1.4 Chemical Equilibrium

- Some reactions go to completion
  - Reactants form products
  - No reactants left (unless in excess)
  - e.g. $Na_2CO_{3(aq)} + 2HCl_{(aq)} \longrightarrow 2NaCl_{(aq)} + H_2O_{(l)} + \underset{\text{gas escapes}}{CO_{2(g)}}$
- Some reactions never reach completion
  - At equilibrium reactant and product concentration remains constant indefinitely
  - Must be a closed system where reactants and products cannot escape but energy can be transferred to and from the system.
    e.g. $CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + H^+_{(aq)}$
  - Rate of forward reaction is equal to the rate of the reverse reaction

Equilibrium Constant

- Every equilibrium can be described by an equilibrium constant (K)
- Equilibrium constant (K) characterises the equilibrium composition of the reaction mixture
  - High K (above 1) – higher % of products in equilibrium mixture
  - Low K (below 1) – lower % of products in equilibrium mixture
- K is measured in terms of the concentration of species at equilibrium (or in terms of partial pressures in gas equilibrium)

  For the reaction $aA + bB \rightleftharpoons cC + dD$

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

A, B, C & D are chemical formulae

a, b, c & d are stoichiometric coefficients (numbers in equation)

- Homogeneous equilibrium is when all species are in the same state
- Heterogeneous equilibrium have species are in more than one state
- Equilibrium constant K has no units
- Equilibrium constant K is independent of the particular concentrations or pressures of species in a given reaction
- When a pure solid is present in an equation or a liquid is present as a solvent, its concentration, at a given temperature, doesn't vary to a measurable extent.
  - It is given the value of 1 in equilibrium equations (due to activity)

Effect of Changing Concentration

For example:

Dilute ethanoic acid has a pH=3.0 but adding a spatula of sodium ethanoate raises pH to 3.5

$$CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + H^+_{(aq)}$$

$$CH_3COONa_{(s)} \longrightarrow CH_3COO^-_{(aq)} + Na^+_{(aq)}$$

- $CH_3COO^-Na^+$ fully ionises on solution
- pH rises as $[H^+]$ falls
    - H^+ ions react with the increased concentration of CH_3COO^- ions to form molecules of CH_3COOH
    - Position of equilibrium shifts to LEFT but value of K remains constant

$$CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + H^+_{(aq)}$$

Equilibrium shifts to left

$$K = \frac{[CH_3COO^-] \times [H^+]}{[CH_3COOH]}$$

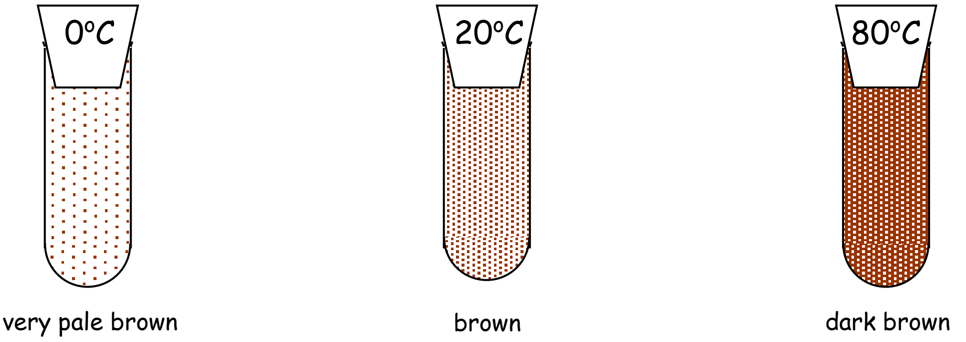
- *increase* in $[CH_3COO^-]$ is balanced by *decrease* in $[H^+]$
  increase in $[CH_3COOH]$

- Value of K remains constant by a combination of these changes

- The value of K remains constant (at the same temperature) as the equilibrium position shifts which results in changes in the concentrations of the species in the reaction
- Le Chatelier's Principle: "When a reaction at equilibrium is subjected to change, the composition alters in such a way as to minimise the effects of the change."

