VOLUMETRIC ANALYSIS

The process of determining the quantity of a substance A by adding measured increments of substance B, with which it reacts (almost always as a standardised solution called the titrant) with provision for some means of recognising (indicating) the endpoint at which essentially all of A has reacted.

DEFINITIONS:

- Primary standard – a pure substance (a solid) which: is easily obtained in a high state of purity, is easily maintained in a high state of purity, has high stability, low hygroscopicity, soluble in appropriate solvent (usually water), high molar mass (minimise weight errors), known formula, non-toxicity and inexpensive.
- Standard solution – a solution in which the concentration of substance is accurately known.
- Standardisation – an experimental procedure in which the accurate molarity of a solution is determined.
- Indicator – a weak acid made from plant extracts that changes colour at particular pH levels, thus assisting in detection of an end point in titrations.
- Concordant titres – a series of titrations in which the volume produced from the burette (titre) differ by a maximum of 0.10mL. For accurate results, at least three concordant titres are needed.
- Strong/weak acid/base – strong acid/base completely ionise in water, whereas weak acid/base partially ionise in water.
- Buffer – an aqueous solution consisting of a mixture of a weak acid and its conjugate base or a weak base and its conjugate acid. Its pH changes very little when a small amount of strong acid or base is added to it and thus it is used to prevent changes in the pH of a solution.
- Buffer capacity – the capacity of a solution to resist changes in pH on addition of acid or base, which may be expressed numerically as the number of moles of strong acid or strong base required to change the pH by one unit when added to one litre of the specified buffer solution.
- End point - The point in a titration at which some property of the solution (as, for example, the colour imparted by an indicator) shows a pronounced change, corresponding more or less closely to the equivalence point.
- Equivalence point - The point in a titration at which the amount of titrant added is chemically equivalent to the amount of substance titrated (stoichiometric ratios).
- Titrant – the solution containing the active agent with which a titration is made (delivered from burette).
- Aliquot – another name for ‘a known volume’.
- Titre – the volume of titrant consumed in a reaction.
- Titration error – the volume difference between the end point value and equivalence point value which should be extremely small to minimise error.

Note: Standard solutions are classified into two types:

- **PRIMARY** – a standard solution prepared from a primary standard substance whose concentration is known from the mass of that substance in a known volume of the solution.
- **SECONDARY** – a solution whose concentration or titre has been obtained by standardisation, or which has been prepared from a known volume of a secondary standard substance.

ERRORS:

- Rinsing incorrectly.
- Not all substance was transferred into volumetric flask/conical flask.
- Indicator error (systematic) because of the different between equivalence and end point.
- Conical flask is not swirled during titration will result in the solution in the flask ceasing to be homogenous and thus the end colour would change earlier than it should.
- Using incorrect indicator that changes at wrong pH.
- Adding more solution after indicator has changed colour (overshooting the end point).
- Incorrectly measuring meniscus level.

RINSING:

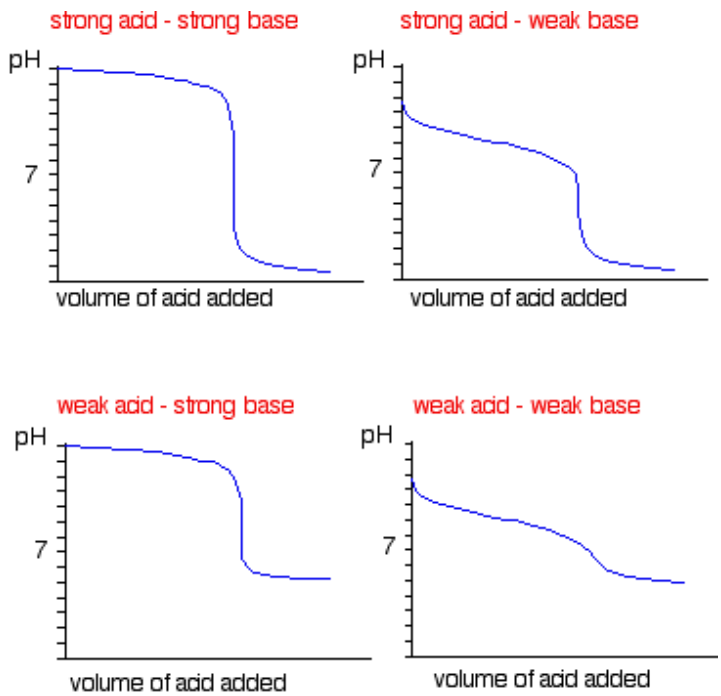
Burette – washed with the solution it is dispensing

Volumetric flask – washed with distilled water

Pipette (bulb or graduated) – washed with the solution it is dispensing

Conical flask – washed with distilled water

TITRATION CURVES:



****Note:**

- The units of concentration can be stated as: % (m/m), % (w/w), % (V/V), % (m/V), ppm or ppb. For example, 3.2% (m/V) means 3.2g of ingredient per 100mL of solution. Also, ppm is equivalent to µg/mL and mg/L, or X (g or mL) per 10^6 (g or mL) of substance.

- The back titration technique is when a deliberate excess of reactant X is added to reactant Y. X is usually in a known volume of a standard solution. Y is either of known mass of a solid (usually impure) or a known volume of a solution of that solid. X and Y react in accordance with a known solution. The quantity of unreacted X is determined in a titration against a standard solution of Z, which reacts with X in accordance with a known equation. From all this, something of interest (% purity, molar mass etc.) about Y may be determined.

- For volumetric analysis, an appropriate indicator should be chosen. An acid/base indicator displays a colour change in response to a pH change. They change colour over a range of pH rather than at a definite pH values. Most indicators used in volumetric work are weak acids and, while their structures are quite involved, we can abbreviate to HIn for the general indicator. Since it is a weak acid, it may undergo acid hydrolysis via:

  $HIn_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + In^-_{(aq)}$

- The colour displayed by an acid-base indicator depends on the pH and hence the $[H_3O^+]$ in solution which varies over the course of a titration.