, NaOH, etc.)			Strong bases completely dissociate in aq solution (Kb > 1, pKb < 1).			
Group II metal hydroxides (Mg(OH) ₂ , Ba(OH) ₂ , etc.)			Conjugate acids (cations) of strong bases are ineffective bases.			

* 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.

ACIDS					
Compound	pK	Ref.			
AgOH	3.96	4	H ₃ PO ₂	2.0, 2.23*	28
Al(OH) ₃	11.2	28	H ₂ PO ₄ ⁻	7.21*	77
As(OH) ₃	9.22	28	HPO ₄ ⁻	12.32*	77
H ₃ AsO ₄	2.22, 7.0, 13.0	28	H ₃ PO ₃	2.0	28
H ₂ AsO ₄ ⁻	6.98*	77	H ₂ PO ₃ ⁻	6.58*	77
HAsO ₄ ⁺	11.53*	77	H ₄ P ₂ O ₇	1.52*	77
As ₂ O ₃	0	4	H ₃ P ₂ O ₇ ⁻	2.36*	77
H ₃ AsO ₃	9.22*		H ₂ P ₂ O ₇ ⁼	6.60*	77
H ₃ BO ₃	9.23*	28	HP ₂ O ₇ ⁼	9.25*	77
H ₂ B ₄ O ₇	4.00	34	HReO ₄	-1.25	30
HB ₄ O ₇	9.00	34	HSCN	4.00	34
Be(OH) ₂	3.7	4	H ₂ SeO ₃	2.6, 8.3, 2.62*	28
HBr	-9.00	31	HSeO ₃	8.32	77
HOBr	8.7	28	H ₂ SeO ₄	Strong, 2.0	28
HOCl	7.53, 7.46	28, 33	HSeO ₄	2.00	34
HClO ₂	2.0	28	H ₃ SiO ₃	10.0	34
HClO ₃	-1.00	28	H ₂ SO ₃	1.9, 7.0, 1.76*	28, 77
HClO ₄ (70%)	-10.00	31	H ₂ SO ₄	-3.0, 1.9	28
CH ₃ SO ₃ H	-0.6	31	HSO ₃	7.21*	77
HCN	9.40	34	HSO ₄ ⁻	1.99*	77
H ₂ CO ₃	6.37, 6.35*, 3.58	34, 32	H ₂ S ₂ O ₄	1.9	29
HCO ₃	10.33*		H ₂ Se	3.89*	77
H ₂ CrO ₄	-0.98	30	HSe ⁻	11.00*	77
HCrO ₄	6.50*	2, 30	H ₂ S	7.00*	77
HOCN	3.92	34	HS ⁻	12.92*	77
HZ	3.17*, 0.59*	77	HSbO ₂	11.0	34
H ₂ GeO ₃	8.59, 12.72	34, 78	HTe	5.00	34
Ge(OH) ₄	8.68, 12.7	28	H ₂ Te	2.64, 11.0	34, 78
HI	-10.0	31	H ₂ TeO ₃	2.7, 8.0	28
HOI	11.0	28	Te(OH) ₆	6.2, 8.8	28
HIO ₃	0.8	28	H ₂ VO ₄ ⁻	8.95	30
H ₄ IO ₆ ⁻	6.00	34	HVO ₄ ⁼	14.4	30
H ₅ IO ₆	1.64, 1.55, 8.27	34, 28	H ₂ CrO ₄	0.74	77
HMnO ₄	-2.25	30	HOCN	3.73	77
NH ₃ OH ⁺	5.98*		HSCN	0.85	77
NH ₄ ⁺	9.24*	77	H ₃ PO ₂	1.07	77
HN ₃	4.72*	77	H ₃ PO ₄	2.12*	77
HNO ₂	3.29	28	H ₂ S ₂ O ₃	0.60*, 1.72*	77
HNO ₃	-1.3	28	H ₃ AuO ₃	13.3, 16.0	78
N ₂ H ₅ ⁺	7.99*	77	H ₃ GaO ₃	10.32, 11.7	78
H ₂ N ₂ O ₂	7.05	34	H ₅ IO ₆	3.29, 6.70, 15.0	78
H ₂ N ₂ O ₂ ⁻	11.0	34		(see above!)	
H ₂ OsO ₅	12.1	34	H ₄ V ₆ O ₁₇	1.96	78
H ₂ O	15.7	none	H ₂ NSO ₃ H	1.0	80
H ₃ O ⁺	-1.7	none			
Pb(OH) ₂	6.48 (10.92)	4 (78)			