The Effects of Changing Temperature

$$\underset{\text{yellow}}{N_2O_4(g)} \rightleftharpoons \underset{\text{brown}}{2NO_2(g)} \qquad \Delta H = +ve$$



more N_2O_4 formed ⟷ more NO_2 formed

- From colour changes, relative concentrations of N_2O_4 and NO_2 have changed with temperature changes
- Value of K has changed
- Value of K is dependant on temperature
- Values of K constants are quoted at particular temperatures

$$N_2O_4(g) \underset{\text{exothermic}}{\overset{\text{endothermic}}{\rightleftharpoons}} 2NO_2(g) \qquad \Delta H = +ve$$

$$K = \frac{[NO_2]^2}{[N_2O_4]}$$

- When temperature 20°C is *lowered* to 0°C
  - More N_2O_4 is formed (as exothermic reaction is favoured)
  - Brown colour (from NO_2) fades

$$K = \frac{\downarrow[NO_2]^2}{\uparrow[N_2O_4]} = \textit{decrease} \text{ in value of K}$$

- When temperature 20°C is *raised* to 80°C
  - More NO_2 is formed (as endothermic reaction is favoured)
  - Brown colour darkens (from more NO_2 produced)

$$K = \frac{\uparrow[NO_2]^2}{\downarrow[N_2O_4]} = \textit{increase} \text{ in value of K}$$

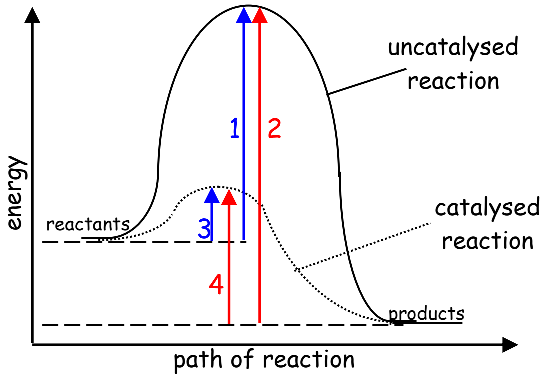
For endothermic reactions

Increase in temperature	*increase* in equilibrium constant K *increase* in product yield

For exothermic reactions

Increase in temperature	*decrease* in equilibrium constant K *decrease* in product yield

Effect of a Catalyst



1 E_a for forward uncatalysed reaction
2 E_a for reverse uncatalysed reaction
3 E_a for forward catalysed reaction
4 E_a for reverse catalysed reaction

- Catalysts lower activation energy E_a for both forward and reverse reactions by the same amount
- No change in the equilibrium concentration so position of equilibrium unchanged
- Equilibrium constant K is unaltered (at the same temperature)
- Catalysts speed up rate at which equilibrium is established

Equilibrium Constant K and Position of Equilibrium

- Value of K gives indication of how far equilibrium lies to the *left* or the *right* of a chemical reaction
    - High K means more products in the equilibrium mixture

    - Low K means more reactants in the equilibrium mixture

- K gives no indication about the rate at which dynamic equilibrium is established

- Catalysts do not increase percentage conversion of reactants to products
    - Catalysts only affect the speed at which equilibrium is attained

- For example

System	Value of K	Position of Equilibrium
$Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]$	1.7×10^7 at 25°C	K >> 1 Equilibrium lies to right (more products at equilibrium)
$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$	1.8×10^{-5} at 25°C	K << 1 Equilibrium lies to left (more reactants at equilibrium)
$N_2O_4 \rightleftharpoons 2NO_2$	0.87 at 55°C	K ~ 1 Equilibrium lies neither to left or right (similar amounts of reactants and products at equilibrium)

Acid/Base Equilibria

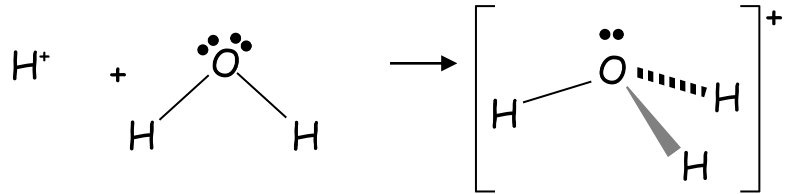
- Acids produce H^+ ions in solutions and bases produce OH^- ions in solution

