Back Titrations

Key Concepts

A back titration, or indirect titration, is generally a two-stage analytical technique:

a. Reactant A of unknown concentration is reacted with excess reactant B of known concentration.
b. A titration is then performed to determine the amount of reactant B in excess.

Back titrations are used when:

- one of the reactants is volatile, for example ammonia.
- an acid or a base is an insoluble salt, for example calcium carbonate
- a particular reaction is too slow
- direct titration would involve a weak acid - weak base titration (the end-point of this type of direct titration is very difficult to observe)

Example : Back (Indirect) Titration to Determine the Concentration of a Volatile Substance

A student was asked to determine the concentration of ammonia, a volatile substance, in a commercially available cloudy ammonia solution used for cleaning.
First the student pipetted 25.00mL of the cloudy ammonia solution into a 250.0mL conical flask.
50.00mL of 0.100M $HCl_{(aq)}$ was immediately added to the conical flask which reacted with the ammonia in solution.
The excess (unreacted) HCl was then titrated with 0.050M $Na_2CO_{3(aq)}$.
21.50mL of $Na_2CO_{3(aq)}$ was required.
Calculate the concentration of the ammonia in the cloudy ammonia solution.

Step 1: Determine the amount of HCl in excess from the titration results

a. Write the equation for the titration:

$$2HCl_{(aq)} + Na_2CO_{3(aq)} \rightarrow 2NaCl_{(aq)} + CO_{2(g)} + H_2O_{(l)}$$

acid + carbonate → salt + carbon dioxide + water

b. Calculate the moles, n, of $Na_2CO_{3(aq)}$ that reacted in the titration:
   $n = M \times V$
   $M = 0.050\ molL^{-1}$
   $V = 21.50mL = 21.50 \times 10^{-3}L$
   $n(Na_2CO_{3(aq)}) = 0.050 \times 21.50 \times 10^{-3} = 1.075 \times 10^{-3}$ mol
c. Use the balanced chemical reaction for the titration to determine the moles of HCl that reacted in the titration.
   From the balanced chemical equation, 1 mole Na_2CO_3 react with 2 moles of HCl
   So, 1.075×10^{-3} mole Na_2CO_3 reacted with $2 \times 1.075 \times 10^{-3}$ moles HCl
   $n(HCl_{titrated}) = 2 \times 1.075 \times 10^{-3} = 2.150 \times 10^{-3}$ mol
d. The amount of HCl that was added to the cloudy ammonia solution in excess was 2.150×10^{-3} mol

Step 2: Determine the amount of ammonia in the cloudy ammonia solution

a. Calculate the total moles of HCl originally added to the diluted cloudy ammonia solution:
   $n(HCl_{total\ added}) = M \times V$
   $M = 0.100\ molL^{-1}$
   $V = 50.00mL = 50.00 \times 10^{-3}L$
   $n(HCl_{total\ added}) = 0.100 \times 50.00 \times 10^{-3} = 5.00 \times 10^{-3}$ mol
b. Calculate the moles of HCl that reacted with the ammonia in the diluted cloudy ammonia solution
   $n(HCl_{titrated}) + n(HCl_{reacted\ with\ ammonia}) = n(HCl_{total\ added})$
   $n(HCl_{total\ added}) = 5.00 \times 10^{-3}$ mol
   $n(HCl_{titrated}) = 2.150 \times 10^{-3}$ mol
   $2.150 \times 10^{-3} + n(HCl_{reacted\ with\ ammonia}) = 5.00 \times 10^{-3}$
   $n(HCl_{reacted\ with\ ammonia}) = 5.00 \times 10^{-3} - 2.150 \times 10^{-3} = 2.85 \times 10^{-3}$ mol
c. Write the balanced chemical equation for the reaction between ammonia in the cloudy ammonia solution and the $HCl_{(aq)}$.

