Acid/Base Equilibria

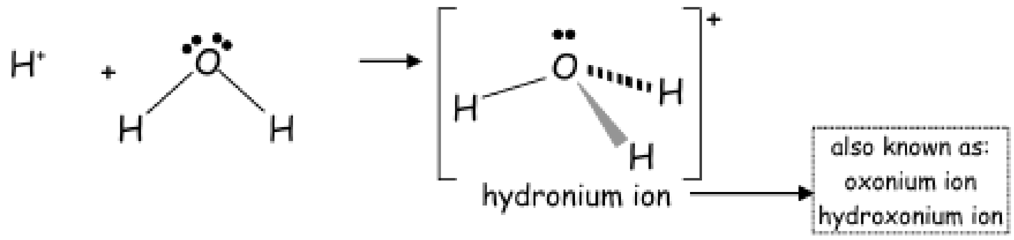
- Acids produce H^+ ions in solutions and bases produce OH^- ions in solution

- Neutralisation: $H^+_{(aq)} + OH^-_{(aq)} \longrightarrow H_2O_{(l)}$

- however
  - HCl gas has no H^+ ions but can neutralise alkalis
  - NH_3 gas can neutralise acid but contains no OH^- ions

- The H^+ ion can be written as follows

$$H^+_{(aq)} + H_2O_{(l)} \longrightarrow H_3O^+_{(aq)}$$



- $H^+_{(aq)}$ is the shorthand form and is often used in stoichiometric and equilibrium equations, despite being an inaccurate representation of the chemical.

<u>Brønsted & Lowry Definitions</u>

- An acid is any substance capable of donating a proton (H^+)
- A base is any substance capable of accepting a proton (H^+)
- For every acid, there is a conjugate base formed by the loss of a proton (H^+)
- For every base, there is a conjugate acid formed by the gaining of a proton (H^+)

	Acid		Base		Conjugate Base		Conjugate Acid
1.	<u>HCl</u>	+	H_2O	$\rightleftharpoons$	Cl^-	+	H_3O^+
2.	CH_3COOH	+	H_2O	$\rightleftharpoons$	CH_3COO^-	+	H_3O^+
3.	H_2O	+	NH_3	$\rightleftharpoons$	OH^-	+	NH_4^+
4.	H_2O	+	CH_3COO^-	$\rightleftharpoons$	OH^-	+	CH_3COOH

- Water can be described as amphoteric since it acts as
  - Proton acceptor (examples 1 & 2)
  - Proton donor (examples 3 & 4)

Dissociation of Water

- Water can dissociate as the following equation shows:

$H_2O_{(l)}$ +	$H_2O_{(l)}$	$\rightleftharpoons$	$H_3O^+_{(aq)}$ +	$OH^-_{(aq)}$
acid	base		conjugate acid (accepts proton)	conjugate base (donated proton)

- The equilibrium constant K for the dissociation of water is:

$$K = \frac{[H_3O^+] \times [OH^-]}{[H_2O]^2}$$

But $[H_2O] = 1$ as water is the solvent in the equation

Ionic Product $K_w = [H_3O^+] \times [OH^-] = 1 \times 10^{-14}$ mol^2 l^{-2} at 25°C

- In pure water
  $H^+_{(aq)} + OH^-_{(aq)} \rightleftharpoons H_2O_{(l)}$ $K_w = [H^+][OH^-] = 1 \times 10^{-14}$
  - For every H^+ ion produced, there is an equal number of OH^- ions produced
  - $[H^+] = [OH^-] = 10^{-7}$ mol l^{-1} in pure water at 25°C

- The Ionic Product K_w varies with temperature

  - $H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$ ΔH=+ve
  - forward reaction is endothermic (bond breaking)
  - increase in temperature favours the endothermic reaction
  - equilibrium moves to RHS more dissociation i.e. ↑$[H^+]$ and ↑$[OH^-]$

- K_w is temperature dependent

Temperature (°C)	Ionic Product K_w
18	0.6×10^{-14}
25	1×10^{-14}
40	2.9×10^{-14}
75	16.9×10^{-14}

- Increase in Temperature increases the K_w and increases the dissociation.