- 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

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



hydronium ion → also known as: oxonium ion hydroxonium ion

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

Brϕnsted & Lowry Definitions

- 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.	HCl	+	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:

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

- 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

  $H^+_{(aq)} + OH^-_{(aq)} \rightleftharpoons H_2O_{(l)}$ $K_w = [H^+][OH^-] = 1\times10^{-14}$
  - 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
  - $H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$ $\Delta H=+ve$
  - forward reaction is endothermic (bond breaking)
  - increase in temperature favours the endothermic reaction
  - equilibrium moves to RHS more dissociation i.e. $\uparrow[H^+]$ and $\uparrow[OH^-]$

- 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

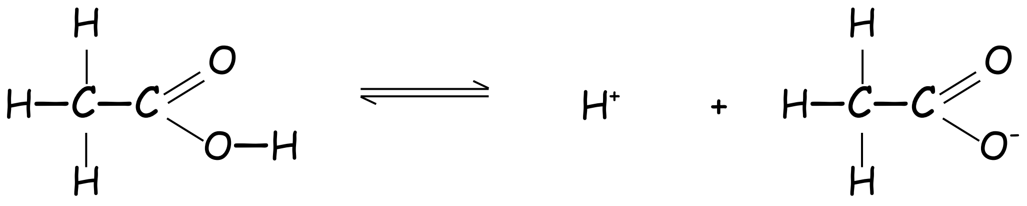
i) Ethanoic Acid (and other alkanoic acids)

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

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

$$CO_2 + H_2O \longrightarrow H_2CO_3$$

$$\underset{\substack{\text{carbonic acid molecule} \\ \text{(mainly molecules)}}}{H_2CO_3} \rightleftharpoons \underset{\text{hydrogen ion}}{2H^+} + \underset{\text{carbonate ion}}{CO_3^{2-}}$$

(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)

$$\underbrace{\underset{\text{ammonia molecule}}{NH_{3(aq)}} + \underset{\text{water molecule}}{H_2O_{(l)}}}_{\text{(mainly molecules)}} \rightleftharpoons \underbrace{\underset{\text{ammonium ion}}{NH_4^+{}_{(aq)}} + \underset{\text{hydroxide ion}}{OH^-_{(aq)}}}_{\text{(few ions)}}$$

- *Ammonia is slightly soluble in water*

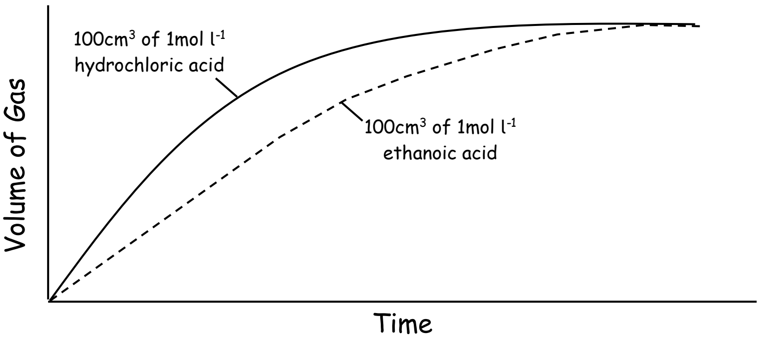
Comparing Strong and Weak Acids/Alkalis

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.

1. Write down ions in the solution	Na^+ CH_3COO^- H^+ OH^-
2. Look for a weak acid or weak alkali from these ions	Na^+ CH_3COO^- H^+ OH^-
3. Follow the following statements to work out the pH	
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	

c) Salt from Strong Acid v Weak Alkali

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

- ammonium chloride is the salt from an ammonium hydroxide v hydrochloric acid neutralisation reaction.

