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

$1\,(Na^+, OH^-) + 1\,(H^+, Cl^-) \rightarrow H_2O + Na^+ + Cl^-$
Reaction of sodium hydroxide with a monobasic acid

$2\,(Na^+, OH^-) + 1\,(SO_4^{2-}, 2H^+) \rightarrow 2\,H_2O + 2\,Na^+ + SO_4^{2-}$
Reaction of sodium hydroxide with a dibasic acid

$1\,(2\,Na^+, CO_3^{2-}) + 2\,(H^+, Cl^-) \rightarrow CO_2 + H_2O + 2\,Na^+ + 2\,Cl^-$
Complete neutralisation of sodium carbonate by hydrochloric acid

$1\,(2\,Na^+, CO_3^{2-}) + 1\,(2\,H^+, SO_4^{2-}) \rightarrow CO_2 + H_2O + 2\,Na^+ + SO_4^{2-}$
Complete neutralisation of sodium carbonate by sulphuric acid

$1\,(Na^+, OH^-) + 1\,(H^+, \text{-OOC-}C_6H_4\text{-COO-}, K^+) \rightarrow H_2O + (Na^+, \text{-OOC-}C_6H_4COO\text{-}, K^+)$
Titration of sodium hydroxide by potassium hydrogen phthalate

$2\,(Na^+, OH^-) + 1\,(C_2O_4^{2-}, 2\,H^+) \rightarrow 2\,H_2O + C_2O_4^{2-} + 2\,Na^+$
Titration of sodium hydroxide by oxalic acid

$1\,(2\,Na^+, B_4O_7^{2-}) + 1\,(2\,H^+, SO_4^{2-}) + H_2O \rightarrow 4\,HBO_2 + SO_4^{2-} + 2\,Na^+$
Titration of borax by sulphuric acid

$1\,(2\,Na^+, B_4O_7^{2-}) + 2\,(H^+, Cl^-) + H_2O \rightarrow 4\,HBO_2 + 2\,Cl^- + 2\,Na^+$
Titration of borax by hydrochloric acid

Example of phosphoric acid H_3PO_4
This is a triacid with the following pKs:
pK_3=2.1, pK_2=7.2 and pK_1=12

In an aqueous medium, only the first two acids can be titrated. The reactions are as follows:
$H_3PO_4 + (Na^+, OH^-) \rightarrow (H_2PO_4^-, Na^+) + H_2O$
(pK_3=2.1)

$(H_2PO_4^-, Na^+) + (Na^+, OH^-) \rightarrow (HPO_4^{2-}, 2\,Na^+) + H_2O$
(pK_2=7.2)

$(HPO_4^{2-}, 2\,Na^+) + (Na^+, OH^-) \rightarrow (PO_4^{3-}, 3\,Na^+) + H_2O$
(pK_1=12)

Redox reactions

$2\,(MnO_4^-, K^+) + 5\,(C_2O_4^{2-}, 2\,Na^+) + 16\,H^+ \rightarrow 10\,CO_2 + 2\,Mn^{2+} + 8\,H_2O + 2\,K^+ + 10\,Na^+$
Reaction of potassium permanganate and sodium oxalate

$1\,(MnO_4^-, K^+) + 5\,(Fe^{2+}, SO_4^{2-}) + 8\,H^+ \rightarrow Mn^{2+} + 5\,Fe^{3+} + 5\,SO_4^{2-} + 4\,H_2O + K^+$
Reaction of potassium permanganate and iron sulphate

$1\,(Cr_2O_7^{2-}, 2\,K^+) + 6\,(Fe^{2+}, SO_4^{2-}) + 14\,H^+ \rightarrow 2\,Cr^{3+} + 6\,Fe^{3+} + 6\,SO_4^{2-} + 2\,K^+ + 7\,H_2O$
Reaction of potassium dichromate and iron sulphate

$1\,(I_2) + 2\,(S_2O_3^{2-}, 2\,Na^+) \rightarrow S_4O_6^{2-} + 4\,Na^+ + 2\,I^-$
Reaction of iodine and sodium thiosulphate

$2\,(Cu^{2+}, SO_4^{2-}) + 4\,(I^-, Na^+) \rightarrow 2\,CuI + I_2 + 2\,SO_4^{2-} + 4\,Na^+$
Reaction of Cu^{2+} and iodide

$1\,(As_2O_3) + 2\,(I_2) + 5\,H_2O \rightarrow 4\,I^- + 2\,AsO_4^{3-} + 10\,H^+$
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:

$1\ Me^{2+} + 1\ H_2Y^{2-} \rightarrow 1\ (MeY^{2-}) + 2\ H^+$

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:

$1\ Ag^+ + 1\ X^- \rightarrow 1\ AgX$

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

$1\ Me^{2+} + 2\ OH^- \rightarrow Me(OH)_2$

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 MW=126.03 g/mol	$(COOH)_2$, 2 H_2O
Potassium hydrogen phthalate MW= 204.22 g/mol	$KOOC\text{-}C_6H_4\text{-}COOH$
Sodium carbonate MW=105.99 g/mol	Na_2CO_3
TRIS or THAM MW=121.14 g/mol	$H_2N\text{-}C(CH_2OH)_3$
Sodium borate (Borax) MW=381.4 g/mol	$Na_2B_4O_7$,10 H_2O

Redox standards

Oxalic acid MW=126.03 g/mol	$(COOH)_2$, 2 H_2O
Potassium dichromate MW=294.19 g/mol	$K_2Cr_2O_7$
Ferrous ammonium sulphate (Mohr's salt) MW=392.14 g/mol	$(NH_4)_2SO_4$, $FeSO_4$, 6 H_2O
Arsenious anhydride MW=169.87 g/mol	As_2O_3
Potassium iodate MW=213.97 g/mol	KIO_3

Complexometric standards

Disodium salt of EDTA MW=372.24 g/mol	Na_2H_2Y, 2 H_2O

Precipitation standards

Silver nitrate MW=169.87 g/mol	$AgNO_3$
Potassium chloride MW=74.56 g/mol	KCl
Sodium chloride MW=58.44 g/mol	NaCl

DOC182.52.20182.Jan15