* Indicates a thermodynamic value.

Please look at →
these two values

Source: R. Williams/Evans' Table of pKa values/Purdue/and many others

- **H⁺ (aq) {or H₃O⁺ (aq)}** is called the **HYDRONIUM ION**.
- When you first encounter them in this Chapter, two sets of numbers will confuse you. *Therefore in order for them **not** to confuse you when you do encounter them, I shall now discuss these two sets of numbers.* I choose to do so because the explanation of the four numbers will take you through an analysis of the very **fundamentals** of the understanding of the **Acid Dissociation Constant, K_a**.
- On page 3 and on this page you will see two tables that contain pK_a values ("pK_a" = -log₁₀K_a). The two tables are from eminently respectable sources, and yet they quote **different** numbers for the same two fundamental species viz. **Water** and the **Hydronium Ion**, H⁺(aq) or H₃O⁺ (aq).

	UCLA		Williams/Evans/et alii	
Ka and pKa values for	Ka	pKa	Ka	pKa
The Hydronium Ion, H ⁺ or H ₃ O ⁺ (aq)	1.0	0.0	55.5	-1.7
Pure Water	1 x 10 ^{-14.0}	14.0	1.8 x 10 ^{-16.0}	15.7
Logic for the discrepancy	Water cannot be both a solute and a solvent		Water can be both a solute and a solvent	

- As you can see the two sources state two different values, and you might reasonably think that *they cannot both be right*.
- One set of numbers is **FIFTY-FIVE TIMES LARGER** than the other set of numbers.
- I am **not** going to try to arbitrate in the difference between the two numbers. All that I am going to do is to explain how the numbers *can be derived*. I will then leave it to very learned people to argue about the rights and the wrongs of the methodologies. As it happens, I believe that **there is no right and wrong involved here**. The discrepancy between the two numbers arises because the starting points between the two numbers is different.

A1) The derivation of K_a and pK_a for the Hydronium ion, H⁺(aq)

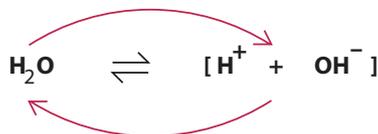
- Let us start by asking a question viz “What is the Concentration of Water in Water?” and one answer to that question is that the **Concentration of any pure solid or liquid must be “1”** because the Concentration of anything **in itself** must be “1”.
- We could therefore arrive at a value for the Concentration of Water viz. [H₂O] = 1.
- I can now ask a second question viz.

What is the concentration of Water molecules dissolved in Water molecules?”

- At first sight this might seem a bizarre, if not even a ridiculous/nonsensical question – until I point out something that we covered last year viz. that in pure Water there are always a truly **TINY** number of Water molecules that have dissociated into H⁺ ions and OH⁻ ions; and, by experimentation, it has been established that at 298K, the Concentration of H⁺ ions in Water, [H⁺] = [OH⁻] = **1 x 10⁻⁷ mol dm⁻³** and we will talk about this in greater detail when we come to talk about the Equilibrium Constant for the Ionic Product of Water (**K_w**) in Chapter 6.
- In a Reversible Reaction, the Reactants are continuously reacting to form the Products *and at exactly the same time, some of the Products are recombining to form the Reactants*. For example, in liquid Water, there will always be some H₂O molecules that will be breaking down into H⁺ ions (Hydronium ions) and OH⁻ ions (Hydroxide ions) – and at exactly the same time there will always be some H⁺ ions and OH⁻ ions that will be joining together to form molecules of Water. **Water therefore ALWAYS consists of a huge number of H₂O molecules, and a tiny proportion of them will be H⁺ ions and OH⁻ ions.**