1. Write down ions in the solution	NH_4^+ Cl^- H^+ OH^-
2. Look for a weak acid or weak alkali from these ions	NH_4^+ Cl^- H^+ OH^-
3. Follow the following statements to work out the pH	
a) OH^- ions in water and dissolved NH_4^+ ions join up to make molecules of NH_3 and H_2O by the following equilibrium: $\underset{\text{(few ions)}}{NH_4^+ + OH^-} \rightleftharpoons \underset{\text{(mainly molecules)}}{NH_3 + H_2O}$	
b) OH^- ions are removed from water and equilibrium in water shifts to replace the removed OH^- ions: $H_2O \rightleftharpoons H^+ + OH^-$	
c) As H_2O molecules splits into equal numbers of H^+ ions and OH^- ions • OH^- ion concentration remains constant as the OH^- ions join up with further NH_4^+ ions • concentration of H^+ ions increases • $[H^+] > [OH^-] \therefore$ acidic pH<7	

Dissociation of Acids

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

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

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.

Indicators and Buffers

Indicators

- Indicators are used to determine the end point in an acid-alkali titration
- Indicators are dyes with pH-sensitive colours
- Indicators are usually weak acids

$$\underset{\text{acid}}{HIn_{(aq)}} + \underset{\text{base}}{H_2O_{(l)}} \rightleftharpoons \underset{\text{conjugate acid}}{H_3O^+_{(aq)}} + \underset{\text{conjugate base}}{In^-_{(aq)}}$$

- The unionised weak acid HIn has a distinctly different colour from the conjugate base In^-.
- The equilibrium constant for indicators is

$$K_{In} = \frac{[H_3O^+] \times [In^-]}{[HIn]}$$

$$\frac{[In^-]}{[HIn]} = \frac{K_{In}}{[H_3O^+]}$$

- The colour of the indicator is determined by the ratio of [HIn] to $[In^-]$ i.e. the relative concentrations of the two coloured forms.
  - Both [HIn] and $[In^-]$ depend on $[H_3O^+]$ i.e. the pH
- Theoretical colour change takes place when $[HIn] = [In^-]$
  - $K_{In} = [H_3O^+]$
  - $\therefore pK_{In} = pH$
- In practice, colour change in only visibly distinguishable when [HIn] and $[In^-]$ differ by a factor of 10
  - pH range over which a colour change can be seen can be estimated by the equation: $pH = pK_{In} \pm 1$

- When choosing an indicator for a titration, the colour change of the indicator (which happens over a very particular pH range) should happen when the pH of the overall titration is changing rapidly.
    - The indicator must change colour with an addition of, roughly, $\frac{1}{2}$drop of reagent if the titration is to have a reliable end-point.

For Example: <u>Strong Acid v Strong Alkali Titration</u>

0.01 mol l^{-1} NaOH titration against 50cm^3 0.01 mol l^{-1} HCl.

- pH of original 50cm^3 HCl = 2 (from 0.01 mol l^{-1} HCl)

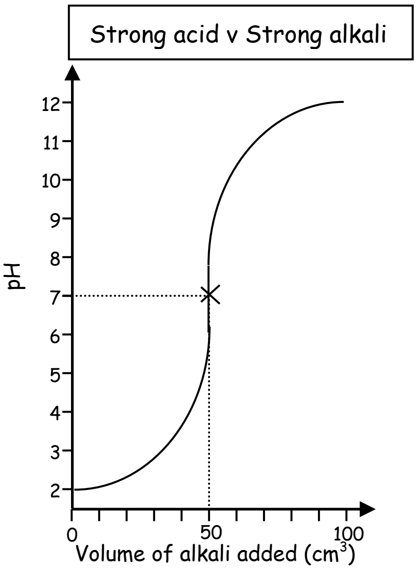
- When 49cm^3 of NaOH has been added, only 1cm^3 HCl remains
    - Total volume is 99cm^3 (~100cm^3)
    - 1cm^3 HCl in 100cm^3 volume is a 1/100 dilution
    - [HCl] is now 0.0001 mol l^{-1}
    - pH = 4