The pH Scale

- $pH = -log_{10} [H^+]$ (or $pH = -log_{10} [H_3O^+]$)

e.g. pure water $[H^+] = 10^{-7}$ mol l^{-1} pH = 7

1M HCl $[H^+] = 1$ mol $l^{-1} = 10^0$ pH = 0

0.2M HCl $[H^+] = 2 \times 10^{-1}$ mol l^{-1}

$log_{10} [H^+] = -0.7$

$-log_{10}[H^+] = 0.7$ pH = 0.7

0.01M NaOH $[OH^-] = 10^{-2}$ mol l^{-1}

$[H^+] = 10^{-12}$ mol l^{-1}

$log_{10} [H^+] = -12$

$-log_{10}[H^+] = 12$ pH = 12

0.5M NaOH $[OH^-] = 5 \times 10^{-1}$ mol l^{-1}

$[H^+] = 2 \times 10^{-14}$ mol l^{-1}

$log_{10} [H^+] = -13.7$

$-log_{10}[H^+] = 13.7$ pH = 13.7

For calculations involving strong acids and strong alkalis, it is assumed that they are 100% dissociated and the number of H^+ ions in the water can be ignored.

Questions

1. Calculate the pH of the following solutions
   a) 0.35 mol l^{-1} HNO_3
   b) 0.14 mol l^{-1} H_2SO_4
   c) 0.78 mol l^{-1} NaOH

Strong & Weak Acids

a) Strong Acids

Strong acids are acids which fully ionise to release H^+ ions

e.g. $HCl_{(g)} \xrightarrow{(aq)} H^+_{(aq)} + Cl^-_{(aq)}$

Strong Acid	hydrochloric acid	sulphuric acid	nitric acid
Formula	HCl	H_2SO_4	HNO_3

- Strong acids fully dissociate into ions

b) Weak Acids

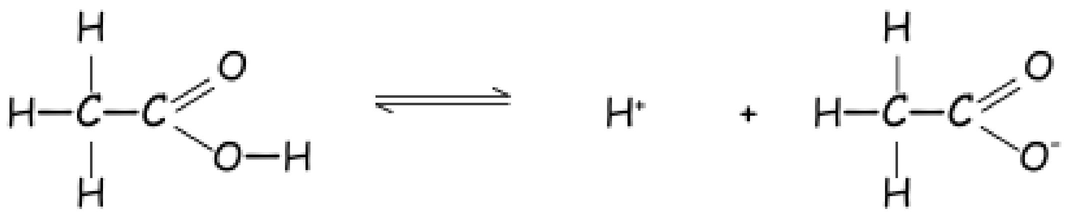
Weak acids do not fully dissociate in water

- Only partial dissociation of H^+ ions from parent molecule

i) Ethanoic Acid (and other alkanoic acids)

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$

ethanoic acid molecule | hydrogen ion | ethanoate ion



(mainly molecules) (few ions)

ii) Sulphur Dioxide Solution

Sulphur Dioxide dissolves in water to form the weak acid sulphurous acid

$$SO_2 + H_2O \longrightarrow H_2SO_3$$

$$H_2SO_3 \rightleftharpoons 2H^+ + SO_3^{2-}$$

sulphurous acid molecule | hydrogen ion | sulphite ion

(mainly molecules) (few ions)

iii) Carbon Dioxide Solution

Carbon Dioxide dissolves in water to form the weak acid carbonic acid

$$CO_2 + H_2O \longrightarrow H_2CO_3$$

$$H_2CO_3 \rightleftharpoons 2H^+ + CO_3^{2-}$$

carbonic acid molecule (mainly molecules) | hydrogen ion | carbonate ion (few ions)

iv) Other Weak Acids

- Phosphoric acid (H_3PO_4)
- Citric acid found in citrus fruits

Strong & Weak Alkalis

a) Strong Alkalis

Strong alkalis are alkalis which fully ionise to release OH^- ions

e.g. $NaOH_{(s)} \xrightarrow{(aq)} Na^+_{(aq)} + OH^-_{(aq)}$

Strong Alkali	sodium hydroxide	potassium hydroxide	lithium hydroxide
Formula	NaOH	KOH	LiOH

- Strong alkalis fully dissociate into ions

b) Weak Alkalis

Weak alkalis partially dissociate to release a few OH^- ions

e.g. ammonia solution (ammonium hydroxide)

$$NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-_{(aq)}$$

ammonia molecule | water molecule (mainly molecules) | ammonium ion | hydroxide ion (few ions)

