

Exercise 0 TITRATION

Theory:

In chemistry a *solution* is a homogeneous mixture composed of two or more substances.

In such a mixture: a *solute* is dissolved in another substance, known as a *solvent*. An *aqueous solution* is a solution in which the solvent is water.

Concentration is the measure of how of a given substance (solute) there is mixed with another substance (solvent). There are a number of different ways to quantitatively express concentration; in this work we will use molar concentration.

Molar concentration (*molarity*) denotes the number of moles (*n*) of a given substance per litre (resp. dm^{-3}) of solution:

$$c = \frac{n}{V} \quad (\text{mol dm}^{-3} \text{ or M}) \quad \text{or} \quad c = \frac{m}{MV} \quad (1)$$

where *V* – is the volume of solution (in dm^3)

m – is the mass of a given substance (in grams)

M – is the molar mass (in g mol^{-1})

Titration is a common laboratory method of quantitative/chemical analysis that can be used to determine the unknown concentration of a known reactant (*analyte*). The basis of the method is a chemical reaction of a *standard solution (titrant)* with a solution of an *analyte*.

The *analyte (described A)* is a solution of the substance whose concentration is unknown and sought in the analysis.

The *titrant (described T)* is a solution in which the concentration of a solute is precisely known.

Because volume measurements play a key role in titration, it is also known as *volumetric analysis*. Usually it is the volume of the titrant required to react with a given quantity of an analyte that is precisely determined during a titration.

Using a calibrated burette (**Figure 1**) to add the titrant, it is possible to determine the exact amount that has been consumed when the *endpoint* of titration is reached. The endpoint is the point at when the titration is complete, as determined by an *indicator* (see below).

At the titration *endpoint*, the quantity of reactant in the titrant added during the titration is stoichiometrically equivalent to the quantity of reactant in the analyte. This is ideally the same volume as the *equivalence point* – the volume of added titrant at which the number of *moles of titrant (n_T)* is equal to the number of *moles of analyte (n_A)*, is in stoichiometric ratio of the given chemical reaction.

Titrations can be classified by the type of reaction. Different types of titration reaction include acid-base titrations, complexometric titrations, etc. Within practicals from physical chemistry we will deal with acid-base titrations.

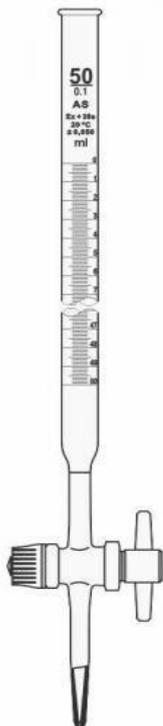
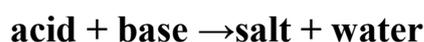


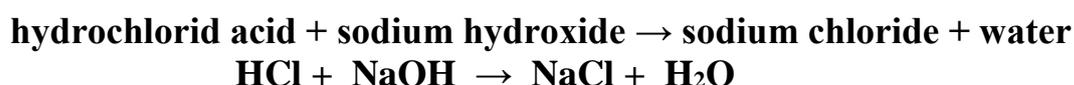
Figure 1 Calibrated burette

Acid-base titrations are based on the neutralization reaction between the analyte and an acidic or basic titrant. These most commonly use a pH meter, or a conductance meter to determine the endpoint. In our experiments we will use a pH indicator to detect the endpoint of the reaction.

Neutralization is a chemical reaction, also called a **water forming reaction**, in which an acid and a base or alkali (soluble base) react and produce a salt and water:



For example, the reaction between hydrochloric acid and sodium hydroxide solutions:



Before starting the titration a suitable pH indicator must be chosen. The endpoint of the reaction, when all the products have reacted, will have a pH dependent on the relative strengths of the acids and bases. The pH of the endpoint can be roughly determined using the following rules:

- A strong acid reacts with a strong base to form a neutral (pH=7) solution.
- A strong acid reacts with a weak base to form an acidic (pH<7) solution.
- A weak acid reacts with a strong base to form a basic (pH>7) solution.

When a weak acid reacts with a weak base, the endpoint solution will be basic if the base is stronger and acidic if the acid is stronger. If both are of equal strength, then the endpoint pH will be neutral.

Frequently, during a titration it is also useful to monitor the progress of the titration with

a graph. This graph is known as a titration curve. Such a curve reflects the changes in pH that occur as titrant is added from a burette to the analyte in the beaker below the burette (**Figure 2**).