- When 49.9cm^3 of NaOH has been added, only 0.1cm^3 HCl remains
    - Total volume is 99.9cm^3 (~100cm^3)
    - 0.1cm^3 HCl in 100cm^3 volume is a 1/1000 dilution
    - [HCl] is now 0.00001 mol l^{-1}
    - pH = 5

- When 49.99cm^3 of NaOH has been added, only 0.01cm^3 HCl remains
    - pH = 6

- When 50cm^3 of NaOH has been added, no HCl remains
    - pH = 7

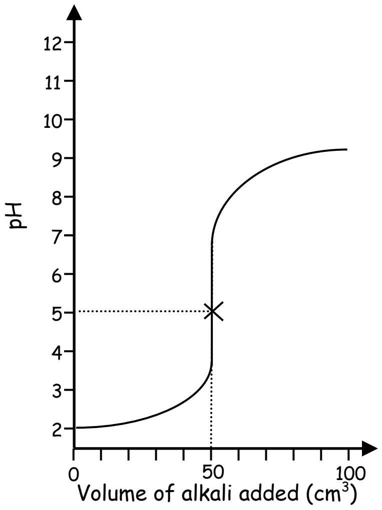
- NB. The rapid rise in pH as the endpoint of the titration is approaching
    - Adding additional NaOH beyond neutralisation endpoint achieves a similar shape of curve.



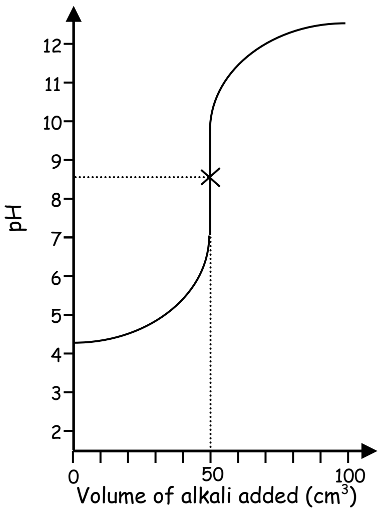
Strong acid v Strong alkali

- Titration using a combination of weak and strong acids & alkalis produces similarly shaped curves:

Strong acid v Weak alkali



Weak acid v Strong alkali



- There is a region of rapid pH change in each of the three curves
  - When choosing an indicator, the indicator should have a colour change pH range which occurs when the pH of the titration is rapid rising.

Indicator	**pH Range of Colour Change**	**Colour (HIn)**	**Colour (In^-)**
Methyl Orange	3.0 – 4.4	Orange	Yellow
Methyl Red	4.2 – 6.3	Red	Yellow
Bromothymol Blue	6.0 – 7.6	Yellow	Blue
Phenolphthalein	8.0 – 9.8	Colourless	red

- It is not possible to select an indicator for weak acid v weak alkali titrations. The titration curve generated from this titration does not produce an upward area of rapidly increasing pH at the endpoint.

Questions

1. Calculate the pK_a and K_a for
   a) Methyl orange
   b) Methyl red
   c) Bromothymol Blue
   d) Phenolphthalein

Buffers

- A Buffer solution is a solution where the pH of the solution remains approximately constant when
  - small amounts of acids or alkalis are added
  - the solution is diluted with water

Acidic Buffers

- Acidic buffers contain
  - A solution of a weak acid

$$HA_{(aq)} + H_2O_{(l)} \xrightleftharpoons{\text{equilibrium}} H_3O^+_{(aq)} + A^-_{(aq)}$$

Equilibrium lies well to *LEFT*

  - One of the salts of that weak acid

$$NaA_{(aq)} \xrightarrow{\text{fully ionises}} Na^+_{(aq)} + A^-_{(aq)}$$

  - Large $[A^-]$ from ionisation of NaA
    - Equilibrium shifts to *LEFT* , increasing [HA]
  - Addition of H^+ ions/acid
    - As $[A^-] >> [H^+]$, buffer has ability to remove large quantity of H^+ ions
    - $H^+ + A^-$ ions re-associate forming HA molecules.
  - Addition of OH^- ions/alkali
    - OH^- ions decrease $[H^+]$ by neutralisation reaction
    - Equilibrium shifts to *RIGHT* to replace H^+ ions
    - HA molecules dissociate to produce H^+ ions and A^- ions
-

