**Back Titrations**

**Key Concepts**

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

1. Reactant A of unknown concentration is reacted with excess reactant B of known concentration.
2. A [titration](http://www.ausetute.com.au/titrcalc.html) is then performed to determine the amount of reactant B [in excess](http://www.ausetute.com.au/exceslim.html).

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](http://www.ausetute.com.au/titrcurv.html)
    (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 Na2CO3(aq).
21.50mL of Na2CO3(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**

1. Write the equation for the titration:

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| 2HCl(aq) | +  | Na2CO3(aq) | →  | 2NaCl(aq)  | +  | CO2(g) | +  | H2O(l) |
| acid | +  | carbonate | →  | salt  | +  | carbondioxide | +  | water |

1. Calculate the moles, n, of Na2CO3(aq) that reacted in the titration:
    n = M x V
    M = 0.050 molL-1
    V = 21.50mL = 21.50 x 10-3L
    n(Na2CO3(aq)) = 0.050 x 21.50 x 10-3 = 1.075 x 10-3 mol
2. 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 Na2CO3 react with 2 moles of HCl
    So, 1.075 x 10-3 mole Na2CO3 reacted with 2 x 1.075 x 10-3 moles HCl
    n(HCltitrated) = 2 x 1.075 x 10-3 = 2.150 x 10-3 mol
3. The amount of HCl that was added to the cloudy ammonia solution in excess was
    2.150 x 10-3 mol

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

1. Calculate the total moles of HCl originally added to the diluted cloudy ammonia solution:
    n(HCltotal added) = M x V
    M = 0.100 molL-1
    V = 50.00mL = 50.00 x 10-3L
    n(HCltotal added) = 0.100 x 50.00 x 10-3 = 5.00 x 10-3 mol
2. Calculate the moles of HCl that reacted with the ammonia in the diluted cloudy ammonia solution
    n(HCltitrated) + n(HClreacted with ammonia) = n(HCltotal added)
    n(HCltotal added) = 5.00 x 10-3 mol
    n(HCltitrated) = 2.150 x 10-3 mol
    2.150 x 10-3 + n(HClreacted with ammonia) = 5.00 x 10-3
    n(HClreacted with ammonia) = 5.00 x 10-3 - 2.150 x 10-3 = 2.85 x 10-3 mol
3. Write the balanced chemical equation for the reaction between ammonia in the cloudy ammonia solution and the HCl(aq).

NH3(aq) + HCl(aq) → NH4Cl(aq)

1. From the balanced chemical equation, calculate the moles of NH3 that reacted with HCl.
    From the equation, 1 mol HCl reacts with 1 mol NH3
    So, 2.85 x 10-3 mol HCl had reacted with 2.85 x 10-3 mol NH3 in the cloudy ammonia solution.
2. Calculate the ammonia concentration in the cloudy ammonia solution.
    M = n ÷ V
    n = 2.85 x 10-3 mol (moles of NH3 that reacted with HCl)
    V = 25.00mL = 25.00 x 10-3L (volume of ammonia solution that reacted with HCl)
    M = 2.85 x 10-3 ÷ 25.00 x 10-3 = 0.114 M
3. 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**

1. Write the equation for the titration:

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| HCl(aq) | +  | NaOH(aq) | →  | NaCl(aq)  | +  | H2O(l) |
| acid | +  | base | →  | salt | +  | water |

1. Calculate the moles, n, of NaOH(aq) that reacted in the titration:
    n = M x V
    M = 0.250 molL-1
    V = 32.12mL = 32.12 x 10-3L
    n(NaOH(aq)) = 0.250 x 32.12 x 10-3 = 8.03 x 10-3 mol
2. 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 x 10-3 mole NaOH reacted with 8.03 x 10-3 moles HCl
3. The amount of HCl that was added to the chalk in excess was
    8.03 x 10-3 mol

**Step 2: Determine the amount of calcium carbonate in chalk**

1. Calculate the total moles of HCl originally added to the chalk:
    n(HCltotal added) = M x V
    M = 0.200 molL-1
    V = 50.00mL = 50.00 x 10-3L
    n(HCltotal added) = 0.200 x 50.00 x 10-3 = 0.010 mol
2. Calculate the moles of HCl that reacted with the calcium carbonate in the chalk
    n(HCltitrated) + n(HClreacted with calcium carbonate) = n(HCltotal added)
    n(HCltotal added) = 0.010 mol
    n(HCltitrated) = 8.03 x 10-3 mol
    8.03 x 10-3 + n(HClreacted with calcium carbonate) = 0.010
    n(HClreacted with calcium carbonate) = 0.010 - 8.03 x 10-3 = 1.97 x 10-3 mol
3. Write the balanced chemical equation for the reaction between calcium carbonate in the chalk and the HCl(aq).

CaCO3(s) + 2HCl(aq) → CaCl2(aq) + CO2(g) + H2O(l)

1. From the balanced chemical equation, calculate the moles of CaCO3 that reacted with HCl.
    From the equation, 1 mol CaCO3 reacts with 2 mol HCl so, 1 mol HCl reacts with ½ mol CaCO3
    So, 1.97 x 10-3 mol HCl had reacted with ½ x 1.97 x 10-3 = 9.85 x 10-4 mol CaCO3 in the chalk.
2. Calculate the mass of calcium carbonate in the chalk.
    n = mass ÷ MM
    n = 9.85 x 10-4 mol (moles of CaCO3 that reacted with HCl)
    MM(CaCO3) = 40.08 + 12.01 + (3 x 16.00) = 100.09 g/mol
    mass = n x MM = 9.85 x 10-4 x 100.09 = 0.099g
3. The mass of calcium carbonate in the chalk was 0.099g