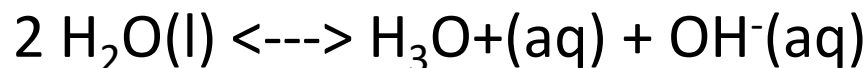


LECTURE 2

Acid- Base Equilibrium in Water

The chemistry of aqueous solutions is dominated by the equilibrium between neutral water molecules and the ions they form.



Strict application of the rules for writing equilibrium constant expressions to this reaction produces the following result.

$$K_c = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2}$$

This is a legitimate equilibrium constant expression, but it fails to take into account the enormous difference between the concentrations of neutral H_2O molecules and H_3O^+ and OH^- ions at equilibrium.

Measurements of the ability of water to conduct an electric current suggest that pure water at 25°C contains 1.0×10^{-7} moles per liter of each of these ions.

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} \text{ M}$$

At the same temperature, the concentration of neutral H_2O molecules is 55.35 molar.

The ratio of the concentration of the H^+ (or OH^-) ion to the concentration of the neutral H_2O molecules is therefore 1.8×10^{-9} .

$$\frac{1.0 \times 10^{-7}}{55.35} = 1.8 \times 10^{-9}$$

In other words, only about 2 parts per billion (ppb) of the water molecules dissociate into ions at room temperature.

The equilibrium concentration of H_2O molecules is so much larger than the concentrations of the H_3O^+ and OH^- ions that it is effectively constant. We therefore build the $[\text{H}_2\text{O}]$ term into the equilibrium constant for the reaction and thereby greatly simplify equilibrium calculations. We start by rearranging the equilibrium constant expression for the dissociation of water to give the following equation.

$$[\text{H}_3\text{O}^+][\text{OH}^-] = K_c \times [\text{H}_2\text{O}]^2$$

We then replace the term on the right side of this equation with a constant known as the water dissociation equilibrium constant, K_w .

$$[\text{H}_3\text{O}^+][\text{OH}^-] = K_w$$

In pure water, at 25C, the $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ ion concentrations are 1.0×10^{-7} M. The value of K_w at 25C is therefore 1.0×10^{-14} .

$$[1.0 \times 10^{-7}][1.0 \times 10^{-7}] = 1.0 \times 10^{-14}$$

Although K_w is defined in terms of the dissociation of water, this equilibrium constant expression is equally valid for solutions of acids and bases dissolved in water. Regardless of the source of the H_3O^+ and OH^- ions in water, the product of the concentrations of these ions at equilibrium at 25C is always 1.0×10^{-14} .

Activity and Concentration

- Activity – “effective concentration”
- Ion-ion and ion-H₂O interactions (hydration shell) cause number of ions available to react chemically ("free" ions) to be less than the number present
- Concentration can be related to activity using the activity coefficient γ , where $[a] = \gamma (c)$

Until now we have assumed that activity, a , is equal to concentration, c , by setting $\gamma = 1$ when dealing with dilute aqueous solutions...

But ions don't behave ideally . . .

- Concentration related to activity using the activity

coefficient γ , where $[a] = \gamma (c)$

- The value of γ depends on:

- Concentration of ions and charge in the solution

- Charge of the ion

- Diameter of the ion

Pure Water

The product of the concentrations of the H_3O^+ and OH^- ions in pure water is equal to K_w .

$$[\text{H}_3\text{O}^+][\text{OH}^-] = K_w$$

But the H_3O^+ and OH^- ion concentrations in pure water are the same.

$$[\text{H}_3\text{O}^+][\text{OH}^-]$$

Substituting the second equation into the first gives the following result.

$$[\text{H}_3\text{O}^+]^2 = K_w$$

The H_3O^+ ion concentration in pure water is therefore equal to the square root of K_w .

Acid and base strengths

The equilibrium constants that define the strengths of an acid and of a base are

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

and

$$K_b = \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]}$$

How are K_a and K_b related?



