

Name:

Volumetric Analysis	Objectives
3. Volumetric Analysis	-carry out a potassium manganate(VII)/ammonium iron(II) sulfate titration -determine the amount of iron in an iron tablet -carry out an iodine/thiosulfate titration -determine the percentage (w/v) of hypochlorite in bleach

Redox Titrations:**1. To prepare a standard solution of Ammonium Iron (II) Sulphate and to use this to standardise a solution of KMnO_4 by titration.**

Potassium Permanganate (KMnO_4) is not a primary standard as it is not available in a very pure state. It also is not stable as it decomposes in sunlight.

Ammonium Iron (II) Sulphate used as our primary standard because it is stable in air and has a high molecular mass. Even though it is not anhydrous, it is stable enough to use as it doesn't lose any water to the air.

We use the Ammonium Iron (II) Sulphate to standardise the Potassium Permanganate.

During this titration there are TWO additions of dilute H_2SO_4 . You need to know the reasons for each addition:

1. When dissolving our crystals in water to make our standard solution, some dilute H_2SO_4 is added to the water to prevent the Fe(II) oxidising to Fe(III) due to oxygen in the air and water.
2. Just before beginning the titration, dilute H_2SO_4 is added to the conical flask containing the Fe(II) . This ensures the full reduction of Mn(VII) to Mn(II) and prevents the formation of a brown precipitate of Mn(IV) .

Oxidising Agent: KMnO_4

Reducing Agent: Fe(II) from Ammonium Iron(II) Sulphate

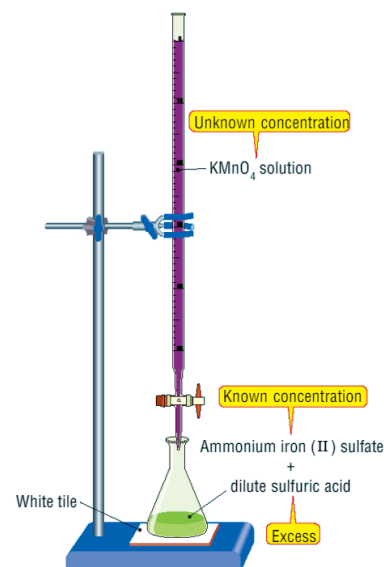
Indicator: KMnO_4 is self indicating.

N.B. At first the pink colour of KMnO_4 will decolourise slowly. As more Mn(II) forms during the titration, this catalyses the decolourisation so that it happens more quickly. This is called autocatalysis.

Colour change: First permanent pale pink (PPP).

Equation: $\text{MnO}_4^- + 5\text{Fe}^{2+} + 8\text{H}^+ \rightarrow \text{Mn}^{2+} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O}$

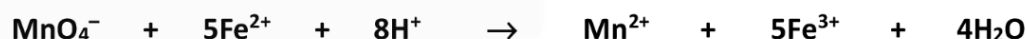
Ratio: $1 \text{ MnO}_4^- : 5 \text{ Fe}^{2+}$



Sample question: (2017 HL Q1)

A solution of $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ (hydrated ammonium iron(II) sulfate), used as a primary standard, was prepared by dissolving 8.82 g of the crystals in dilute sulfuric acid and making the solution up to exactly 250 cm^3 with deionised water. This standard solution was titrated in 25.0 cm^3 portions, to which some more dilute sulfuric acid had been added, with a solution of potassium manganate(VII) (KMnO_4). On average, 20.45 cm^3 of the potassium manganate(VII) solution were required for complete oxidation of the Fe^{2+} ions.

