Summary sheet of volumetric analysis.

Know your definitions

Standard solution – A solution whose concentration is accurately known, This solution usually goes into the burette

Primary standard – A substance that is used to make a standard solution. A primary standard should:

- have a high molecular mass. This will reduce the error in calculations.
- have a known formula mass.
- have a high degree of purity.
- not react with the atmosphere or decompose
- be highly soluble

Equivalence point – Is a point in the titration where the mol of the titrant is in the exact stoichiometric ratio as the mol of the substance being titrated. In other words, the reaction is complete as all the substance in the conical flask has fully reacted with the substance titrated from the burette. The equivalence point is not obvious to the person performing the titration.

End point – Is a point in the titration where the indicator changes colour to signal the end of the titration procedure. Ideally the end point should be reached in the next drop delivered by the burette.

Indicator – is a substance that changes colour within a certain pH range and is used to indicate the end point of a titration. Ideally the indicator should change colour as close to the equivalence point as possible.

Titre - The volume of solution delivered by the burette, as shown on the right, in order to reach the end point.

Concordant titres – titres whose highest value differs from the lowest value by no more than 0.10 mL.
eg 21.80 mL, 21.75 mL, 20.70 mL.

Aliquot – an *accurate fixed* volume of solution delivered with a pipette.

Burette – delivers *an accurate variable* volume of solution. Volume of the titre should be read to two decimal places

Ph Curve - shows how the pH of a solution in the conical flask changes as the titration proceeds. A pH curve os the titration of a weak acid against a strong base is shown on the right.

Volumetric flask – Is used to dilute concentrated solutions of unknown substances before titrating.
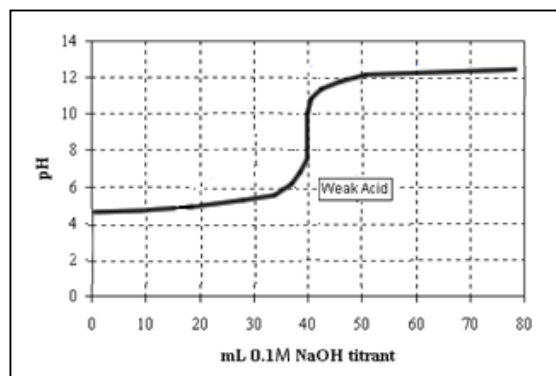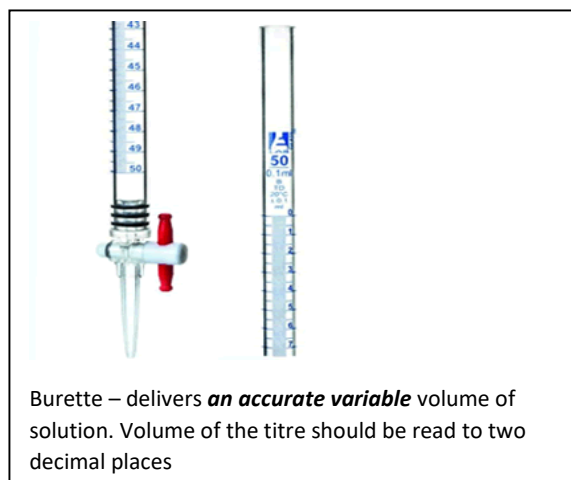
What can a pH curve tell us? Consider the pH curve shown on the right of a titration of two monoprotic acids. Information that can be obtained from the curves includes:
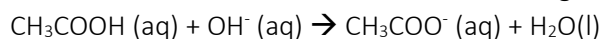- The strength of the acid or base used. Judging by the shape of each curve we can tell that A is a weak acid and B is a strong acid. The final pH of around 13 indicates that the base used is a strong base.
- The equivalence point of a weak acid vs strong base titration is above pH 7 while the equivalence point of strong acid is around pH 7.
- Judging by where the equivalence point is on the curve an appropriate indicator can be found.
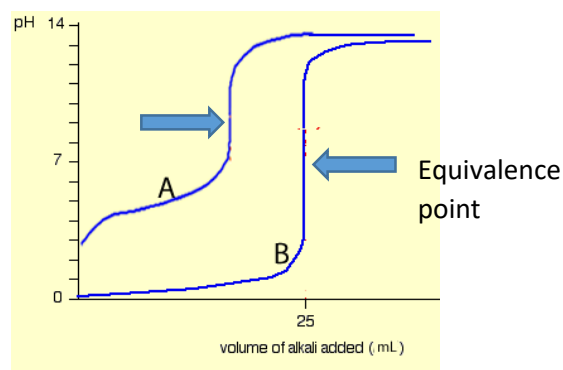

 The reason why the equivalence point is not always at pH 7 is linked to the conjugate acids and bases of the reactants.
For example, consider the titration of acetic (ethanoic acid) with NaOH, the pH curve is shown on the right.
The reaction between acetic acid and NaOH is given below.
$CH_3COOH (aq) + OH^- (aq) \rightarrow CH_3COO^- (aq) + H_2O(l)$
CH_3COO^- is a medium strength base so at the point where CH_3COOH and OH^- have reacted in the stoichiometric ratio the solution will have acetate (CH_3COO^-) ions present thus forming a basic or alkaline solution.
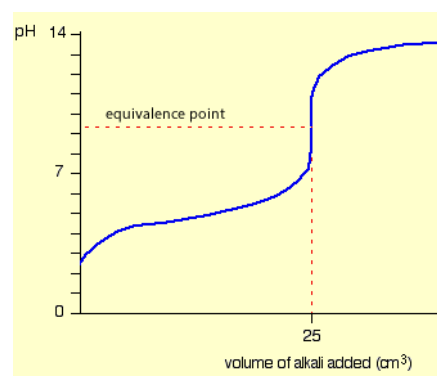
Just to summarise:
-- when titrating a strong acid with a strong base, pH = 7 at equivalence point
-- when titrating a weak acid with a strong base, pH > 7 at equivalence point
-- when titrating a strong acid with a weak base, pH < 7 at equivalence point