Since the sum of the first two equations represents the dissociation of water (we are using H^+ instead of H_3O^+ for simplicity), the equilibrium constant for the third reaction must be the product of the first two equilibrium constants:

$$K_a K_b = K_w$$

Clearly, as the strength of a series of acids increases, the strengths of their conjugate bases will decrease, hence the inverse relation between K_a and K_b .

pK values You will recall that the pH scale serves as a convenient means of compressing a wide range of $[H^+]$ -values into a small range of numbers. Just as we defined the pH as the negative logarithm of the hydrogen ion concentration, we can define

$$pK = -\log K$$

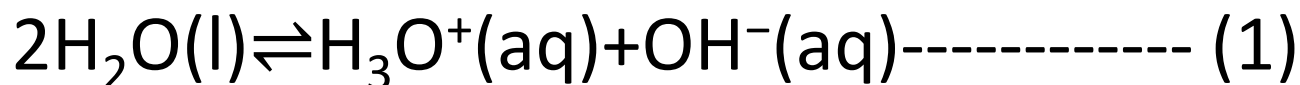
for any equilibrium constant. Acid and base strengths are very frequently expressed in terms of pK_a and pK_b . From Eq. it should be apparent that

$$pK_a + pK_b = pK_w (= 14.0 \text{ at } 25^\circ\text{C})$$

The pH Scale

Self-Ionization of Water

Because of its amphoteric nature (i.e., acts as both an acid or a base), water does not always remain as H₂O molecules. In fact, two water molecules react to form hydronium and hydroxide ions:



This is also called the self-ionization of water. The concentration of H₃O⁺ and OH⁻ are equal in pure water because of the 1:1 stoichiometric ratio of Equation 1.

The molarity of H_3O^+ and OH^- in water are also both $1.0 \times 10^{-7} \text{M}$ at 25°C . Therefore, a constant of water (K_w) is created to show the equilibrium condition for the self-ionization of water. The product of the molarity of hydronium and hydroxide ion is always 1.0×10^{-14} .

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} \text{-----}(2)$$

This equations also applies to all aqueous solutions. However, K_w does change at different temperatures, which affects the pH range discussed below.

Note

H^+ and H_3O^+ is often used interchangeably to represent the hydrated proton, commonly call the hydronium ion.

The equation for water equilibrium is



- If an acid (H^+) is added to the water, the equilibrium shifts to the left and the OH^- ion concentration decreases
- If base (OH^-) is added to water, the equilibrium shifts to left and the H^+ concentration decreases.

pH and pOH

Because the constant of water, K_w is always 1.0×10^{-14} , the pK_w is 14, the constant of water determines the range of the pH scale.

To understand what the pK_w is, it is important to understand first what the "p" means in pOH, and pH.

The Danish biochemist Søren Sørensen proposed the term pH to refer to the "potential of hydrogen ion." He defined the "p" as the negative of the logarithm, $-\log$, of $[H^+]$. Therefore the pH is the negative logarithm of the molarity of H. The pOH is the negative logarithm of the molarity of OH^- and the pK_w is the negative logarithm of the constant of water. These definitions give the following equations:

$$\text{pH} = -\log[\text{H}^+] \text{-----} (4a)$$

$$\text{pOH} = -\log[\text{OH}^-] \text{-----} (4b)$$

$$\text{pKw} = -\log[\text{Kw}] \text{-----} (4c)$$

A logarithm, used in the above equations, of a number is how much a power is raised to a particular base in order to produce that number. To simplify this, look at the equation: $\log_b a = x$. This correlates to $b^x = a$. A simple example of this would be $\log_{10} 100 = 2$, or $10^2 = 100$. It is assumed that the base of Logarithms is ten if it is not stated. So for the sake of pH and pOH problems it will always be ten. When x is a negative number that means you are dividing it by the power. So, if $\log_{10} 0.01 = -2$ which can be written $10^{-2} = 0.01$, then 10^{-2} also means $1/10^2$. The log function can be found on your scientific calculator. Now if we apply this to pH and pOH we can better understand how we calculate the values.

At room temperature,

$$K_w = 1.0 \times 10^{-14} \text{-----} (4d)$$

So

$$pK_w = -\log[1.0 \times 10^{-14}] \text{-----} (4e)$$

Using the properties of logarithms, Equation 4e can be rewritten as

$$10 - pK_w = 14 \text{-----} (4f)$$

By substituting, we see that pK_w is 14. The equation also shows that each increasing unit on the scale decreases by the factor of ten on the concentration of H^+ . For example, a pH of 1 has a molarity ten times more concentrated than a solution of pH 2.

Since

$$pK_w = 14 \text{-----} (5a)$$

$$pK_w = pH + pOH = 14 \text{-----} (5b)$$

Example 1

If the concentration of NaOH in a solution is $2.5 \times 10^{-4} \text{M}$, what is the concentration of H_3O^+ ?

