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.

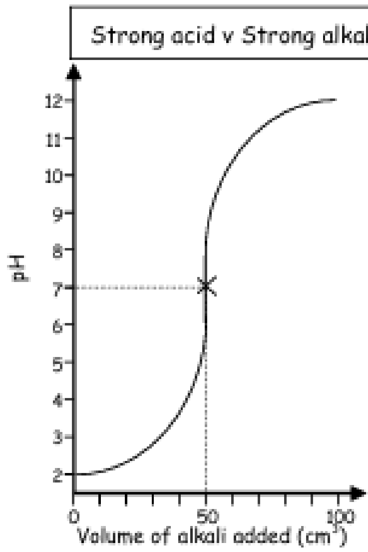
- pH of original 50cm^3 HCl = 2 (from 0.01 mol l^{-1} HCl)

- 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.

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    - 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 $99cm^3$ ($\sim100cm^3$)
    - $1cm^3$ 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 $99.9cm^3$ ($\sim100cm^3$)
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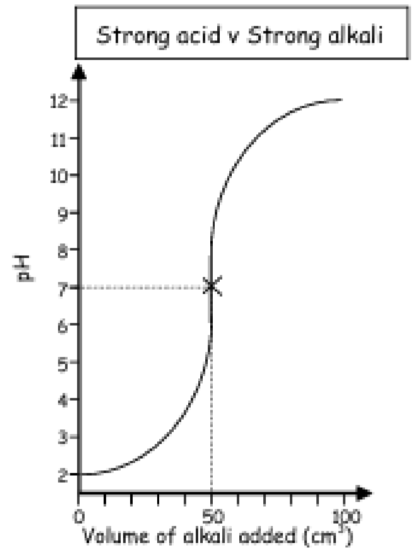
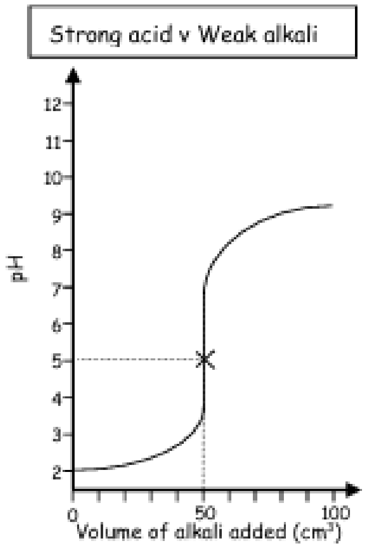
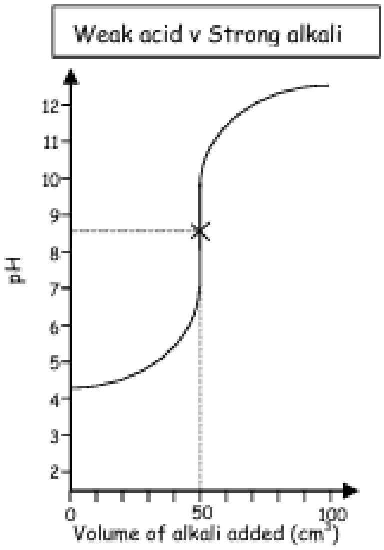


- NB. The rapid rise in pH as the endpoint of the titration is approaching
    - Adding additional NaOH beyond neutralisation endpoint achieves a similar shape of curve.

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





- 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

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

$\boxed{\text{Equilibrium lies well to } \textit{LEFT}}$

  - 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)

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

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

- 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