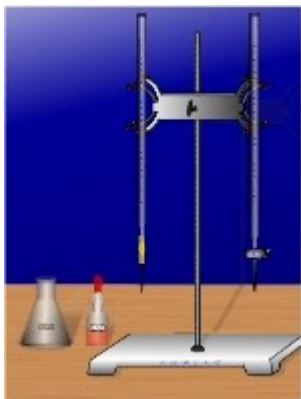


### §3.1.5 Stoichiometric Relationships in Titrimetry

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To determine the relationship of mole between analyte and titrant



(1) Direct titration (one reaction) reaction formula between titrant and analyte:

$a A + b B = c C + d D$  if it is at the stoichiometric point,  $a$  moles of  $A$  just completely react with  $b$  moles of  $B$ , where  $A$  is the analyte and  $B$  is the titrant:  
 Thus:  $n_A / n_B = a / b$ ,  $n_A = (a / b) \cdot n_B$   $(c \cdot V)_A = (a / b) \cdot (c \cdot V)_B$  or:  $(c \cdot V)_A = (a / b) \cdot (m / M)_B$   
 In acid-base titrations, the concentration of standard solutions are around  $0.1 \text{ mol/L}$ , the volumes of titrant used are  $20\text{--}30\text{mL}$ , thus the mass of the analyte needed can be estimated.

(2) Back titration (two reactions):

A known excess of one standard reagent is added to the analyte. Then a second standard reagent is used to titrate the excess of the first reagent. e.g. aluminum (complexometric titration)  
 Reaction 1:  $\text{Al}^{3+} + Y^{4-} \rightarrow \text{AlY}$  (accurate, excessive)  
 Reaction 2:  $\text{Zn}^{2+} + Y^{4-} \rightarrow \text{ZnY}^{2-}$   
 $(n_{\text{EDTA}})_{\text{total}} - (n_{\text{EDTA}})_{\text{excessive}} = (n_{\text{Al}})$   
 $(n_{\text{EDTA}})_{\text{excessive}} = (a / b)n_{\text{Zn}}$ ;  $a / b = 1$   $(cV)_{\text{EDTA total}} - (cV)_{\text{Zn}} = (cV)_{\text{Al}}$   
 substitute experimental data for the above formula, the concentration of aluminium is obtained.

(3) Indirect titration (two or more reactions)

The stoichiometric relationship between the reactions should be found out from the overall reactions.

For example, in standardization of  $\text{Na}_2\text{S}_2\text{O}_3$  solution by using  $\text{KBrO}_3$  as a primary standard under acidic condition. (two steps) Example: In standardization of  $\text{Na}_2\text{S}_2\text{O}_3$  solution by using  $\text{KBrO}_3$  as a primary standard under acidic condition (two steps).

(can not be direct titrated for complex products) (1)  $\text{KBrO}_3$  reacts with an excess  $\text{KI}$  to release  $\text{I}_2$  in an acidic solution:  $\text{BrO}_3^- + 6 \text{I}^- + 6\text{H}^+ = 3 \text{I}_2 +$

$\text{Br}^- + 3\text{H}_2\text{O} \rightarrow \text{BrO}_3^- + 6\text{H}^+ + 6\text{e}^-$   $n(\text{BrO}_3^-) = 1/3 n(\text{I}_2)$  (2) The released  $\text{I}_2$  is titrated with  
 $\text{Na}_2\text{S}_2\text{O}_3$  solution  $2\text{S}_2\text{O}_3^{2-} + \text{I}_2 = 2\text{I}^- + \text{S}_4\text{O}_6^{2-}$   $n(\text{I}_2) = 1/2 n(\text{S}_2\text{O}_3^{2-})$  (3) the  
relationship between  $n$  of  $\text{BrO}_3^-$  and  $\text{S}_2\text{O}_3^{2-}$   $n(\text{BrO}_3^-) = 1/3 n(\text{I}_2) = 1/6 n(\text{S}_2\text{O}_3^{2-})$   
 $(cV)\text{S}_2\text{O}_3^{2-} = 6(W/M)\text{BrO}_3^-$  Example 2 Determination of  $\text{Ca}^{2+}$  by  $\text{KMnO}_4$  (several steps)  
 $\text{Ca}^{2+} + \text{CaC}_2\text{O}_4 \downarrow$  dissolve  $\text{C}_2\text{O}_4^{2-}$   $\text{KMnO}_4 + 2\text{C}_2\text{O}_4^{2-} + 16\text{H}^+ = 2$   
 $\text{Mn}^{2+} + 10\text{CO}_2 + 8\text{H}_2\text{O}$   $n(\text{Ca}^{2+}) = n(\text{C}_2\text{O}_4^{2-}) = 5/2 n(\text{MnO}_4^-)$   $(W/M)$   
 $(\text{Ca}^{2+}) = 5/2 (cV)(\text{MnO}_4^-)$  The key point in this page: For four titration  
types, the stoichiometric relationship and relevant calculations, especially the  
relationship for the reactions of several steps. Problems in this page: what  
other substances being of no oxidant or reductant can be determined with the  
principle of determining calcium with redox method