Direct titration and back titration

When a titrant reacts directly with an analyte, the procedure is termed a direct titration. It is some times necessary to add an excess of standard titrant and then determine the excess amount by back titration with a second standard titrant. In other wards back titration is a process in which the excess of standard solution used to react with an analyte is determined by titration with a second standard solution. Back – titration are often required when the rate of reaction between the analyte and reagent is slow or when the standard solution lacks stability.

In back – titration, the equivalence point corresponds to the point when the amount of initial titrant is chemically equivalent to the amount af analyte plus the amount of back titrant.
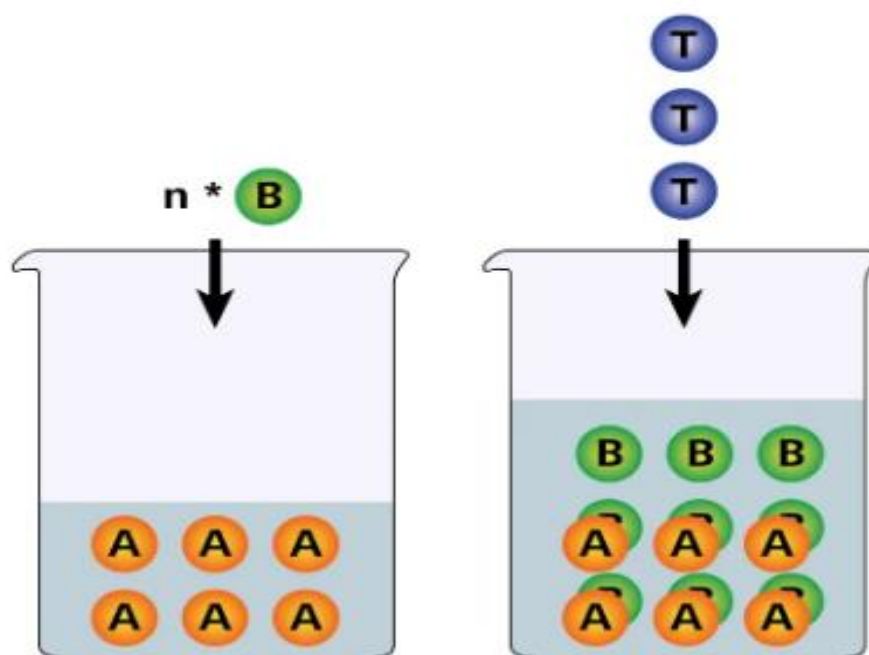

Figure 1. Reaction principle of a back-titration: Reagent B is added in excess to analyte A. After a defined waiting period which allows for the reaction between A and B, the excess of reagent B is titrated with titrant T.

In contrast to direct titrations, where analyte A directly reacts with titrant T, back-titrations are a subcategory of indirect titrations. Indirect titrations are used when, for example, no suitable sensor is available or the reaction is too slow for a practical direct titration.

During a back-titration, an exact volume of reagent B is added to the analyte A. Reagent B is usually a common titrant itself. The amount of reagent B is chosen in such a way that an excess remains after its interaction with analyte A. This excess is then titrated with titrant T. The amount of analyte A can then be determined from the difference between the added amount of reagent B and the remaining excess of reagent B.

As with any titration, both involved reactions must be quantitative, and stoichiometric factors involved for both reactions must be known.

Calculation in back titration

a) calculation based on normality of solution:

To calculate a substance like (B)

A + B= product + Excess A

Excess A +C= Product

Back titration term of normalty

meqB =[(N_A*V_A) - (V_C*N_C)]

wt B= meqB x eq. wtB

wt B=[(N_A*V_A) - (V_C*N_C)] eq. wtB

b) calculation based on molarity of solution :

$$aA + bB = product + excess\ A$$

$$R_1 = \frac{b\ un\ known}{a\ known}$$

$$cC + dA(excess) = product$$

$$R_2 = \frac{d}{c}$$

m g B =[(M_A*V_A)-(V_C*M_C * R_2)] R_1x M. wtB

Example 1: Calculate % CaO in sample of limestone from the following data :

Weight of Sample =1.5 gm

Volume of HCl used =40 mL

Volume of NaOH used =3mL

If 1 mL HCl=1.5 mL of NaOH

N_{NaOH}=0.333

Solve:

$$\% \, CaO = \frac{wt. \; CaO}{wt. \; of \; Sample} * 100$$

$$meq. \, Hcl = meq. \, NaOH$$

$$(N * V)_{acid} = (N * V)_{base} \implies 1 * N = 1.5 * 0.333$$

$$\therefore N_{acid} = 0.4995 \quad meq/ml$$

$$eq. \, wt \, CaO = \frac{Mwt}{2} = \frac{56.08}{2} = 28.04$$

$$mg \, CaO = \left[(N*V)_{Hcl} - (N*V)_{base} \right] * eq. \, wt \, CaO$$

$$= \left[(0.4995 * 40) - (0.333 * 3) \right] * 28.04$$

$$= 532.7 \; mg$$

$$\% \, CaO = \frac{532.7}{1.5 * 1000} * 100 = 35.52 \, \%$$

Example2: 45 ml, 0.1163 N H_2SO_4 was added to 0.4 gm sample of Soda ash which is 67.72% Na_2CO_3. What is the volume of 0.1053 N NaOH that required for back titration?