SOLUTION

Because

$$1.0 \times 10^{-14} = [\text{H}_3\text{O}^+][\text{OH}^-]$$

to find the concentration of H_3O^+ , solve for the $[\text{H}_3\text{O}^+]$.

$$1.0 \times 10^{-14} [\text{OH}^-] = [\text{H}_3\text{O}^+]$$

$$1.0 \times 10^{-14} 2.5 \times 10^{-4} = [\text{H}_3\text{O}^+] = 4.0 \times 10^{-11} \text{M}$$

- **Example 2**

- a. Find the pH of a solution of 0.002 M of HCl.
- b. Find the pH of a solution of 0.00005 M NaOH.

- **SOLUTION**

- a. The equation for pH is $-\log [\text{H}^+]$

$$[\text{H}^+] = 2.0 \times 10^{-3} \text{M}$$

$$\text{pH} = -\log[2.0 \times 10^{-3}] = 2.70$$

- b. The equation for pOH is $-\log [\text{OH}^-]$

$$[\text{OH}^-] = 5.0 \times 10^{-5} \text{M}$$

$$\text{pOH} = -\log[5.0 \times 10^{-5}] = 4.30$$

$$pK_w = pH + pOH$$

and

$$pH = pK_w - pOH$$

then

$$pH = 14 - 4.30 = 9.70$$

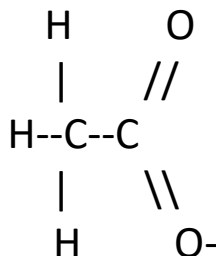
Example 3:

If moist soil has a pH of 7.84, what is the H^+ concentration of the soil solution?

Weak Acids and Bases

Weak acids and bases are only partially ionized in their solutions, whereas strong acids and bases are completely ionized when dissolve in water.

Ionization of Weak Acids



Acetic acid, CH_3COOH , is a typical weak acid, and it is the ingredient of vinegar. It is partially ionized in its solution.



The structure of the acetate ion, CH_3COO^- , is shown on the right

Example 1

In a solution of acetic acid, the equilibrium concentrations are found to be $[\text{CH}_3\text{COOH}] = 1.000$; $[\text{CH}_3\text{COO}^-] = 0.0042$. Evaluate the pH of this solution and the equilibrium constant of ionization of acetic acid.

Solution

From the ionization of acetic acid,



0.100 0.0042 0.0042 we conclude that

$$[\text{H}^+] = [\text{CH}_3\text{COO}^-]$$

$$= 0.0042.$$

Thus, $\text{pH} = -\log 0.0042 = 2.376$.

The equilibrium constant of ionization,

$$(0.0042)^2$$

$$K = \frac{(0.0042)^2}{1.000} = 1.78 \times 10^{-5}$$

Calculate pOH of Basic Solutions

The discussion on weak acids provide a paradigm for the discussion of weak bases. For weak base B, the ionization is $B^- + H_2O = HB + OH^-$

and

$$K_b = \frac{[HB][OH^-]}{[B^-]}$$

The pOH can be calculated for a basic solution if K_b is given. In this case, the discussion is similar and parallel to that given above for the calculation of pH of weak acids when K_a is know.

Buffer Solutions

Definition

A buffer solution is one which resists changes in pH when small quantities of an acid or an alkali are added to it.

Acidic buffer solutions

An acidic buffer solution is simply one which has a pH less than 7. Acidic buffer solutions are commonly made from a weak acid and one of its salts - often a sodium salt.

Alkaline buffer solutions

An alkaline buffer solution has a pH greater than 7. Alkaline buffer solutions are commonly made from a weak base and one of its salts.

How do buffer solutions work?

A buffer solution has to contain things which will remove any hydrogen ions or hydroxide ions that you might add to it - otherwise the pH will change. Acidic and alkaline buffer solutions achieve this in different ways.

Henderson-Hasselbach Equation: pH and pKa

The relationship between pH, pKa, and the buffering action of any weak acid and its conjugate base is best explained by the Henderson-Hasselbach equation.

How to calculate pH of buffer solution containing both acid and conjugate base? Dissociation constant definition 1.1 can be rearranged into

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

or

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$$

(note that due to sign change $[A^-]$ was moved to nominator).

This is so called **Henderson-Hasselbalch equation** (or **buffer equation**). It can be used for pH calculation of solution containing pair of acid and conjugate base - like HA/A^- , HA^-/A^{2-} or B^+/BOH . For solutions of weak bases sometimes it is more convenient to use equation in the form

$$pOH = pK_b + \log\left(\frac{[B^+]}{[BOH]}\right)$$

Two common types of buffer solutions are :

(1) a weak acid together with a salt of the same acid with a strong base. These are called Acid buffers e.g. $CH_3COOH + CH_3COONa$.