- If you go on to read Chemistry at University, you will learn about the Debye-Hückel (1923) modifications of the Arrhenius theory and Onsager's (1925) modifications thereto, but I am going to keep this discussion very simple.
- At any time a tiny part of water is always undergoing a reversible reaction viz.

→ *Water molecules breaking down into H⁺ ions and OH⁻ ions*



← *H⁺ ions and OH⁻ ions recombining to form Water molecules*

but please could you remember that a Hydrogen ion or 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 Water² surrounded by other molecules of Water to give H₃O⁺(aq) – and, in modern Chemistry, in Britain we depict this situation as H⁺(aq). An H₃O⁺(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 H₃O⁺(aq), whereas we in Great Britain tend to use the label H⁺(aq).

- In a sense therefore, one could say that Water molecules have been broken down by/have been ‘dissolved’ by other Water molecules – therefore the dissociated Water molecules can be regarded as a **solute**, and the other molecules of Water can be regarded as a **solvent**, and the reversible reaction for the dissociation of Water (or autoionisation of Water) can thus be written as



or if we use the label H⁺ instead of H₃O⁺ we could write it as



and from this reaction equation we can then calculate a K_a value for molecules of solute Water dissolved in molecules of solvent Water.

- Let us now ask “What is the concentration of solute Water dissolved in solvent Water?”, and we can answer the question by stating that 1 mole of molecules of Water has a mass of 18.0 g.
- We should also note that 1 cubic decimetre (1 dm³) of Water, by definition, has a mass of 1,000g. We can therefore say that

if	1 mol of Water	has a mass of	18.0 g
then	X mol of Water	has a mass of	1,000g

 Where $X = \frac{1 \text{ mol} \times 1,000\text{g}}{18.0\text{g}} = 55.5 \text{ mol}$ (the plural of the SI unit “mol” is still “mol”).

On earth, Oxygen exists as three isotopes O-16 / O-17 / and O-18, and if we were to use the Relative Isotopic Avefrage Atomic Mass of Oxygen (18.01528) in the calculation, then the answer for [H₂O] would be 55.5084 g mol⁻¹. **Here I shall use [H₂O] = 55.5 mol per dm³ or [H₂O] = 55.5 mol dm⁻³.**

² Grotthus showed that a Proton keeps hopping from one molecule of Water to another, but let us not bother with that here.

- In other words
55.5 moles of Water have a **mass** of 1,000 g, and
55.5 moles of Water occupy a **volume** of 1 dm³, and the
RMM or M_r of Water = 55.5 mol dm⁻³ and
since **Concentration** = $\frac{\text{Number of moles}}{\text{Volume}}$ = **55.5 moles of Water in every litre or dm³**, i.e.

$$[\text{H}_2\text{O}] = 55.5 \text{ mol dm}^{-3}.$$

- We have now arrived at two different answers for the Concentration of Water viz.

$$[\text{H}_2\text{O (solute)}] = 55.5 \text{ mol dm}^{-3} \quad \text{and from page 5} \quad [\text{H}_2\text{O (solvent)}] = 1$$

- Let us now consider the specific case of the dissociation of Water into H⁺ ions and OH⁻ ions, in other words where Water is acting like an Acid by dissociating Protons (i.e. where Water is acting as both a **solute** and a **solvent**)



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

then, since $[\text{H}^+(\text{aq})] = 55.5 = [\text{OH}^-(\text{aq})]$ *(both concentrations must be the same)*

and $[\text{H}_2\text{O (solute)}] = 55.5$

and $[\text{H}_2\text{O (solvent)}] = 1.0$

then for Water molecules dissociated in other Water molecules,

$$K_c \times [\text{H}_2\text{O (solvent)}] = K_a = \frac{55.5 \times \cancel{55.5}}{\cancel{55.5}} = 55.5$$

and since $\text{p}K_a = -\log_{10}55.5$ then **$\text{p}K_a$ for H⁺ = $-\log_{10}55.5 = -1.74$** .