The equation for the titration reaction is:



(d) Calculate

- (i) the number of moles of Fe^{2+} ion in a 25.0 cm^3 portion of the standard solution,
- (ii) the number of moles of potassium manganate(VII) required to oxidise this quantity of Fe^{2+} ion,
- (iii) the molarity of the potassium manganate(VII) solution. (15)

(i) We have $8.82 \text{ g}/250\text{cm}^3$ $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$

$$M_r \text{ of } (\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O} = 2[14+4(1)] + 32 + 4(16) + 56 + 32 + 4(16) + 6[2(1)+16] = 392$$

We have $8.82 \text{ g}/250\text{cm}^3$ $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$

$$\div 392 \quad [\text{g to mol} \rightarrow \div M_r]$$

$$0.0225 \text{ mol}/250\text{cm}^3 (\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$$

$$= 0.0225 \text{ mol}/250\text{cm}^3 \text{Fe}^{2+}$$

$$\frac{0.0225}{250} \times 25$$

$$= 0.00225 \text{ mol}/25 \text{ cm}^3 \text{Fe}^{2+}$$

(ii) MnO_4^- : Fe^{2+}
 1 : 5
 0.00045 : 0.00225

$$= 0.00045 \text{ mol MnO}_4^-$$

(iii) $0.00045 \text{ mol}/20.45 \text{ cm}^3 \text{MnO}_4^-$

$$\frac{0.00045}{20.45} \times 1000$$

$$= 0.022 \text{ mol/L MnO}_4^-$$

2. To determine the amount of iron in an iron tablet

Oxidising Agent: KMnO_4

Reducing Agent: Fe(II) from FeSO_4

Indicator: KMnO_4 is self indicating.

Colour change: First permanent pale pink.

Equation: $\text{MnO}_4^- + 5\text{Fe}^{2+} + 8\text{H}^+ \rightarrow \text{Mn}^{2+} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O}$

Ratio: $1 \text{ MnO}_4^- : 5 \text{ Fe}^{2+}$

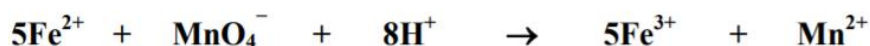
Notes: The tablets are ground up using a pestle and mortar. This is done in dilute H_2SO_4 to prevent the oxidation of Fe^{2+} to Fe^{3+} due to oxygen in the air or water. Further dilute H_2SO_4 is added just before the titration to ensure the full reduction of Mn(VII) to Mn(II) and to prevent the formation of a brown precipitate of Mn(IV) .

Iron tablets are prescribed by doctors to treat anaemia.

Sample calculation: (2009 HL Q1)

The Fe^{2+} content of iron tablets was determined by titration with a freshly standardised potassium manganate(VII), KMnO_4 .

The equation for the titration reaction is



(c) Describe how exactly 250 cm^3 of Fe^{2+} solution was prepared from five iron tablets, each of mass 0.325 g . Why was some dilute sulfuric acid used in making up this solution? (12)

(e) On average, 18.75 cm^3 of 0.01 M potassium manganate(VII) was required to react with 25.0 cm^3 portions of the iron solution prepared from the five tablets.

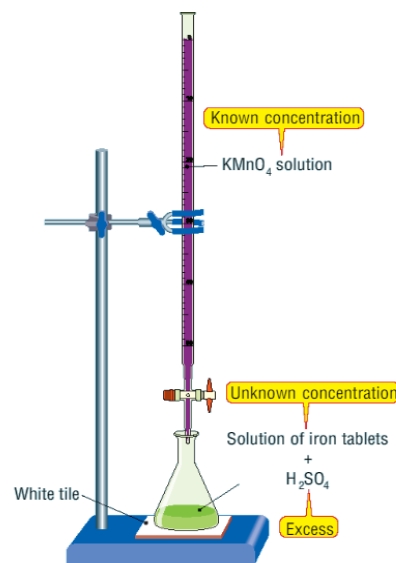
Calculate

- the molarity of the Fe^{2+} solution,
- the total mass of iron in the 250 cm^3 of solution,
- the percentage by mass of iron in the tablets.

(18)

(c)

- Crush tablets using a mortar and pestle, using dilute H_2SO_4
- Transfer with rinsings to a beaker with some deionised water and dilute H_2SO_4 .
- Stir to dissolve.
- Using a funnel, transfer solution and rinsings to a 250 cm^3 volumetric flask.
- Drop by drop, add deionised water to the volumetric flask until the bottom of the meniscus reaches the graduation mark at eye level.
- Stopper and invert 20 times.