(2) a weak base and its salt with a strong acid. These are called Basic buffers. e.g. $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$.

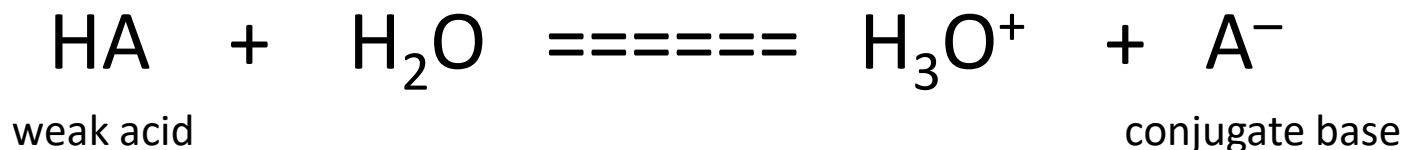
Let us illustrate buffer action by taking example of a common buffer system consisting of solution of acetic acid and sodium acetate ($\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$).

Hydrolysis:-Reaction between a salt (ion or ions in a salt) and water to produce an acidic or basic solution.

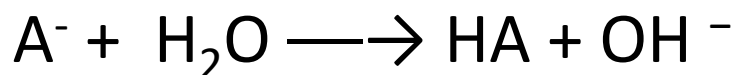
The term hydrolysis is derived from hydro, meaning water, and lysis, meaning breaking.

BRONSTED-LOWRY CONCEPT OF HYDROLYSIS

HA and A⁻ are conjugate acid-base pair

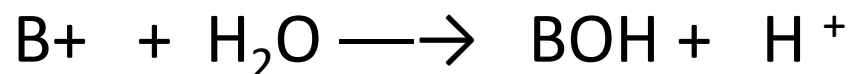


Since HA is a weak acid (poor proton donor), its conjugate base, A^- , must be relatively strong (good proton acceptor). Owing to this fact, A^- ions tend to react with water by accepting proton from the latter to form HA molecule (anionic hydrolysis),



The presence of OH^- ions makes the solution basic.

Similarly, BOH and B^+ are a conjugate acid-base pair. Since BOH is a weak base, its conjugate acid, B^+ , would be relatively strong. Thus B^+ would accept OH^- ions from water to form BOH molecules.



The presence of excess H^+ ions makes the solution acidic.

EXAMPLES OF HYDROLYSIS

The different salts may be classified into the following types according to their hydrolytic behaviour

1-Salts of Strong acids and Strong bases

2-Salts of Weak acids and Strong bases

3-Salts of Weak bases and Strong acids

4-Salts of Weak acids and Weak bases

Salts made from strong acids and strong bases

For example the salt NaCl $\text{NaOH}_{(\text{aq})} + \text{HCl}_{(\text{aq})} \longrightarrow \text{NaCl}_{(\text{aq})} + \text{H}_2\text{O}(\text{l})$

The Na^+ comes from the base NaOH and the Cl^- comes from the acid HCl.

Anions of salts formed by the addition of a strong acid and a strong base will NOT hydrolyze. In the above example the anion is Cl^- and is a **weak conjugate base**, therefore it is too weak a base to pull H^+ ions from H_2O .

Cations of salts formed by the addition of a strong acid and a strong base will NOT hydrolyze. The cation Na^+ is a weak conjugate acid, therefore it is too weak an acid to remove OH^- ions from H_2O . Metallic cations from Group IA or IIA, except Be, do not hydrolyze.

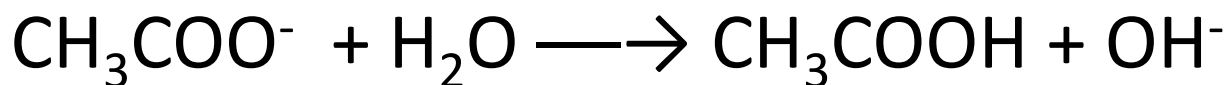
A solution of a salt formed by a strong acid and a strong base will be neutral because:

(Neither the cation or the anion hydrolyzes, \therefore the solution has a pH of 7)

Salts of Weak acids and Strong bases

Sodium acetate, CH_3COONa , and sodium cyanide, NaCN , are examples of this type of salts.

Sodium acetate, CH_3COONa . This is a salt of the weak acid, CH_3COOH , and strong base, NaOH . It ionises in aqueous solution to form the anion CH_3COO^- . Being the conjugate base of a weak acid, CH_3COOH , it is a relatively strong base. Thus CH_3COO^- accepts H^+ ion from water and undergoes hydrolysis.