- Therefore, on a number line (with minus infinity on the left of the line, and plus infinity on the right of the line, and "0" in the middle), anything that has a pK_a of less than the pK_a of the Hydronium ion (i.e. anything less than "-1.74" on the number line) is considered to be a Strong Acid.
- Anything therefore that has a pK_a of less than "-1.74" is a Strong Acid. (NB In some pK_a Tables you may see the pK_a of H₃O⁺ (aq) or H⁺ (aq) given as either "0.0" or as "-1.74". Equally, the pK_a for pure Water may be given as "14.0" or as "15.74". (Please do not concern yourself with this dispute. It is not relevant to your studies.)**

A2) The derivation of K_a and pK_a for pure Water

- We know that for the **Equilibrium Constant for the Ionic Product of Water** (cf. Chapter 6)

$$K_w = [\text{H}^+(\text{aq})] \cdot [\text{OH}^-(\text{aq})] = 1 \times 10^{-14.0}$$

- Then from



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

and we know that

$$\begin{aligned} [\text{H}_2\text{O (solute)}] &= 55.5, \text{ and} \\ [\text{H}_2\text{O (solvent)}] &= 1.0, \text{ and} \\ K_c \times [\text{H}_2\text{O (solute)}] &= K_a, \text{ and} \\ [\text{H}_2\text{O (solvent)}] &= 1.0 \end{aligned}$$

$$K_a \text{ for pure Water} = \frac{1 \times 10^{-14.0}}{55.5} = 1.8 \times 10^{-16}$$

$$\text{p}K_a \text{ for pure Water} = -\log_{10}(1.8 \times 10^{-16}) = 15.74 .$$

- We have now derived the two numbers for pKa
 $\text{p}K_a \text{ for H}^+ = -\log_{10}55.5 = -1.74$, and
 $\text{p}K_a \text{ for pure Water} = -\log_{10}(1.8 \times 10^{-16}) = 15.74$.

Please do keep in mind that all that I am trying to do is to derive two differing sets of numbers for the value of the Ka and the pKa for (i) the Hydronium ion and for (ii) pure Water viz.

	UCLA		Williams	
Ka and pKa values for	Ka	pKa	Ka	pKa
The Hydronium Ion, H ⁺ or H ₃ O ⁺ (aq)	1.0	0.0	55.5	-1.7
Pure Water	1 x 10 ^{-14.0}	14.0	1.8 x 10 ^{-16.0}	15.7

B1) An alternative derivation for the value for K_a and pK_a for the Hydronium ion

- If we were to not allow the possibility of Water being both a **solute** and a **solvent**, then Ka must = 1.0, because the Products and the Reactants would be exactly the same.³
- If **K_a = 1.0** , then **pK_a = -log₁₀(1.0) = "0"** (cf. the Table above under UCLA).

³ In fact no reaction would have taken place!

B2) An alternative derivation for the value for K_a and pK_a for pure Water

- If we use a different starting point from Section (A2), we can derive different numbers for the values of K_a and pK_a .
- We already know that the **Concentration of any pure solid or liquid must be “1”** because the Concentration of anything **in itself** must be “1”. We therefore know the value for the Concentration of Water viz. $[H_2O] = 1$.
- However, were we to refuse to allow the possibility of Water being both a **solute** and a **solvent**, then in the reaction equation



the Concentration of Water would have only one value viz. $[H_2O] = 1$.