$$NH_{3(aq)} + HCl_{(aq)} \rightarrow NH_4Cl_{(aq)}$$

d. From the balanced chemical equation, calculate the moles of NH_3 that reacted with HCl.
   From the equation, 1 mol HCl reacts with 1 mol NH_3
   So, 2.85×10^{-3} mol HCl had reacted with 2.85×10^{-3} mol NH_3 in the cloudy ammonia solution.
e. Calculate the ammonia concentration in the cloudy ammonia solution.
   $M = n \div V$
   $n = 2.85 \times 10^{-3}$ mol (moles of NH_3 that reacted with HCl)
   $V = 25.00mL = 25.00 \times 10^{-3}L$ (volume of ammonia solution that reacted with HCl)
   $M = 2.85 \times 10^{-3} \div 25.00 \times 10^{-3} = 0.114$ M
f. The concentration of ammonia in the cloudy ammonia solution was 0.114M

Example : Back (Indirect) Titration to Determine the Amount of an Insoluble Salt

A student was asked to determine the mass, in grams, of calcium carbonate present in a 0.125g sample of chalk.
The student placed the chalk sample in a 250mL conical flask and added 50.00mL 0.200M HCl using a pipette.
The excess HCl was then titrated with 0.250M NaOH.
The average NaOH titre was 32.12mL
Calculate the mass of calcium carbonate, in grams, present in the chalk sample.

Step 1: Determine the amount of HCl in excess from the titration results

a. Write the equation for the titration:

$$HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$$
$$\text{acid} + \text{base} \rightarrow \text{salt} + \text{water}$$

b. Calculate the moles, n, of $NaOH_{(aq)}$ that reacted in the titration:
   $n = M \times V$
   $M = 0.250\ molL^{-1}$
   $V = 32.12mL = 32.12 \times 10^{-3}L$
   $n(NaOH_{(aq)}) = 0.250 \times 32.12 \times 10^{-3} = 8.03 \times 10^{-3}$ mol

c. Use the balanced chemical reaction for the titration to determine the moles of HCl that reacted in the titration.
   From the balanced chemical equation, 1 mole NaOH reacts with 1 mole of HCl
   So, 8.03×10^{-3} mole NaOH reacted with 8.03×10^{-3} moles HCl
d. The amount of HCl that was added to the chalk in excess was
   8.03×10^{-3} mol

Step 2: Determine the amount of calcium carbonate in chalk

a. Calculate the total moles of HCl originally added to the chalk:
   $n(HCl_{\text{total added}}) = M \times V$
   $M = 0.200\ molL^{-1}$
   $V = 50.00mL = 50.00 \times 10^{-3}L$
   $n(HCl_{\text{total added}}) = 0.200 \times 50.00 \times 10^{-3} = 0.010$ mol
b. Calculate the moles of HCl that reacted with the calcium carbonate in the chalk
   $n(HCl_{\text{titrated}}) + n(HCl_{\text{reacted with calcium carbonate}}) = n(HCl_{\text{total added}})$
   $n(HCl_{\text{total added}}) = 0.010$ mol
   $n(HCl_{\text{titrated}}) = 8.03 \times 10^{-3}$ mol
   $8.03 \times 10^{-3} + n(HCl_{\text{reacted with calcium carbonate}}) = 0.010$
   $n(HCl_{\text{reacted with calcium carbonate}}) = 0.010 - 8.03 \times 10^{-3} = 1.97 \times 10^{-3}$ mol
c. Write the balanced chemical equation for the reaction between calcium carbonate in the chalk and the $HCl_{(aq)}$.

$$CaCO_{3(s)} + 2HCl_{(aq)} \rightarrow CaCl_{2(aq)} + CO_{2(g)} + H_2O_{(l)}$$

d. From the balanced chemical equation, calculate the moles of $CaCO_3$ that reacted with HCl.
   From the equation, 1 mol $CaCO_3$ reacts with 2 mol HCl so, 1 mol HCl reacts with ½ mol $CaCO_3$
   So, 1.97×10^{-3} mol HCl had reacted with $\frac{1}{2} \times 1.97 \times 10^{-3} = 9.85 \times 10^{-4}$ mol $CaCO_3$ in the chalk.
e. Calculate the mass of calcium carbonate in the chalk.
   $n = mass \div MM$
   $n = 9.85 \times 10^{-4}$ mol (moles of $CaCO_3$ that reacted with HCl)
   $MM(CaCO_3) = 40.08 + 12.01 + (3 \times 16.00) = 100.09$ g/mol
   $mass = n \times MM = 9.85 \times 10^{-4} \times 100.09 = 0.099g$
f. The mass of calcium carbonate in the chalk was 0.099g