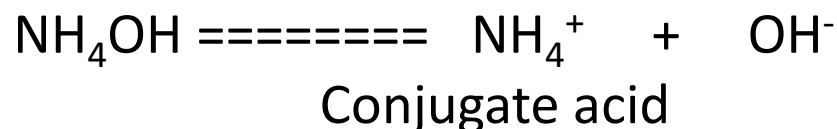


The resulting solution is slightly basic due to excess OH^- ions present.

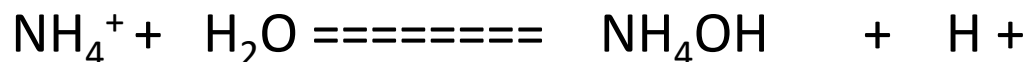
Salts of Weak bases and Strong acids

Some salts of weak bases and strong acids undergo cationic hydrolysis and yield slightly acidic solutions.

Ammonium chloride is a typical example of this class of salts. It is the salt of a weak base, NH_4OH , and strong acid, HCl . It ionises in aqueous solution to form the cation, NH_4^+ .



NH_4^+ is a Bronsted conjugate acid of the weak base NH_4OH . Therefore, it is a relatively strong acid. It accepts OH^- ion from water (H_2O) and forms the unionised NH_4OH and H^+ ion.



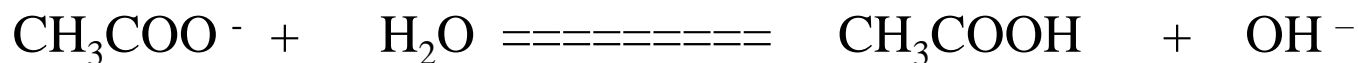
The accumulation of H^+ ions in solution makes it acidic.

The other examples of this type of salts are ferric chloride, aluminium chloride, and copper sulphate.

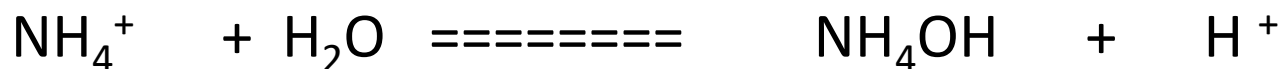
Salts of Weak acids and Weak bases

The examples of this type of salts are ammonium acetate, ammonium cyanide and ammonium fluoride. Both the anion and the cation produced by ionisation of the salt undergo hydrolysis. The resulting solution is neutral, basic or acidic depending on the relative hydrolysis of the anions and the cations.

Ammonium acetate, $\text{CH}_3\text{COONH}_4$. It is the salt of weak acid, CH_3COOH , and weak base, NH_4OH . In aqueous solution it ionises to form the anion CH_3COO^- and the cation NH_4^+ . Since the acid and the base are both weak, their conjugate base (CH_3COO^-) and conjugate acid (NH_4^+) are relatively strong. They accept H^+ and OH^- ions respectively from water and undergo considerable hydrolysis

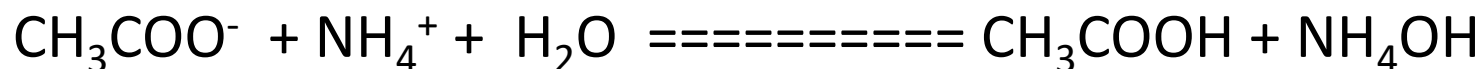


conjugate base



conjugate acid

The overall hydrolysis may be represented as



We have stated that pH of the resulting solution will depend on the relative extent of anionic hydrolysis and cationic hydrolysis. If both the ions react to the same extent (as shown for $\text{CH}_3\text{COONH}_4$), $[\text{OH}^-] = [\text{H}^+]$ and the solution is neutral. If the cation reacts to a greater extent, the solution is slightly acidic. If the anion is a little more reactive, the solution will be basic.

Thus, a solution of $\text{CH}_3\text{COONH}_4$ is neutral, a solution of NH_4CN is slightly basic and a solution of NH_4F is slightly acidic.

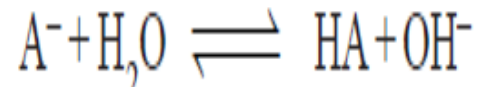
QUANTITATIVE ASPECT OF HYDROLYSIS

Hydrolysis is a reversible reaction. The equilibrium constant derived by application of Law of Mass action to a hydrolysis (or hydrolytic) reaction is called the Hydrolysis constant or Hydrolytic constant. The hydrolysis constant is represented by K_h .