Calculation of the pH of a Buffer

- To calculate the pH of a buffer, the following equation can be used:

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

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

where
[HA] = concentration of weak acid (little dissociation of HA to A^-)

$[A^-]$ = concentration of fully ionised salt (little A^- from dissociation of acid)

$$\boxed{[H_3O^+] = \frac{K_a \times [Acid]}{[Salt]}}$$

$$\boxed{pH = pK_a - \log_{10}\frac{[Acid]}{[Salt]}}$$

- If the buffer has water added, both [salt] and [acid] are equally diluted and this has no effect on the ratio of [acid] to [salt]
    - $[H_3O^+]$ is unaffected
    - pH is unaffected

- good buffers must have reasonable reserves of A^- and HA
    - adding H^+ ions removes A^-
    - adding OH^- dissociates $HA \longrightarrow H^+ + A^-$
    - if buffer has [salt] = [acid], then buffer has equal ability in resisting pH change by the addition of H^+ or OH^-.

Questions

1. Calculate the pH of the buffer solution made from 1.0 mol l^{-1} methanoic acid and 1.78 mol l^{-1} sodium methanoate solution. The pK_a of methanoic acid is 3.8.
2. Calculate the pH of the buffer solution made from 0.1 mol l^{-1} solutions of ethanoic acid *and* potassium ethanoate. The pK_a of ethanoic acid is 4.8.

- The composition of an acid buffer can be calculated from the same equation

e.g. Calculate the concentration ratio of [acid]:[salt] for a propanoic acid buffer with pH=5. The pK_a of propanoic acid = 4.9

$$pH = pK_a - \log_{10}\frac{[Acid]}{[Salt]}$$

$$5.0 = 4.9 - \log_{10}\frac{[Acid]}{[Salt]}$$

$$\log_{10}\frac{[Acid]}{[Salt]} = -0.1$$

$$\frac{[Acid]}{[Salt]} = 0.794$$

<u>Answer</u>: Dissolve 0.794 moles of propanoic acid and 1 mole of sodium propanoate in 1 litre of water (or similar proportionate amounts)

Questions

1. Calculate the concentrations of acid and salt solutions required to make:
    a) a buffer of pH=6.0, made with carbonic acid (pK_a = 6.4) and sodium hydrogencarbonate
    b) a buffer of pH=3.1, made from chloroethanoic acid (pK_a=2.9) and its potassium salt.

Examples of Buffers

Buffers are important chemical systems in chemistry and in biological systems:

- enzymes work in narrow pH environments
    - amylase in saliva and the small intestine require a slightly alkaline pH to function with optimum activity

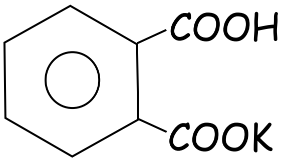
- Blood is buffered at pH=7.4
    - CO_2/bicarbonate equilibrium (bicarbonate = hydrogencarbonate)
    - Excess CO_2 removed by exhalation in lungs
    - Excess bicarbonate removed by excretion in urine

- The sea is buffered to a particular pH
    - Marine life required stable pH for survival
    - Sea water contains significant concentration of carbonate and bicarbonate ions

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \rightleftharpoons 2H^+ + CO_3^{2-}$$

- Phosphate solutions act as buffers
    - 2nd and 3rd dissociations of H_3PO_4 are weak
    - $H_3PO_4 \longrightarrow H^+ + H_2PO_4^-$
    - $H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$
    - $HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$

- A useful all-in-one buffer is potassium hydrogenphthalate
    - The weak acid and its salt are in the same molecule



Partition Coefficient

- When a solute is shaken in 2 immiscible liquids
    - If solute is soluble in both liquids
    - Some solute dissolves in both liquids

- Solute partitions (distributes) itself between the liquids in a definite ratio called the partition coefficient.