Examples of a weak acid include.
- HF, CH_3COOH, H_2CO_3, H_3PO_4
Examples of strong acid
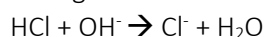- HCl, H_2SO_4 , HNO_3
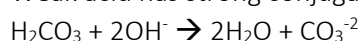Examples of weak base
- NH_3
Examples of a strong base
- KOH, NaOH, LiOH

Summary of strength of acid and conjugate base
        strong acid has a weak conjugate base eg
        $HCl + OH^- \rightarrow Cl^- + H_2O$
        Weak acid has strong conjugate base eg
        $H_2CO_3 + 2OH^- \rightarrow 2H_2O + CO_3^{-2}$

In a titration two things are needed to calculate the concentration of the unknown solution.

1 – The exact volume of the standard solution delivered.
- With which to calculate the mol of primary standard delivered in each titre.

2 – A balanced chemical equation for the reaction between the reactants in each solution.
- A balanced chemical equation will give the stoichiometric ratio between the two reactants, hence knowing the mole of primary standard we can find the mole of unknown present.

Errors

Washing glassware

- Burette- always rinsed with the solution that will be delivered by the burette.
  errors – rinsing with water – dilutes the solution in the burette.
  impact on titre – increased

- Pipette – washed with the solution it will deliver
  errors – rinsing with water – dilutes the solution in the pipette
  impact on titre – decrease

- Flask – can be washed with water.

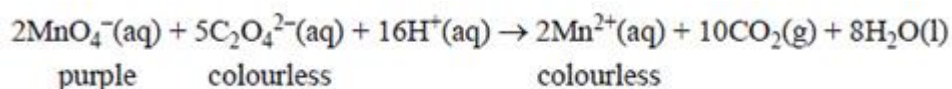- Volumetric flask – can be washed with water.

Reading the burette.

There is always an uncertainty of ± ½ of the smallest unit marked on the scale of the instrument. In the case of the burette the smallest unit marked is 0.10mL hence the uncertainty in reading the burette is ± 0.05 mL
When taking the difference of two readings, such as when calculating the titre we add the uncertainties of each reading. Eg a titre of 21.11 mL has an uncertainty of ± 0.10 mL.
The percentage uncertainty is given by the expression (0.10/21.11) X 100 = 0.47%

When answering a volumetric analysis question involving many steps of dilution of the original sample a diagram is essential to back track. Consider the example below.

A clear, colourless liquid extract of the rhubarb plant was analysed for the concentration of oxalic acid, $H_2C_2O_4$, by direct titration with a recently standardised and acidified potassium permanganate solution, $KMnO_4(aq)$. The balanced equation for this titration is shown below.

$$2MnO_4^-(aq) + 5C_2O_4^{2-}(aq) + 16H^+(aq) \rightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l)$$
$$\text{purple} \quad \text{colourless} \quad\quad\quad \text{colourless}$$

The steps in the titration were as follows:
Step 1 – A 20.00 mL aliquot of the rhubarb extract was placed in a 250 mL volumetric flask and made to the mark with distilled water
Step 2 – A 20.00 mL aliquot of the diluted rhubarb extract from the volumetric flask was placed in a 200 mL conical flask.
Step 3 – The burette was filled with acidified 0.0200 M $KMnO_4$ solution.
Step 4 – The acidified 0.0200 M $KMnO_4$ solution was titrated into the rhubarb extract in the conical flask. The titration was considered to have reached the end point when the solution in the conical flask showed a permanent change in colour to pink. The volume of the titre was recorded.
Step 5 - The titration was repeated until three concordant results were obtained. The average of the concordant titres was 21.7 mL.

Find the concentration of $H_2C_2O_4$ in the original sample of rhubarb extract in %(w/v)

Unpacking all this information is difficult so draw a flow diagram.

20.00mL
original
sample

20.00mL
aliquot is
taken

21.7 mL
average titre

Step 1 Calculate the mol of MnO_4^- *delivered in the 21.7 mL titre.*
=> n = C X V = 0.0200 X 0.0217 = 4.34 X 10⁻⁴ mol
Step 2 Calculate the mol of $C_2O_4^{-2}$ present in the flask. using the stoichiometric ratio.
=> (5/2) X 4.34 X 10⁻⁴ mol = 1.085 X 10⁻³
Step 3 Find the total amount of $C_2O_4^{-2}$ present in the volumetric flask
=> (250 / 20) X 1.085 X 10⁻³ = 0.01356
Step 4 Find the concentration of the original sample in %w/v
=> mass of $H_2C_2O_4$ *= 0.01356 X 90.0 = 1.22 grams*
=> (1.22 / 20.00) X 100 = 6.10 %(w/v)