- The reaction equation above would thus become



where $[H_2O] = 1.0$.

- The K_c for Water thus becomes

$$K_c = \frac{[H^+] \cdot [OH^-]}{1.0 \times 1.0} \quad \text{and then}$$

and since $[H^+] \cdot [OH^-] = 1 \times 10^{-14}$, and by definition $K_a = K_c \cdot [H_2O]$, then

K_a (the Equilibrium Dissociation Constant for pure Water) can be expressed as

$$K_c \times [H_2O] = K_a = \frac{1 \times 10^{-14}}{1.0} = 1 \times 10^{-14}$$

- **If therefore the K_a for pure Water = 1×10^{-14} , then $pK_a = -\log_{10}(1 \times 10^{-14}) = 14.0$.**

We have therefore now derived BOTH sets of numbers for the K_a and pK_a values of

- i) the Hydronium ion, and
- ii) pure Water

	UCLA		Williams	
	K_a	pK_a	K_a	pK_a
The Hydronium Ion, H^+ or H_3O^+ (aq)	1.0	0.0	55.5	-1.7
Pure Water	$1 \times 10^{-14.0}$	14.0	$1.8 \times 10^{-16.0}$	15.7

and in doing so we have discussed the theory for the ‘A’ Level Syllabus for the Acid Dissociation Equilibrium Constant, K_a .

- Luckily we do not have to worry about the discrepancy between the two sets of numbers that we have examined because in an examination you will be given all the K_a and pK_a numbers that the examiners want you to use. All that I need to do now is to give you some practice in doing the calculations that are involved.

NB Please also do not confuse pK_a with pH.

the “p” of something = $-\log_{10}$ (of that thing)
 therefore **the pH of an Acid** = $-\log_{10}$ (the Hydrogen ion concentration of the Acid) = $-\log_{10}[H^+]$
 and the **pOH of a base** = $-\log_{10}$ (the dissociated Hydroxide, OH^- concentration in Water)
 and the **pH of a base** = **14.0 – pOH.**

Please make sure that you have got all that lodged firmly in your brain!

- Let me remind you of the numbers that are associated with **Strong Acids** and **Weak Acids**. Technically, the definition of a Strong Acid is
 - one that has a K_a **greater** than that of the Hydronium ion H_3O^+ (aq), or as we tend to write it in Europe, H^+ (aq), or
 - it is one that a pK_a **less than** that of a Hydronium ion.
 You can use either definition because they amount to the same thing.
- Please note that even though the **pH** scale is normally quoted as 0-14, it is in fact possible to have Acid pH values that are **NEGATIVE** (i.e. less than “0”), and base pH values that are **LARGER THAN** 14.0. Please also note that the exact pH value of a substance depends on
 - whether it is an Acid or a base
 - how Strong or how Weak it is (and there are many factors that influence this⁴)
 - the size of the concentration of H^+ ions in it (i.e. the number of H^+ ions per dm^3)
 - how diluted it is (and this is also a function of item (iii))
 - the temperature of the solution
 - and so on.
- The generalised formula for an Acid is HA**, where H^+ is the dissociable proton that defines an Acid and A^- is any **anionic** spectator salt such as a Chloride (Cl^-)/a Sulphate (SO_4^{2-})/a Nitrate (NO_3^-)/ etc ion.
- The general formula for a base is BOH**, where B^+ is a **cationic** spectator ion (such as Na^+ / K^+ / NH_4^+ /etc) and OH^- is the Hydroxide ion that is normally present in the reaction of a base with Water. If the Hydroxide ion is not present in the base itself, then it could be generated when the base reacts with Water e.g. $Na_2O(s) + H_2O(l) \rightarrow 2Na^+(aq) + 2OH^-(aq)$.

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: $HA(g/s/l) + H_2O(l) \rightarrow H^+(aq) + A^-(aq)$
Base: $BOH(g/s/l) + H_2O(l) \rightarrow B^+(aq) + OH^-(aq)$
 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 EXTREMELY important.

