

THEME
1

The chemical world

Topic 1: Quantitative and qualitative analysis

Performance objectives

After studying this Topic, you should be able to do the following:

- 1.1 Titrate accurately and perform relevant calculations.
- 1.2 Analyse different salts for anions and cations.
- 1.3 Carry out simple tests for common gases.
- 1.4 Carry out simple redox titrations.
- 1.5 Test for fats, oils, proteins, starch, etc.

Qualitative analysis is based on the qualities present, for example, the type of elements in a substance. Quantitative analysis is based on the number and ratio of quantities present, for example, the concentration of a substance. In this topic, we will look at quantitative analysis of acid-base titrations and redox titrations. We will discuss the qualitative analysis on how to identify oxidants and reductants, how to identify cations and anions, how to test for common gases, and how to identify fats, oils, simple sugars, proteins and starch.

Acid-base titrations

Titration is a method for determining the amount or concentration of an unknown substance. The method is easy to use if the quantitative relationship between two reacting substances is known. The titration method can be used for acid-base and redox reactions. An acid-base titration determines the concentration of an acid or a base by exactly neutralising the acid/base with a base

or acid of known concentration. A solution of known concentration is a **standard solution**. **Neutralisation** occurs at the equivalence point (or endpoint) of the reaction. This is the point where equal molar amounts of the acid and base have reacted according to the molar concentration ratio in the chemical equation. Neutralisation occurs between the H^+ ions from the acid and the OH^- ions from the base. Before starting a titration, a suitable pH indicator must be chosen. The **endpoint** of a titration is that point where the indicator changes colour.

Titration to determine percentage purity

The substances that we use in titrations are not always completely pure – they may contain impurities. Some substances are mixtures of different compounds. For example, an acid or a base may be contaminated by one of its salts, for instance NaOH may be contaminated by NaCl. Sometimes we have to calculate how pure the sample is or what percentage by mass there exists in a sample.

Chemical analysis can determine the composition of substances and from the composition we can work out the percentage purity. To calculate the percentage purity, we use this formula:

$$\text{percentage purity} = \frac{\text{mass of the pure substance}}{\text{mass of the sample}} \times 100\%$$

When finding the percentage purity of a sample of impure compounds, a standard solution of the impure solid is made. Titration with the other solution enables you to find the mass of the pure substance and from there you can calculate the percentage purity. It should be kept in mind that the neutralisation reaction is between the pure acid and the pure base – the impurities remain in solution.

Worked example: Calculate percentage purity

3.68 g of washing soda crystals ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$) are dissolved in water and made up to a volume of 275 cm^3 . Of this washing soda sample, 25.0 cm^3 is neutralised by 23.5 cm^3 of HCl of concentration $0.11 \text{ mol} \cdot \text{dm}^{-3}$. Calculate the percentage Na_2CO_3 in the washing soda. The balanced equation for the reaction is as follows:



Solution:

The aim of our calculation is to determine how much of the 3.68 g of washing soda is actually Na_2CO_3 .

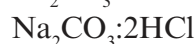
- **Step 1:** Calculate the number of moles of the pure acid used in the titration.

$$c = \frac{n}{V}$$

$$0.11 \text{ mol} \cdot \text{dm}^{-3} = \frac{n}{0.0235 \text{ dm}^{-3}}$$

$$n = 2.59 \times 10^{-3} \text{ mol}$$

- **Step 2:** Use the mole ratio to find the number of moles of Na_2CO_3 used in the titration.