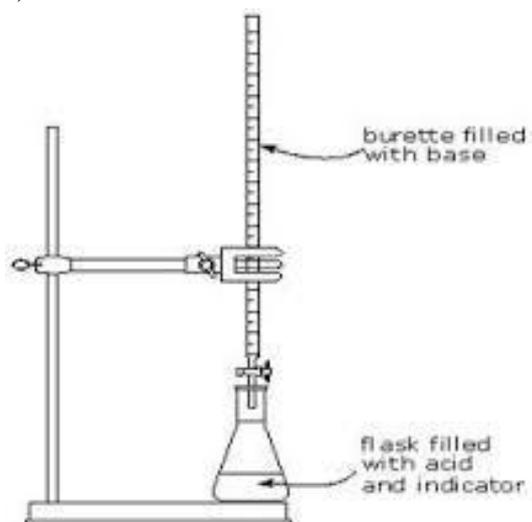


Figure 2 Scheme of titration

There are two different types of acids that can be titrated, besides being strong or weak. They are known as being monoprotic or polyprotic:

Monoprotic acids contain one acidic hydrogen, for example hydrochloric acid (HCl), nitric acid (HNO₃), acetic acid (CH₃COOH), etc. Titration curve of strong monoprotic acid with strong base is shown in Figure 3A.

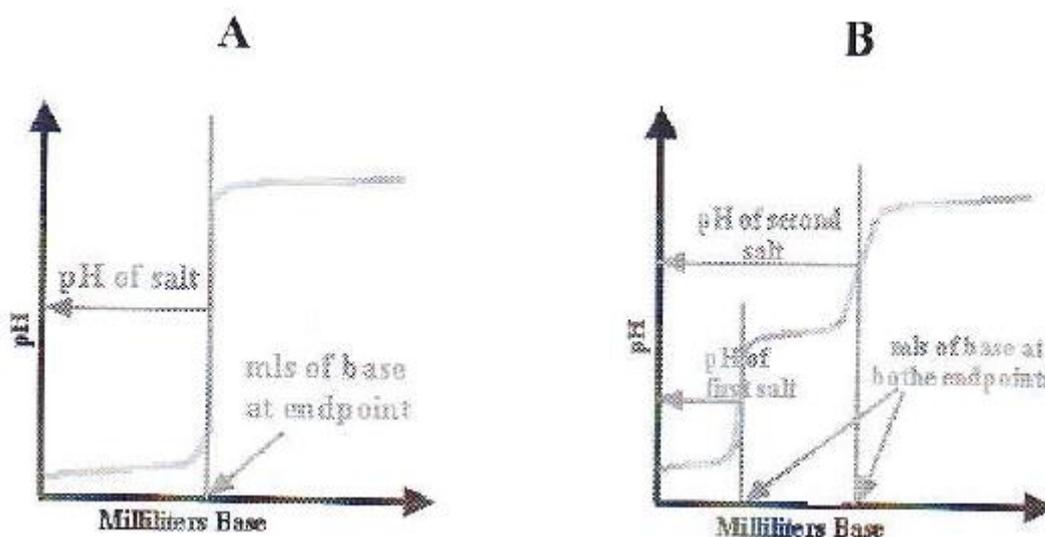
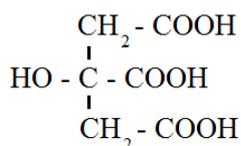


Figure 3 Titration curve of strong monoprotic and polyprotic acids with strong base

Polyprotic acids contain more than one acidic hydrogen. They are always identified by their formulas showing more than one H. Specifically, a **diprotic acid** will have two hydrogens – sulphuric acid (H₂SO₄), succinic acid [(CH₂)₂-(COOH)₂], a **triprotic acid** will have three hydrogens – phosphoric acid (H₃PO₄), citric acid:



Titration curve of strong diprotic acid with strong base is shown in **Figure 3B**.

A suitable indicator should be chosen, that will experience a change in color close to the end-point of the reaction.

pH indicators are generally very complex organic molecules (frequently weak acids or bases). When introduced into a solution, they bind to H^+ or OH^- ions. They will contain a structural component that is called a chromophoric group, or chromophore. This group will have a structure that changes slightly when the pH of the system changes. The indicator will have one structure through one range of pH values, and a second structure through a second range of pH values. When the structure changes, as a response to pH, the chromophore will also change its color, for more information see e.g.

<http://www.bcpl.net/~kdrews/titration/indicators.html>

In our exercises we will titrate weak acids (acetic, succinic, citric) (resp. strong acid HCl) with a strong base (NaOH). We will use phenolphthalein ($\text{C}_{20}\text{H}_{14}\text{O}_4$) – **Figure 4** as pH indicator. It is colorless in acidic solutions ($\text{pH} < 8.2$), and in basic solutions it turns from weak pink up to fuchsia color ($\text{pH} \sim 10$).