(e)

(i) 0.01 mol/L MnO_4^-

$$\frac{0.01}{1000} \times 18.75$$

$$= 1.875 \times 10^{-4} \text{ mol/18.75 cm}^3 \text{ MnO}_4^-$$

$$\begin{array}{ccc} \text{MnO}_4^- & : & \text{Fe}^{2+} \\ 1 & : & 5 \\ 1.875 \times 10^{-4} & : & 9.375 \times 10^{-4} \end{array}$$

$$9.375 \times 10^{-4} \text{ mol/25 cm}^3 \text{ Fe}^{2+}$$

$$\frac{9.375 \times 10^{-4}}{25} \times 1000$$

$$= 0.0375 \text{ mol/L Fe}^{2+}$$

(ii) 0.0375 mol/L Fe^{2+}

$$\div 4$$

$$9.375 \times 10^{-3} \text{ mol/250 cm}^3 \text{ Fe}^{2+}$$

$$\times 56 \quad [\text{mol to g} \rightarrow \times M_r] \quad M_r \text{ of Fe} = 56$$

$$= 0.525 \text{ g/250 cm}^3 \text{ Fe}^{2+}$$

(iii) $\% = \frac{\text{Mass of iron in 1 tablet}}{\text{Mass of 1 tablet}} \times 100$

$$0.525 \text{ g of Fe in 5 tablets.}$$

$$\div 5$$

$$= 0.105 \text{ g Fe in 1 tablet.}$$

From question, each tablet weighs 0.325g.

$$\% = \frac{0.105}{0.323} \times 100$$

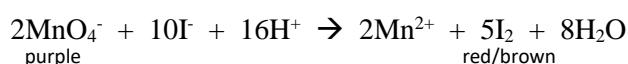
$$= 32.5\%$$

3. To prepare a solution of Sodium Thiosulphate and standardise it by titration against a solution of Iodine.

Sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$) is not a primary standard as it is not available in a pure enough state. It is also not anhydrous as it contains water of crystallisation.

Iodine is not a primary standard as it vaporises at room temperature (not stable) and it is not soluble in water. To make iodine soluble in water, there must be a source of iodide (I^-) ions, such as from potassium iodide (KI).

To make a standard solution of iodine we react a standard solution of potassium permanganate (KMnO_4) with excess sulphuric acid (H_2SO_4) and excess potassium iodide (KI). This forms a standard iodine solution, according to the equation below:



From this we can calculate the concentration of the iodine (I_2) solution using stoichiometric ratios. Making an I_2 solution from KMnO_4 has never been asked about in SEC exams, but it IS examinable.

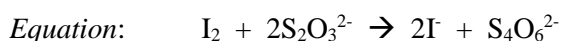
Oxidising Agent: I_2

Reducing Agent: $\text{S}_2\text{O}_3^{2-}$ (thiosulphate)