1:2

$$\begin{aligned} \therefore n(\text{Na}_2\text{CO}_3) &= 2(2.59 \times 10^{-3} \text{ mol}) \\ &= 1.29 \times 10^{-3} \text{ mol} \end{aligned}$$

- **Step 3:** Determine the number of moles of Na_2CO_3 in the original 275 cm^3 sample. $1.29 \times 10^{-3} \text{ mol}$ is the number of moles in 25 cm^3 of Na_2CO_3 solution, and we need to know the number of moles in the original 275 cm^3 sample.

$$n = \frac{1.29 \times 10^{-3} \text{ mol}}{25 \text{ cm}^3} \times 275 \text{ cm}^3$$

$$= 1.42 \times 10^{-2} \text{ mol}$$

$\therefore 1.42 \times 10^{-2} \text{ mol Na}_2\text{CO}_3$ in 275 cm^3 sample

- **Step 4:** Calculate the mass of Na_2CO_3 in the original 275 cm^3 sample.

$$n = \frac{m}{M}$$

$$1.42 \times 10^{-2} \text{ mol} = \frac{m}{106 \text{ g} \cdot \text{mol}^{-1}}$$

$$m = 1.51 \text{ g Na}_2\text{CO}_3$$

- **Step 5:** Calculate the percentage of Na_2CO_3 in the original sample.

Percentage purity

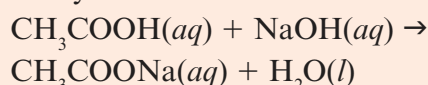
$$= \frac{\text{mass of the pure substance}}{\text{mass of the sample}} \times 100\%$$

$$\% \text{ purity} = \frac{1.51 \text{ g}}{3.68 \text{ g}} \times 100\% = 41\%$$

Therefore, the percentage purity of Na_2CO_3 is 41%

Experiment 1.1 Determine the percentage acetic acid in vinegar

In this experiment, you will determine the concentration of acetic acid in vinegar and calculate the percentage acetic acid in vinegar. The acetic acid reacts with the sodium hydroxide as follows:



Vinegar should contain about 5% acetic acid by volume.

Aim: To determine the percentage acetic acid in vinegar

Materials/apparatus:

- 250 cm³ volumetric flask
- vinegar
- sodium hydroxide
- 25.0 cm³ pipette
- phenolphthalein indicator
- burette
- conical flask

Method:

1. Make a standard solution of sodium hydroxide in a 250 cm³ volumetric flask.
2. Clean the burette and rinse with a small amount of sodium hydroxide solution. Fill the burette with NaOH and zero the reading.
3. Using a pipette, add 25.0 cm³ of vinegar to a conical flask.
4. Add a few drops of phenolphthalein indicator to the conical flask.
5. Using the burette, slowly add sodium hydroxide solution to the conical flask while swirling the conical flask until the

colour of the solution is a light pink. The colour in the solution must remain for 20 seconds.

6. Record the final burette reading.
7. Repeat the procedure twice and record your titration results in a table. Take the average of the three final burette readings.

In this experiment, assume that the density of vinegar is 1 g·ml⁻¹, thus 25 ml = 25 g

Questions:

1. Calculate the concentration of the acetic acid from the titration results.
2. Calculate the mass of acetic acid in the 25 cm³ sample of vinegar used in the titration.
3. Calculate the percentage of acetic acid in the vinegar sample.

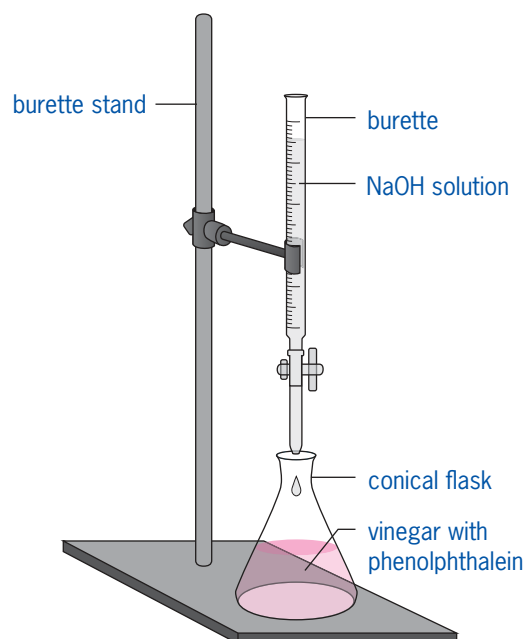


Figure 1.1 Diagram of experimental setup

Titration to determine heat of neutralisation

During a neutralisation reaction, the hydrogen ion (H^+) or proton from the acid is neutralised by the hydroxide ions (OH^-) from the alkali to form a water molecule (H_2O). The heat of neutralisation is the amount of heat liberated when 1 gram equivalent of an acid is completely neutralised in a base. The heat of neutralisation is the energy change that occurs when one mole of water is formed from the neutralisation between one mole of hydrogen ions (H^+) from an acid and one mole of hydroxide ions (OH^-) from a base.

