

## Back Titrations

### Key Concepts

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

- Reactant A of unknown concentration is reacted with excess reactant B of known concentration.
- 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<sub>(aq)</sub> was immediately added to the conical flask which reacted with the ammonia in solution.

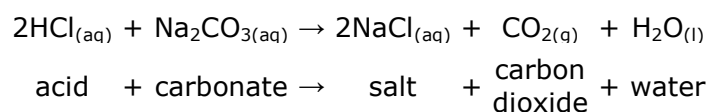
The excess (unreacted) HCl was then titrated with 0.050M Na<sub>2</sub>CO<sub>3(aq)</sub>.

21.50mL of Na<sub>2</sub>CO<sub>3(aq)</sub> 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

- Write the equation for the titration:



- Calculate the moles,  $n$ , of Na<sub>2</sub>CO<sub>3(aq)</sub> that reacted in the titration:

$$n = M \times V$$

$$M = 0.050 \text{ molL}^{-1}$$

$$V = 21.50\text{mL} = 21.50 \times 10^{-3}\text{L}$$

$$n(\text{Na}_2\text{CO}_{3(\text{aq})}) = 0.050 \times 21.50 \times 10^{-3} = 1.075 \times 10^{-3} \text{ mol}$$

- 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<sub>2</sub>CO<sub>3</sub> react with 2 moles of HCl

So,  $1.075 \times 10^{-3}$  mole Na<sub>2</sub>CO<sub>3</sub> reacted with  $2 \times 1.075 \times 10^{-3}$  moles HCl

$$n(\text{HCl}_{\text{titrated}}) = 2 \times 1.075 \times 10^{-3} = 2.150 \times 10^{-3} \text{ mol}$$

- The amount of HCl that was added to the cloudy ammonia solution in excess was  $2.150 \times 10^{-3}$  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:

$$n(\text{HCl}_{\text{total added}}) = M \times V$$

$$M = 0.100 \text{ molL}^{-1}$$

$$V = 50.00\text{mL} = 50.00 \times 10^{-3}\text{L}$$

$$n(\text{HCl}_{\text{total added}}) = 0.100 \times 50.00 \times 10^{-3} = 5.00 \times 10^{-3} \text{ mol}$$

- b. Calculate the moles of HCl that reacted with the ammonia in the diluted cloudy ammonia solution

$$n(\text{HCl}_{\text{titrated}}) + n(\text{HCl}_{\text{reacted with ammonia}}) = n(\text{HCl}_{\text{total added}})$$

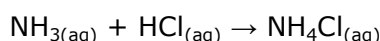
$$n(\text{HCl}_{\text{total added}}) = 5.00 \times 10^{-3} \text{ mol}$$

$$n(\text{HCl}_{\text{titrated}}) = 2.150 \times 10^{-3} \text{ mol}$$

$$2.150 \times 10^{-3} + n(\text{HCl}_{\text{reacted with ammonia}}) = 5.00 \times 10^{-3}$$

$$n(\text{HCl}_{\text{reacted with ammonia}}) = 5.00 \times 10^{-3} - 2.150 \times 10^{-3} = 2.85 \times 10^{-3} \text{ mol}$$

- c. Write the balanced chemical equation for the reaction between ammonia in the cloudy ammonia solution and the  $\text{HCl}_{(\text{aq})}$ .



- d. From the balanced chemical equation, calculate the moles of  $\text{NH}_3$  that reacted with HCl.

From the equation, 1 mol HCl reacts with 1 mol  $\text{NH}_3$

So,  $2.85 \times 10^{-3}$  mol HCl had reacted with  $2.85 \times 10^{-3}$  mol  $\text{NH}_3$  in the cloudy ammonia solution.

- e. Calculate the ammonia concentration in the cloudy ammonia solution.

$$M = n \div V$$

$$n = 2.85 \times 10^{-3} \text{ mol (moles of } \text{NH}_3 \text{ that reacted with HCl)}$$

$V = 25.00\text{mL} = 25.00 \times 10^{-3}\text{L}$  (volume of ammonia solution that reacted with HCl)

$$M = 2.85 \times 10^{-3} \div 25.00 \times 10^{-3} = 0.114 \text{ M}$$

- 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.

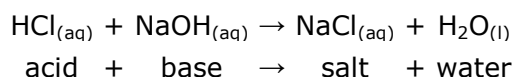
The excess HCl was then titrated with 0.250M NaOH.

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:



- b. Calculate the moles,  $n$ , of  $\text{NaOH}_{(\text{aq})}$  that reacted in the titration:

$$n = M \times V$$

$$M = 0.250 \text{ molL}^{-1}$$

$$V = 32.12\text{mL} = 32.12 \times 10^{-3}\text{L}$$

$$n(\text{NaOH}_{(\text{aq})}) = 0.250 \times 32.12 \times 10^{-3} = 8.03 \times 10^{-3} \text{ mol}$$

- 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,  $8.03 \times 10^{-3}$  mole NaOH reacted with  $8.03 \times 10^{-3}$  moles HCl

- d. The amount of HCl that was added to the chalk in excess was  
 $8.03 \times 10^{-3}$  mol

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

- a. Calculate the total moles of HCl originally added to the chalk:

$$n(\text{HCl}_{\text{total added}}) = M \times V$$

$$M = 0.200 \text{ molL}^{-1}$$

$$V = 50.00 \text{ mL} = 50.00 \times 10^{-3} \text{ L}$$

$$n(\text{HCl}_{\text{total added}}) = 0.200 \times 50.00 \times 10^{-3} = 0.010 \text{ mol}$$

- b. Calculate the moles of HCl that reacted with the calcium carbonate in the chalk

$$n(\text{HCl}_{\text{titrated}}) + n(\text{HCl}_{\text{reacted with calcium carbonate}}) = n(\text{HCl}_{\text{total added}})$$

$$n(\text{HCl}_{\text{total added}}) = 0.010 \text{ mol}$$

$$n(\text{HCl}_{\text{titrated}}) = 8.03 \times 10^{-3} \text{ mol}$$

$$8.03 \times 10^{-3} + n(\text{HCl}_{\text{reacted with calcium carbonate}}) = 0.010$$

$$n(\text{HCl}_{\text{reacted with calcium carbonate}}) = 0.010 - 8.03 \times 10^{-3} = 1.97 \times 10^{-3} \text{ mol}$$

- c. Write the balanced chemical equation for the reaction between calcium carbonate in the chalk and the  $\text{HCl}_{(\text{aq})}$ .



- d. From the balanced chemical equation, calculate the moles of  $\text{CaCO}_3$  that reacted with HCl.

From the equation, 1 mol  $\text{CaCO}_3$  reacts with 2 mol HCl so, 1 mol HCl reacts with  $\frac{1}{2}$  mol  $\text{CaCO}_3$

So,  $1.97 \times 10^{-3}$  mol HCl had reacted with  $\frac{1}{2} \times 1.97 \times 10^{-3} = 9.85 \times 10^{-4}$  mol  $\text{CaCO}_3$  in the chalk.

- e. Calculate the mass of calcium carbonate in the chalk.

$$n = \text{mass} \div \text{MM}$$

$$n = 9.85 \times 10^{-4} \text{ mol (moles of CaCO}_3 \text{ that reacted with HCl)}$$

$$\text{MM}(\text{CaCO}_3) = 40.08 + 12.01 + (3 \times 16.00) = 100.09 \text{ g/mol}$$

$$\text{mass} = n \times \text{MM} = 9.85 \times 10^{-4} \times 100.09 = 0.099\text{g}$$

- f. The mass of calcium carbonate in the chalk was 0.099g