Now, we proceed to discuss the mathematics of hydrolysis of the various types of salts.

Salt of a Weak acid and Strong base

The general hydrolysis reaction of a salt of weak acid (HA) and strong acid can be written as



This leads to the equilibrium constant expression

$$K_h = \frac{[HA][OH^-]}{[A^-][H_2O]}$$

The concentration of water, $[H_2O]$, is very large and is regarded as practically constant. Thus the hydrolysis constant expression assumes the form

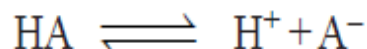
$$K_h = \frac{[HA][OH^-]}{[A^-]} \quad \dots(1)$$

Relation between K_h , K_w and K_a

We know that the ionic product of water, K_w , is expressed as

$$K_w = [H^+][OH^-] \quad \dots(2)$$

For the dissociation of a weak acid, HA,



the acid dissociation constant, K_a , is expressed as

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad \dots(3)$$

Dividing (2) by (3)

$$\frac{K_w}{K_a} = \frac{[OH^-][HA]}{[A^-]} = K_h \quad [\text{by equation (1)}]$$

or

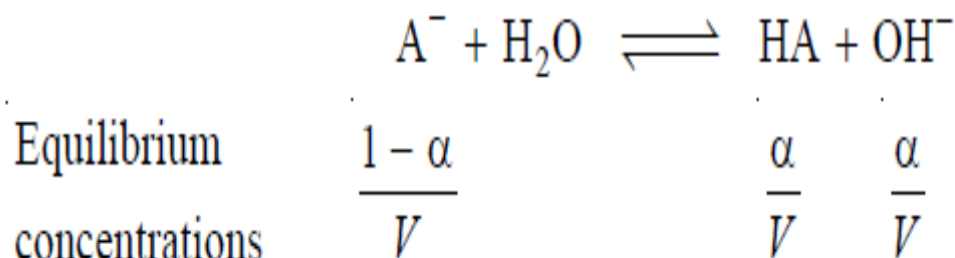
$$\frac{K_w}{K_a} = K_h \quad \dots(4)$$

It is clear from (4) that the hydrolysis constant (K_h) of the salt varies inversely as the dissociation constant K_a of the weak acid. Therefore, **weaker the acid greater is the hydrolysis constant of the salt.**

Relation between Hydrolysis constant and Degree of hydrolysis

The degree of hydrolysis is the fraction of the salt which has undergone hydrolysis when equilibrium is established. It is generally represented by α .

Suppose we start with one mole of the salt dissolved in V litres of solution. Then the equilibrium concentrations are :



Hence the hydrolysis constant K_h is given by

$$K_h = \frac{[HA][OH^-]}{[A^-]} = \frac{\alpha/V \times \alpha/V}{1 - \alpha/V} = \frac{\alpha^2}{(1 - \alpha)V}$$

If α is small, $(1 - \alpha)$ may be taken as equal to one. Then,

$$K_h = \frac{\alpha^2}{V}$$

or

$$\alpha^2 = K_h V = \frac{K_w}{K_a} V$$

\therefore

$$\begin{aligned}\alpha &= \sqrt{\frac{K_w V}{K_a}} \\ &= \sqrt{\frac{K_w}{K_a C}}\end{aligned}$$

where C is the initial concentration of the salt. Knowing the values of K_w , K_a and C, the degree of hydrolysis can be calculated.

Derivation of pH. The pH of an aqueous solution of weak acid and strong base can be derived as follows :

From earlier discussion, we know that

$$[\text{OH}^-] = \frac{\alpha}{V} = \alpha C$$

and

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]}$$

\therefore

$$[\text{H}^+] = \frac{K_w}{\alpha C}$$

But

$$\alpha = \sqrt{\frac{K_w}{K_a C}}$$

\therefore

$$[H^+] = \frac{K_w}{C} \sqrt{\frac{K_a C}{K_w}} = \sqrt{\frac{K_w K_a}{C}}$$

Taking logarithms and reversing the sign throughout

$$-\log[H^+] = -\frac{1}{2}\log K_w - \frac{1}{2}\log K_a + \frac{1}{2}\log C$$

$$\text{pH} = \frac{1}{2}\text{p}K_w + \frac{1}{2}\text{p}K_a + \frac{1}{2}\log C$$

$$= 7 + \frac{1}{2}\text{p}K_a + \frac{1}{2}\log C$$