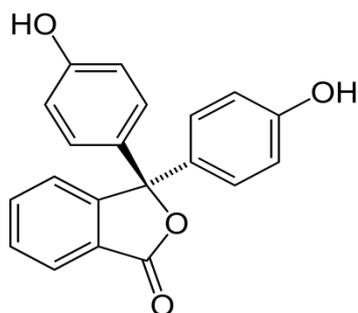


Figure 4 Structure of phenolphthalein

Titration procedure:

- 1 The burette is filled with a standard solution (**titrant, base**) of known concentration c_T (mol dm^{-3} or M).
- 2 A known volume V_A of the **analyte (acid)** is placed in a titration flask.
- 3 Before the titration is started, 1 drop of indicator (phenolphthalein) is placed in the titration flask with the analyte (acid).
The chosen indicator must be colorless, when the solution is acidic.
- 4 A base solution is then slowly added from the burette, drop by drop.
The titration continues, drop by drop, until the indicator suddenly achieves the color (weak pink) which corresponds to the **point of equivalence**, that is the end of the titration. Over titrated mixture has **fuchsia color**. Over titration is when too much titrant is added to the analyte in a titration procedure
The endpoint will correspond to a perfect stoichiometric ratio between the acid and the base.

- Once the endpoint has been reached, the burette must be read. The bottom of the meniscus line determines the quantity of the base V_T that was required to reach the endpoint.
- Once the titration is completed, the final calculations can be done.

Calculations:

Calculating the concentration c_A (M) of the analyte (acid):

- From the chemical equilibrium

moles analyte (acid) = moles titrant (NaOH)

$$n_A = n_T \quad (2)$$

- moles titrant: $n_T = V_T c_T$ (3)

- for monoprotic acid $n_T = n_A$,

the concentration of the analyte (monoprotic acid) $c_A = \frac{n_A}{V_A}$ (4)

Polyprotic acids contain more than one acidic hydrogen, so stoichiometric ratio between the acid and the base is for:

diprotic acids $2 n_A = n_T$

triprotic acids $3 n_A = n_T$

Task:

Determination of the molar concentration of acids by titration

Equipments and chemicals:

burette, pipettes, titration flask, funnel, beaker, distilled water, phenolphthalein,

analyte: hydrochlorid acid, acetic acid, citric acid

titrant: sodium hydroxide (0.2 mol dm^{-3})

Determination of the molar concentration of HCl by titration with NaOH

Chemical reaction: $\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O}$

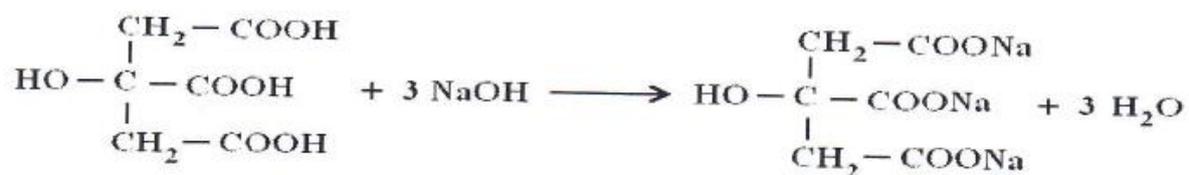
Procedure:

- Fill the burette (**Figure 1** and **2**) with a standard solution of NaOH (titrant). Read the concentration of titrant c_T (mol dm^{-3}) from the bottle and write it down to the table 1.
- Fill the titration flask with $V_A = 10 \text{ ml}$ of HCl from the stock HCl solution. An approximated concentration c_{APP} (mol dm^{-3}) of the stock solution is marked on the bottle with HCl, write it down to the **Table 1**.
- Add 1 drop of phenolphthalein to the solution of acid.
- Perform the titration.
- When the endpoint of titration has been reached, read the used volume of NaOH from the burette (V_T). Write it down to the **Table 1**.
- Repeat the procedure.

- Each student must perform two titrations of each analyte - acid. Determine the average volume of titrant from two titrations V_T (ml).
- Applying **Equations 2 – 4**, calculate the precise concentration of HCl, c_A (mol dm⁻³).

Determination of the molar concentration of citric acid by titration with NaOH

Chemical reaction:



Repeat the same procedure as above. Citric acid is a triprotic acid, so correct the **Equations 2 – 4** for stoichiometric ratio according the reaction.

Determination of the molar concentration of acetic acid by titration with NaOH

- Write the chemical reaction of acetic acid with NaOH.
- Repeat the same procedure as for titration of hydrochloric acid. The concentration of acetic is unknown.

Table 1 Measured and calculated values

Acid	V_A (ml)	c_{APP} *	titrant c_T *	V_T (ml)		\overline{V}_T ** (ml)	c_A (mol dm ⁻³)
				I	II		
HCl	10						
citric	10						
acetic	10	-----					

* unit: mol dm⁻³

**average volume from two titrations of acids (I and II)

Compare concentrations c_{APP} and c_A in conclusions of your report. Express the deviation in %, supposing the value of c_{APP} is 100%

Report

The report must include:

- Theory
- Equipments and chemicals
- Method and used procedure
- Table of results and calculations
- Conclusion

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