

Appendix – Titration: Theory + Practice

Colour changes of some indicators in pH measurement

| | |
|-----------------------------|-------------------|
| Methyl orange (helianthine) | pH 3.1 to pH 4.4 |
| Bromophenol blue | pH 3.0 to pH 4.0 |
| Bromocresol green | pH 4.0 to pH 5.6 |
| Methyl red | pH 4.2 to pH 6.2 |
| Bromothymol blue | pH 6.2 to pH 7.6 |
| Phenolphthalein | pH 8.0 to pH 10.0 |

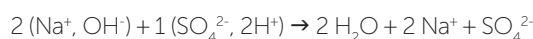
Equations of some titration reactions

The syntax below is used to show the relationship between titrant and analyte during the reaction which helps explain the stoichiometry of the reactions.

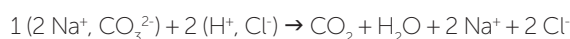
Acid/base reactions



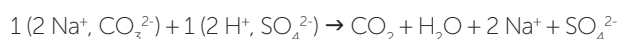
Reaction of sodium hydroxide with a monobasic acid



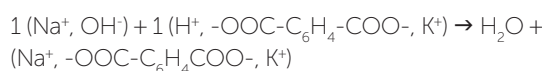
Reaction of sodium hydroxide with a dibasic acid



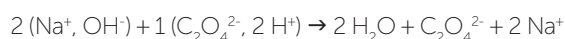
Complete neutralisation of sodium carbonate by hydrochloric acid



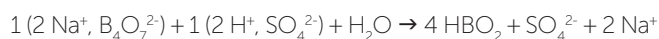
Complete neutralisation of sodium carbonate by sulphuric acid



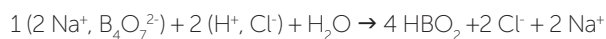
Titration of sodium hydroxide by potassium hydrogen phthalate



Titration of sodium hydroxide by oxalic acid



Titration of borax by sulphuric acid



Titration of borax by hydrochloric acid

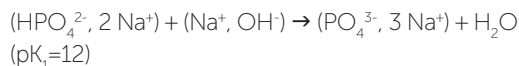
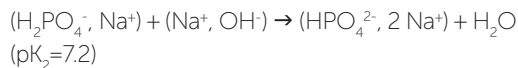
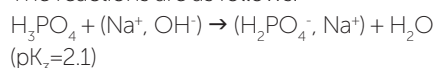
Example of phosphoric acid H_3PO_4

This is a triacid with the following pKs:

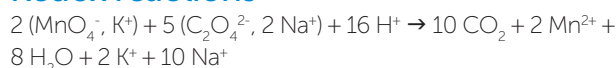
$\text{pK}_3=2.1$, $\text{pK}_2=7.2$ and $\text{pK}_1=12$

In an aqueous medium, only the first two acids can be titrated.

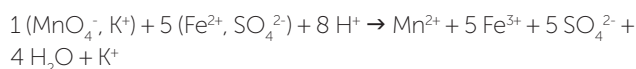
The reactions are as follows:



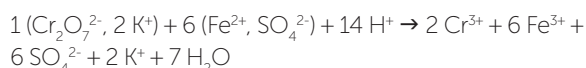
Redox reactions



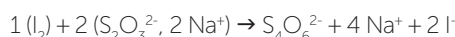
Reaction of potassium permanganate and sodium oxalate



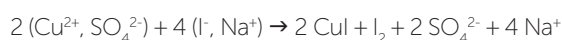
Reaction of potassium permanganate and iron sulphate



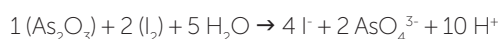
Reaction of potassium dichromate and iron sulphate



Reaction of iodine and sodium thiosulphate



Reaction of Cu^{2+} and iodide

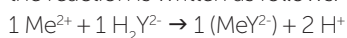


Reaction of iodine and arsenious anhydride

Complexometric reactions

The most common complexing agent used is disodium salt of ethylenediaminetetraacetic acid, or EDTA, usually expressed in its simple form as H_2Y^{2-} .

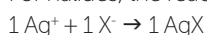
As it is often used to complex divalent metals of the Me^{2+} type, the reaction is written as follows:



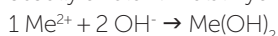
Precipitation reactions

The most important use of precipitation reactions is silver nitrate used to titrate halides (Cl^- , Br^- , I^-) and CN^- and SCN^- used to titrate Ag^+ ions.

For halides, the reaction is as follows:



Some other reactions correspond to the precipitation of usually divalent metal hydroxides:



Characteristics of some standards

We consider a standard to be a commercially available substance of sufficient purity, delivered with a certificate. Such a standard can be weighed to make stable solutions.

pH standards

Oxalic acid $(COOH)_2 \cdot 2 H_2O$
MW=126.03 g/mol

Potassium hydrogen phthalate $KOOC-C_6H_4-COOH$
MW= 204.22 g/mol

Sodium carbonate Na_2CO_3
MW=105.99 g/mol

TRIS or THAM $H_2N-C(CH_2OH)_3$
MW=121.14 g/mol

Sodium borate (Borax) $Na_2B_4O_7 \cdot 10 H_2O$
MW=381.4 g/mol

Redox standards

Oxalic acid $(COOH)_2 \cdot 2 H_2O$
MW=126.03 g/mol

Potassium dichromate $K_2Cr_2O_7$
MW=294.19 g/mol

Ferrous ammonium sulphate (Mohr's salt) $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6 H_2O$
MW=392.14 g/mol

Arsenious anhydride As_2O_3
MW=169.87 g/mol

Potassium iodate KIO_3
MW=213.97 g/mol

Complexometric standards

Disodium salt of EDTA $Na_2H_2Y \cdot 2 H_2O$
MW=372.24 g/mol

Precipitation standards

Silver nitrate $AgNO_3$
MW=169.87 g/mol

Potassium chloride KCl
MW=74.56 g/mol

Sodium chloride $NaCl$
MW=58.44 g/mol