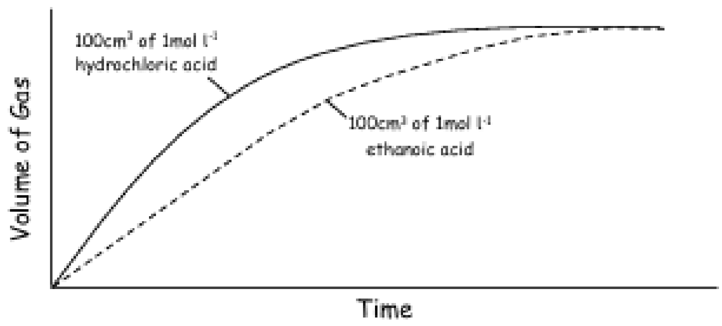
- Ammonia is slightly soluble in water

a) Comparing Hydrochloric Acid and Ethanoic Acid

- Strong acids have 100% of the H^+ ions available to react at all times
- Weak acids have only a small proportion of the H^+ ions present at any time
    - $CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$
- As the H^+ ions react with another chemical, they are removed from the equilibrium
    - concentration of product is reduced
    - equilibrium shifts to RIGHT to replace removed H^+ ions
    - more molecules of CH_3COOH dissociate to replace removed H^+ ions
    - CH_3COOH molecules will continue to dissociate to replace H^+ ions as they continue to be removed by reacting.

Property	Reaction with 100cm^3 of 1 mol l^{-1} hydrochloric acid	Reaction with 100cm^3 of 1 mol l^{-1} ethanoic acid
Degree of Dissociation	Full	Partial
Type	Strong	Weak
pH	0	4
Acidity	Higher	Lower
Electrical Conductivity	High due to many ions	Low due to few ions
Moles of alkali required for complete neutralisation	Same	Same
Rate of Reaction with 10g calcium carbonate	Faster	Slower
Reaction with 10g calcium carbonate	Same volume of gas	Same volume of gas

Reaction of acid with 10g of chalk



Same volume and concentration of strong and weak acid will

- neutralise the same volume of alkali
- give off the same volume of gas with excess chalk

NB: HCl and CH_3COOH both release one H^+ ion

- they are both described as monoprotic
- they both have a power p=1 in volumetric calculations

$$V_{acid} \times C_{acid} \times P_{acid} = V_{alkali} \times C_{alkali} \times P_{alkali}$$

- Care must be taken when comparing any acid to sulphuric acid H_2SO_4
  - H_2SO_4 fully dissociates to release $2H^+$ ions per molecule
  - H_2SO_4 is a diprotic acid (power p=2)
  - $50cm^3$ of 1 mol l^{-1} H_2SO_4 has the same neutralising ability as $100cm^3$ of 1mol l^{-1} hydrochloric acid or ethanoic acid.

b) Comparing Sodium Hydroxide and Ammonium Hydroxide

Alkali	Type	Dissociation	pH	Conductivity	Rate of Reaction	Volume of acid neutralised
Sodium Hydroxide	strong	full	higher	higher	faster	same
Ammonium Hydroxide (ammonia solution)	weak	partial	lower	lower	slower	

pH of Salts

Not all salts are pH neutral when dissolved in water.

Salts are made when the H^+ ion in an acid is replaced by a metal ion (or an ammonium ion) from a base/alkali.

There are 4 combinations of strong/weak acids and strong/weak alkalis:

Acid in Salt	Alkali in Salt	Example of Salt	pH of Salt in Water	
Strong	Strong	sodium chloride potassium sulphate	pH = 7	neutral
Weak	Strong	sodium ethanoate potassium carbonate	pH > 7	Alkaline
Strong	Weak	ammonium chloride ammonium nitrate	pH < 7	Acidic
Weak	Weak	ammonium ethanoate ammonium carbonate	This is not covered until University	

a) Salt from Strong Acid v Strong Alkali

Salts from **strong acid** v **strong alkali** neutralisation are pH=7 neutral.