⁴ For example, the larger the oxidation number on the central atom of like (or similar) Acids, the stronger will be the Acid e.g. sulphuric (VI) Acid $H_2S^{6+}O_4$ is a stronger Acid than $H_2S^{4+}O_3$ sulphurous (IV) Acid. Could you now please calculate the oxidation numbers of $HClO_4$ / $HClO_3$ / $HClO_2$ /and $HClO$ and then work out the order of their Acid strengths.

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 of calculating 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.
- **K_a is a number that has been arrived at by experimentation (at 298K) for many different acidic substances.** NB In this context, anything that dissociates a Proton can be regarded as an Acid. Even if it has a pK_a greater than that of Water, **it can still be regarded as an Acid.**
- Weak Acids dissociate very few protons before they reach a position of dynamic equilibrium (e.g. at 298K, the K_a for Ethanoic Acid is only 1.76 x 10⁻⁵), therefore it is appropriate to talk about K_a for Weak Acids (and K_b for Weak bases), but Strong Acids (and Strong bases) **do not engage in reversible reactions.** By very definition, Strong Acids and Strong bases go straight to completion
$$\text{HA} \longrightarrow \text{H}^+ + \text{A}^-$$
otherwise they could not be classed as “Strong Acids” (or as Strong bases), therefore
 - the concept of K_a **is not applicable to Strong Acids** (such as HCl and H₂SO₄), and
 - the concept of K_b **is not applicable to Strong bases** (such as NaOH and KOH).
- **Please therefore never bother doing K_a and pK_a calculations for Strong Acids (nor K_b and pK_b for Strong bases). In normal circumstances such concepts are just not relevant.**
- Let me therefore start with the calculations that involve Strong Acids and Strong bases.

A) Calculations for Strong Acids/Strong Bases (where K_a and pK_a do not apply)

- pH = -log₁₀[H⁺], therefore if you are given the concentration of H⁺ ions in a Strong Acid then you can easily calculate its pH. A Strong Acid is generally considered to have a pH of 0–3, **but a very concentrated Strong Acid can have a negative pH value** (cf. page 18).
- **For a Strong base you have first to calculate the pOH = -log₁₀[OH⁻], and then to get the pH of the Strong base you must use the equation**
$$\text{pH} = 14.0 - \text{pOH}$$
- A Strong base will have a pH value of 11-14 (but a highly concentrated solution of a Strong base can have a pH value of more than 14).
- **However, the vast bulk of pH values lie in the range 0–14.**
- If you are not given the concentration of H⁺ ions for an Acid (or OH⁻ ions for a base), then you must work out what those numbers are – and you derive those numbers from the concentration of the Acid (or the base).

- English schools can routinely buy Acids with a concentration of say 6.00 mol dm^{-3} , but for your experiments in a school in England you will not *normally* be given an Acid with a concentration higher than 0.1 mol dm^{-3} . If therefore you are told that the concentration of a Strong Acid (such as Hydrochloric Acid/Sulphuric Acid/Nitric Acid) is 0.1 mol dm^{-3} , then since a Strong Acid dissociates to completion (or almost to completion)



then to all intents and purposes, the value of concentration of H^+ ions in the solution will be the same as the value of the concentration of the Acid that you were given i.e. $[\text{H}^+] = [\text{HA}]$.

- If therefore $[\text{HA}] = 0.1 \text{ mol dm}^{-3}$, then $[\text{H}^+] = 0.1 \text{ mol dm}^{-3}$, and $\text{pH} = -\log_{10}[\text{H}^+] = -\log_{10}(0.1) = 1.0$.

NB The units do not form a part of the calculations for logs, and you ignore the units when you are doing your **log** calculations **but you MUST NOT ignore the units when calculating K_a** .