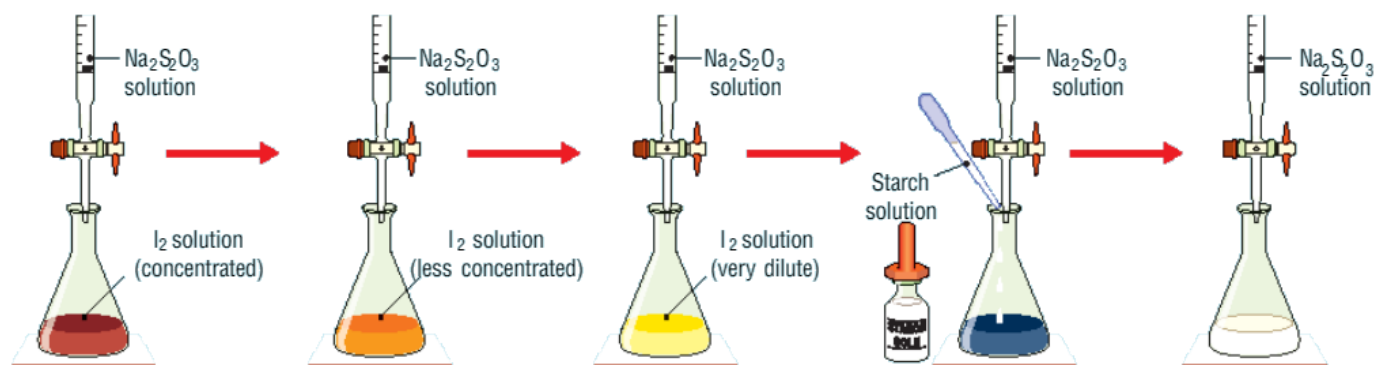
Indicator: Starch

Only add starch at straw yellow stage (most of the iodine has reacted with thiosulphate). Adding starch too early can cause iodine to form a strong complex with starch which won't decolourise.

Colour change: red/brown \rightarrow straw yellow $\xrightarrow{\text{add starch}}$ blue/black \rightarrow colourless

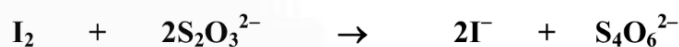


Ratio: 1 I_2 : 2 $\text{S}_2\text{O}_3^{2-}$



Sample Calculation (2015 HL Q1):

Sodium thiosulfate is a reducing agent that reacts with iodine according to the following balanced equation.



To determine the concentration of a sodium thiosulfate solution, a student titrated it against 25.0 cm³ portions of a standard iodine solution.

- (d) Given that there were 6.35 g of iodine (**I₂**) in 500 cm³ of the iodine solution, calculate
- the number of moles of iodine in each 25.0 cm³ portion,
 - the number of moles of sodium thiosulfate required to reduce this quantity of iodine,
 - the concentration of the sodium thiosulfate solution in moles per litre, 17.85 cm³ of which were required to reduce 25.0 cm³ of the iodine solution,
 - the concentration of the sodium thiosulfate solution in grams per litre of its crystals (**Na₂S₂O₃·5H₂O**).

(d)

- (i) We have 6.35 g/500 cm³ I₂

$$M_r \text{ of I}_2 = 2(127) = 254$$

$$\text{We have } 6.35 \text{ g}/500\text{cm}^3 \text{ I}_2$$

$$\div 254 \quad [\text{g to mol} \rightarrow \div M_r]$$

$$0.025 \text{ mol}/500\text{cm}^3 \text{ I}_2$$

$$\frac{0.025}{500} \times 25$$

$$=0.00125 \text{ mol}/25 \text{ cm}^3 \text{ I}_2$$

- (ii)
$$\begin{array}{lll} \text{I}_2 & : & \text{S}_2\text{O}_3^{2-} \\ 1 & : & 2 \\ 0.00125 & : & 0.0025 \end{array} = 0.0025 \text{ mol S}_2\text{O}_3^{2-}$$

- (iii) 0.0025 mol/17.85 cm³ S₂O₃²⁻

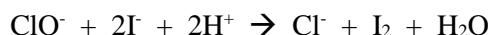
$$\frac{0.0025}{17.85} \times 1000$$

$$=0.14 \text{ mol/L S}_2\text{O}_3^{2-}$$

- (iv)
$$\begin{array}{l} M_r \text{ of Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O} = 2(23) + 2(32) + 3(16) + 5[2(1) + 16] = 248 \\ \times 254 \quad [\text{mol to g} \rightarrow \times M_r] \\ 34.72 \text{ g/L Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O} \end{array}$$

4. To determine the percentage (w/v) of sodium hypochlorite (NaClO) in bleach.

In household bleach, the concentration of ClO^- (hypochlorite) is too high so we dilute it first. Note your dilution factor. Before titrating, we react the dilute bleach with excess KI and excess dilute H_2SO_4 to form an iodine solution, as in the following equation:



When we carry out the titration we will find the concentration of the iodine solution we just formed, and use the ratios in the equation above to find the concentration of ClO^- .