Solution:

net wt. $Na_2CO_3 = 0.4 * 0.6772 = 0.27088$ gm
$$= 270.88 \text{ mg}$$

$$mg\ Na_2CO_3 = [(N*V)_{H_2SO_4} - (N*V)_{NaOH}] * eq.wt.\ Na_2CO_3$$

$$eq.wt.\ Na_2CO_3 = \frac{mwt.}{2} = \frac{106}{2} = 53\ mg/meq$$

$$270.88 = [(0.1163 * 45) - (0.1053 * V)] * 53$$

$$270.88 = 277.375 - 5.5809\ V$$

$$\therefore V = 1.1638\ ml$$

B - Molarity:

$$aA + bB \longrightarrow \text{Product} + \text{Excess } A \qquad R_1 = \frac{b}{a}$$

$$cC + dA \longrightarrow \text{Product} \qquad\qquad R_2 = \frac{d}{c}$$
$$\underset{\text{Excess}}{}$$
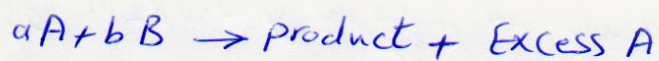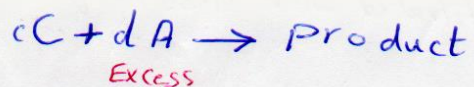
$$\boxed{m M_B = (m M_A - m M_C * R_2) * R_1}$$

$$\boxed{mg_B = [(M*V)_A - (M*V)_C * R_2] * R_1 \cdot Mwt_B}$$

Example: A 0.2gm sample of impure magnesium carbonate was treated with 50 ml, 0.1023 M. HCl. The solution was boiled to expel CO_2 then titrated with 5.04 ml, 0.1181 M NaOH. Calculate % purity of $MgCO_3$?
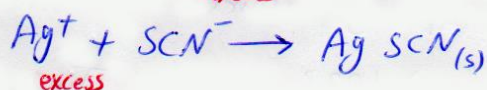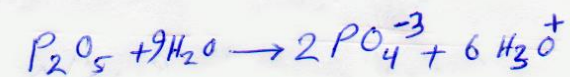
Solve:

$$MgCO_3 + 2HCl \longrightarrow MgCl_2 + CO_2 \overset{+H_2O}{} + \text{Excess HCl} \quad R_1 = \frac{1}{2}$$

$$\underset{\text{excess}}{HCl} + NaOH \longrightarrow H_2O + NaCl \qquad\qquad R_2 = \frac{1}{1}$$
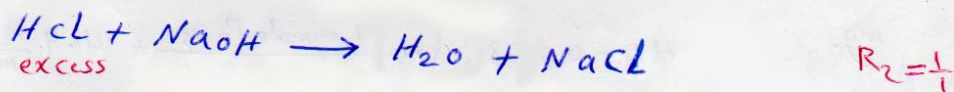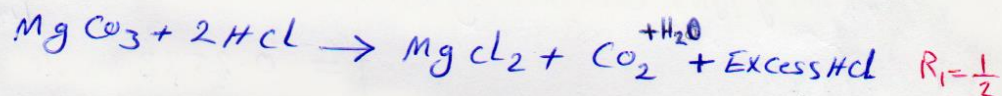
$$mg_{MgCO_3} = [m M_{HCl} - m M_{NaOH} * R_2] * R_1 * Mwt_{MgCO_3}$$

$$= [(50 * 0.1023) - (5.04 * 0.1181) * 1] * \frac{1}{2} * 84$$

$$= 190.55 \text{ mg}$$

$$\% \text{ Purity} = \frac{190.55 \text{ mg}}{0.2 * 1000 \text{ mg}} * 100 = 95.27\%$$

Example:[2] The phosphorus in a 4.258 gm sample of a plant food was dissolved in water to convert to PO_4^{-3} and precipitated as Ag_3PO_4 through the addition of 50 ml of 0.082 M $AgNO_3$. The excess $AgNO_3$ was back titrated with 4.06 ml of 0.0625 M KSCN. Calculate % P_2O_5?

The chemical reactions are:

$$P_2O_5 + 9H_2O \longrightarrow 2PO_4^{-3} + 6H_3O^+$$

$$2PO_4^{-3} + \underset{excess}{6Ag^+} \longrightarrow 2Ag_3PO_{4(s)}$$

$$\underset{excess}{Ag^+} + SCN^- \longrightarrow AgSCN_{(s)}$$

Solution:

$$mg\, P_2O_5 = \left[(M*V)_{AgNO_3} - (M*V)_{KSCN} * R_2 \right] * R_1 * Mwt.\,P_2O_5$$

total moles of $AgNO_3 = 50 * 0.082 = 4.1$ mmole

mmoles of $AgNO_3$ consumed by KSCN $= 4.06 * 0.0625 * \dfrac{1\, mmole\, AgNO_3}{1\, mmole\, KSCN}$

$$= 0.2538\, mmole$$

$$mg.\, P_2O_5 = \left[4.1 - 0.2538 \right] * \dfrac{1\, mmole\, P_2O_5}{6\, mmole\, AgNO_3} * 141.9\, \dfrac{mg}{mmole}$$

$$= 90.96\, mg$$

$$\%\, P_2O_5 = \dfrac{wt.\, P_2O_5}{wt.\, sample} * 100$$

$$= \dfrac{90.96\, mg}{4.258 * 10^3\, mg} * 100 = 2.14\%$$