- There are no weak ions from strong acids and strong alkalis

b) Salt from Weak Acid v Strong Alkali

Salts from **weak acid** v **strong alkali** neutralisations are alkaline pH>7
e.g. sodium ethanoate

- Sodium ethanoate is the salt from a sodium hydroxide v ethanoic acid neutralisation reaction.

a) H^+ ions in water and dissolved CH_3COO^- ions join up to make molecules of CH_3COOH by the following equilibrium: $\underset{\text{(few ions)}}{H^+ + CH_3COO^-} \rightleftharpoons \underset{\text{(mainly molecules)}}{CH_3COOH}$

b) H^+ ions are removed from water and equilibrium in water shifts to replace the removed H^+ ions: $H_2O \rightleftharpoons H^+ + OH^-$

c) As H_2O molecules splits into equal numbers of H^+ ions and OH^- ions

- H^+ ion concentration remains constant as the H^+ ions join up with further CH_3COO^- ions
- concentration of OH^- ions increases
- $[OH^-] > [H^+]$ $\therefore$ alkaline pH>7

pH of Salts

Not all salts are pH neutral when dissolved in water.

Salts are made when the H^+ ion in an acid is replaced by a metal ion (or an ammonium ion) from a base/alkali.

There are 4 combinations of strong/weak acids and strong/weak alkalis:

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a) Salt from Strong Acid v Strong Alkali

Salts from **strong acid** v **strong alkali** neutralisation are pH=7 neutral.

- There are no weak ions from strong acids and strong alkalis

b) Salt from Weak Acid v Strong Alkali

Salts from **weak acid** v **strong alkali** neutralisations are alkaline pH>7
e.g. sodium ethanoate

- Sodium ethanoate is the salt from a sodium hydroxide v ethanoic acid neutralisation reaction.

a) H^+ ions in water and dissolved CH_3COO^- ions join up to make molecules of CH_3COOH by the following equilibrium: $\underset{\text{(few ions)}}{H^+ + CH_3COO^-} \rightleftharpoons \underset{\text{(mainly molecules)}}{CH_3COOH}$

b) H^+ ions are removed from water and equilibrium in water shifts to replace the removed H^+ ions: $H_2O \rightleftharpoons H^+ + OH^-$

c) As H_2O molecules splits into equal numbers of H^+ ions and OH^- ions

- H^+ ion concentration remains constant as the H^+ ions join up with further CH_3COO^- ions
- concentration of OH^- ions increases
- $[OH^-] > [H^+]$ $\therefore$ alkaline pH>7

Dissociation of Acids

$HA_{(aq)}$ +	$H_2O_{(l)}$	$\rightleftharpoons$	$H_3O^+_{(aq)}$ +	$A^-_{(aq)}$
acid	base		conjugate acid (accepts proton)	conjugate base (donated proton)

$$K_a = \frac{[H_3O^+] \times [A^-]}{[HA]}$$

NB: H_2O omitted as $[H_2O] = 1$

- K_a is a measure of the strength of the acid
- The dissociation constant of an acid can be represented by pK_a
    - where $pK_a = -\log_{10} K_a$
- For strong acids equilibrium lies to the *RIGHT*
    - Effectively complete dissociation
    - K_a has little meaning for strong acids
- For weak acids equilibrium lies to the *LEFT*
    - Little dissociation e.g. less than 5% dissociation
    - K_a is a measure of the degree of dissociation
    - The smaller the K_a value, the weaker the acid

Calculation of pH of a Weak Monobasic Acid

- There is an equation to calculate the pH of a weak acid from its pK_a value and its concentration

$$K_a = \frac{[H_3O^+] \times [A^-]}{[HA]} \qquad \text{but } [H_3O^+] = [A^-]$$

$$= \frac{[H_3O^+]^2}{[HA]}$$

$$\log_{10}K_a = \log_{10}[H_3O^+]^2 - \log_{10}[HA]$$

$$\log_{10}K_a = 2\times\log_{10}[H_3O^+] - \log_{10}[HA]$$

$$\log_{10}K_a = -2pH - \log_{10}[HA]$$

$$-\log_{10}K_a = 2pH + \log_{10}[HA]$$

$$pK_a = 2pH + \log_{10}[HA]$$

- For weak acid HA of concentration c mol l^{-1}
    - [HA] at equilibrium ~ original concentration c mol l^{-1}

$$pK_a = 2pH + \log c$$

$$2pH = pK_a - \log c$$

$$pH = \tfrac{1}{2}pK_a - \tfrac{1}{2}\log c$$

The equation is only valid for weak acids where the [HA] at equilibrium is almost equal to the original concentration of HA i.e. small degree of dissociation.

- The weaker the acid, the truer the calculated pH will be from the above equation.
    - The stronger the acid, the less accurate the calculated pH will be.