- The procedure for calculating the pH of Strong bases is very similar, because Strong bases such as NaOH and KOH dissociate to completion (or almost to completion)



where "B" stands for the base involved e.g.



- If therefore you are given (say) a 0.1 mol dm^{-3} solution of NaOH, then $[\text{OH}^-] = [\text{NaOH}]$, and since $\text{pOH} = -\log_{10}[\text{OH}^-]$, then $\text{pOH} = -\log_{10}(0.1) = 1.0$.
- For a base you then use the equation, $\text{pH of a base} = 14.0 - \text{pOH}$, and you get

$$\text{pH of the NaOH} = 14.0 - 1.0 = 13.0$$

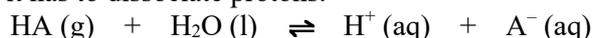
- The procedure involved for Strong Acids and Strong bases is therefore very simple
 - Strong Acids and Strong bases go to completion (or almost to completion) therefore
 - $[\text{H}^+]$ for a Strong Acid = the concentration of the Acid itself, and $\text{pH} = -\log_{10}[\text{H}^+]$, and
 - $[\text{OH}^-]$ for a Strong base = the concentration of the base itself, and $\text{pOH} = -\log_{10}[\text{OH}^-]$, and $\text{pH} = 14.0 - \text{pOH}$.

It really is rather simple (once when you have understood what is going on).

- OK, now let us talk about the slightly more complicated calculations for Weak Acids.

B) Calculations for the pH of Weak Acids (and here we MUST use K_a and an ICE table to calculate the pH of the Weak Acid)

- For a Weak Acid, H^+A^- (where H^+ is a proton and A^- is the anionic salt), in order to act as an Acid in an aqueous solution it has to dissociate protons.



therefore (leaving out the state symbols)

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

but, K_c is just a constant, and $[\text{H}_2\text{O}]$ is also another constant ($[\text{H}_2\text{O}] = 55.5$ recurring = $55.\dot{5}$) that is arrived at by experimentation, therefore we can write " $K_c \cdot [\text{H}_2\text{O}]$ " as another constant " K_a ".

- Therefore

K_a is called the Acid Dissociation Constant.

- If $K_a = K_c \cdot [H_2O]$, and $[H_2O] = 55.5$ then just as a nice little yardstick, since

$K_c = \frac{\text{The product of the concentrations of the Products to their stoichiometric ratios}}{\text{The product of the concentrations of the Reactants to their stoichiometric ratios}}$

then (ignoring the complicated stuff) we can say that if

$K_a > 1$, then the position of dynamic equilibrium lies to the right and we are almost certainly **not** dealing with a Weak Acid

$K_a = 1$, then the position of dynamic equilibrium is in the middle and we are probably still **not** dealing with a Weak Acid

$K_a < 1$, then the position of dynamic equilibrium lies to the left and if K_a is very small then **we ARE certainly dealing with a Weak Acid.**

- Weak Acids dissociate very few protons before they reach a position of dynamic equilibrium, therefore the position of dynamic equilibrium lies **very far to the left**, (e.g. at 298K, the K_a for Ethanoic Acid is only 1.76×10^{-5}) i.e.

$$\frac{1.76}{100,000} = 0.000,017,6 \quad (\text{i.e. a rather small number})$$

- The application of the concept of K_a (for Acids) and K_b (for bases) is therefore totally appropriate because we **ARE** dealing with reversible reactions that are in dynamic equilibrium at a given temperature – so let us see how we can apply the concept. However, before we start, let me repeat something that you need to remember viz.

The LARGER the K_a , the stronger the Acid, and the SMALLER the pK_a , the stronger the Acid.

- This next statement sums it all up

It does not matter at all how much the concentrations of the substances in the equation change, provided that you do not change the temperature, then K_a will not alter!

K_a WILL REMAIN CONSTANT

IRRESPECTIVE OF THE CHANGES THAT TAKE PLACE IN THE CONCENTRATIONS.