Oxidising Agent: ClO^- (sometimes given as I_2)

Reducing Agent: $\text{S}_2\text{O}_3^{2-}$ (thiosulphate)

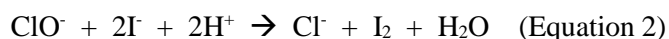
Indicator: Starch

Only add starch at straw yellow stage (most of the iodine has reacted with thiosulphate). Adding starch too early can cause iodine to form a strong complex with starch which won't decolourise.

Colour change: red/brown $\xrightarrow{\text{add starch}}$ straw yellow \rightarrow blue/black \rightarrow colourless

Equation: $\text{I}_2 + 2\text{S}_2\text{O}_3^{2-} \rightarrow 2\text{I}^- + \text{S}_4\text{O}_6^{2-}$ (Equation 1)

If we combine this with the equation to form I_2 from ClO^- ,



We see that each ClO^- forms 1 I_2 (equation 2). Each I_2 then reacts with 2 $\text{S}_2\text{O}_3^{2-}$ ions (Equation 1)

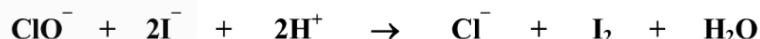
From this we get our overall ratio.

Ratio: $1 \text{ ClO}^- : 1 \text{ I}_2 : 2 \text{ S}_2\text{O}_3^{2-}$
 $\equiv 1 \text{ ClO}^- : 2 \text{ S}_2\text{O}_3^{2-}$

Sample Calculation (2011 HL Q1):

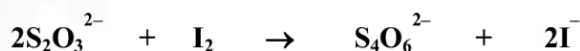
A chemist determined the concentration of a bleach solution containing **NaClO** by volumetric analysis. A 25.0 cm^3 sample of the bleach was first diluted to exactly 500 cm^3 .

A pipette was used to measure a 25.0 cm^3 volume of the diluted bleach and to transfer it into a conical flask. Solutions of potassium iodide, **KI**, and sulfuric acid were added. The following reaction took place in the conical flask.



The solution in the conical flask was next titrated with a 0.10 M solution of sodium thiosulfate (**Na₂S₂O₃**). The average volume of sodium thiosulfate required, when the procedure was repeated a number of times, was 16.1 cm^3 .

The balanced equation for the titration reaction was:



(e) Calculate the concentration of **NaClO** in moles per litre in

(i) the diluted bleach,

(ii) the original bleach.

(12)

(f) What was the concentration of **NaClO** in the original bleach

(i) in grams per litre,

(ii) as a % (w/v)?

(8)

(e)

(i) $0.10 \text{ mol/L S}_2\text{O}_3^{2-}$

$$\frac{0.10}{1000} \times 16.1$$

$$0.00161 \text{ mol/16.1 cm}^3 \text{ S}_2\text{O}_3^{2-}$$

$$\begin{array}{ccc} \text{ClO}^- & : & \text{S}_2\text{O}_3^{2-} \\ 1 & : & 2 \\ 0.000805 & : & 0.00161 \end{array}$$

$$0.000805 \text{ mol/25 cm}^3 \text{ ClO}^- \text{ (dil)}$$

$$\frac{0.000805}{25} \times 1000$$

$$= 0.0322 \text{ mol/L ClO}^- \text{ (dil)}$$

(ii) Dilution Factor = $\frac{500}{25} = 20$

$$\begin{aligned} &0.0322 \times 20 \\ &= 0.644 \text{ mol/L ClO}^- \text{ (original)} \end{aligned}$$

(f)

(i) $M_r \text{ of NaClO} = 23 + 35.5 + 16 = 74.5$
 0.644×74.5 [mol to g $\rightarrow \times M_r$]
 $= 47.978 \text{ g/L NaClO}$

(ii) $\%(\text{w/v}) = \text{g/100 cm}^3 \text{ NaClO}$
 $47.978 \div 10$
 $4.7978 \%(\text{w/v}) \text{ NaClO}$