- The value of the partition coefficient depends on
    - The solute used
    - two immiscible liquids
    - the temperature

e.g. I_2 dissolves in both $KI_{(aq)}$ and $CHCl_{3(l)}$

$$K = \frac{[I_2] \text{ in } KI_{(aq)}}{[I_2] \text{ in } CHCl_{3(l)}}$$

Solvent Extraction

- The most common application of partition coefficients is solvent extraction

- This is often used for purification of chemicals

  e.g. impure carboxylic acid dissolved in water

  - Carboxylic acid can be extracted from aqueous solution by adding another immiscible liquid (ethoxyethane/ether)
  - Carboxylic acid dissolves in ether but the impurities stay in the water

- It is more efficient to use small volumes of organic solvent in repeated extractions rather than one larger volume in a single extraction.

Worked Example: 10 g of carboxylic acid dissolved in 100cm^3 of water

a) Single extraction with 100cm^3 ether (with *v* grams extracted)

$$K = \frac{[\text{Acid}]_{\text{ether}}}{[\text{Acid}]_{\text{water}}} = 5$$

$$\frac{v/100}{(10-v)/100} = 5$$

$$\frac{v}{10-v} = 5$$

$$\begin{aligned} v &= 5\,(10 - v) \\ v &= 50 - 5v \\ 6v &= 50 \\ v &= 50 / 6 \\ &= 8.33\text{g} \end{aligned}$$

b) w, x, y and z grams of carboxylic acid are extracted in successive extractions using 25cm^3 of ether each time.

Extraction 1:

$$K = \frac{[\text{Acid}]_{\text{ether}}}{[\text{Acid}]_{\text{water}}} = 5$$

$$\frac{w/25}{10 - w/100} = 5$$

$$\frac{4w}{10 - w} = 5$$

$$\begin{aligned} 4w &= 5\,(10 - w) \\ 4w &= 50 - 5w \\ 9w &= 50 \\ w &= 50 / 9 \\ &= 5.56\text{g} \end{aligned}$$

Mass of carboxylic acid remaining in water = 10g – 5.56g = <u>4.44g remaining</u>

Extraction 2:

$$K = \frac{[\text{Acid}]_{\text{ether}}}{[\text{Acid}]_{\text{water}}} = 5$$

$$\frac{x/25}{4.44 - x/100} = 5$$

$$\frac{4x}{4.44 - x} = 5$$

$$\begin{aligned} 4x &= 5\,(4.44 - x) \\ 4x &= 22.2 - 5x \\ 9x &= 22.2 \\ x &= 22.2 / 9 \\ &= 2.47\text{g} \end{aligned}$$

Mass of carboxylic acid remaining in water = 4.44g – 2.47g = <u>1.97g remaining</u>

Extraction 3:

$$K = \frac{[\text{Acid}]_{\text{ether}}}{[\text{Acid}]_{\text{water}}} = 5$$

$$\frac{y/25}{1.97 - y/100} = 5$$

$$\frac{4y}{1.97 - y} = 5$$

$$\begin{aligned} 4y &= 5\,(1.97 - y) \\ 4y &= 9.85 - 5y \\ 9y &= 9.85 \\ y &= 9.85 / 9 \\ &= 1.09\text{g} \end{aligned}$$

Mass of carboxylic acid remaining in water = 1.97g – 1.09g = <u>0.88g remaining</u>

Extraction 4:

$$K = \frac{[\text{Acid}]_{\text{ether}}}{[\text{Acid}]_{\text{water}}} = 5$$

$$\frac{z/25}{0.88 - z/100} = 5$$

$$\frac{4z}{0.88 - z} = 5$$

$$\begin{aligned} 4z &= 5\,(0.88 - z) \\ 4z &= 4.40 - 5z \\ 9z &= 4.40 \\ z &= 4.40 / 9 \\ &= 0.49\text{g} \end{aligned}$$

Total Carboxylic Acid Extracted $= w + x + y + z$

$= 5.56 + 2.47 + 1.09 + 0.49$

$= 9.61\text{g}$