In any calorimeter, the heat released or absorbed is given by the following equation:

Heat of neutralisation = mass \times specific heat capacity of H_2O \times change in temperature

$$Q = m \times C_{\text{H}_2\text{O}} \times \Delta T$$

$$C_{\text{H}_2\text{O}} = \text{specific heat capacity of water} \\ = 4.18 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$$

$$\Delta T = \text{temperature change}$$

In other words, it takes 4.18 J of heat energy to raise the temperature of 1 g of water by 1 degree.

m = mass of the water absorbing the heat

You have to relate this heat change to the mass or molar mass quantities used to get the ΔH enthalpy change in $\text{kJ} \cdot \text{mol}^{-1}$. At constant volume and pressure, the enthalpy change is approximately equal to the heat of the reaction.

Worked example: Calculate heat of neutralisation

50 ml (about 50 g) of NaOH was added to a calorimeter connected to a thermometer and the initial temperature of the solution was measured. 25 ml (about 50 g) of HCl was added to the NaOH in the calorimeter. The temperature rose from 23 °C to 55 °C.

Questions:

- Calculate the heat of neutralisation by using the formula:
 $Q = \text{mass of solution } (m) \times \text{specific heat of water } (C) \times \text{change in temperature of solution } (\Delta T)$
- Why do we use a polystyrene (Styrofoam) cup in this experiment?
- What conclusion can we draw from these results?

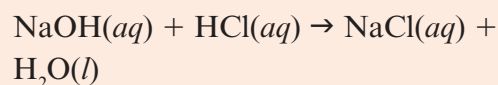
Solutions:

- $Q_{\text{neutralisation}} = m \times C \times \Delta T = (100) (4.18)(55 - 23) = 13.376 \text{ kJ}$
- To prevent heat loss to the surroundings. Polystyrene is a heat insulator.
- A neutralisation reaction can occur when you combine an acid and a base. Neutralisation reactions give off energy, which is known as the heat of neutralisation.

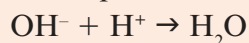
In the following experiment, we will measure the heat of neutralisation when an acid and base react to form 1 mole of water. This quantity of heat is measured experimentally by allowing the reaction to take place in a thermally insulated polystyrene cup calorimeter. The heat liberated in the neutralisation reaction will cause an increase in the temperature of the solution and the calorimeter.

Experiment 1.2 Determine heat of neutralisation of an acid and a base

When aqueous solutions of HCl and NaOH are mixed, a reaction takes place and the products formed are a salt and water.



This is a neutralisation reaction since the H^+ ion, which is responsible for acidic properties, has reacted with the hydroxide ion (OH^-), which is responsible for basic properties.



Aim: To determine the heat change for the neutralisation reaction between NaOH and HCl

Materials/apparatus:

- 2 × 50 ml measuring cylinders
- beakers
- polystyrene cup calorimeter
- thermometer
- 0.5 M HCl
- 0.5 M NaOH
- 0.5 M HNO_3

Method:

Using NaOH as the base and HCl and HNO_3 as the acids, proceed as follows, performing the neutralisation in duplicate:

1. Pour 40 ml of 0.5 M NaOH into one measuring cylinder and 40 ml of the acid into the other.
2. Measure accurately and record the temperature of each solution.
3. Simultaneously, pour the acid and base together into the polystyrene cup calorimeter.
4. Stir gently with the thermometer and record the highest temperature reached.
5. Wash the beaker and repeat the experiment twice.
6. Repeat the above procedure, but now use HNO_3 as the acid.

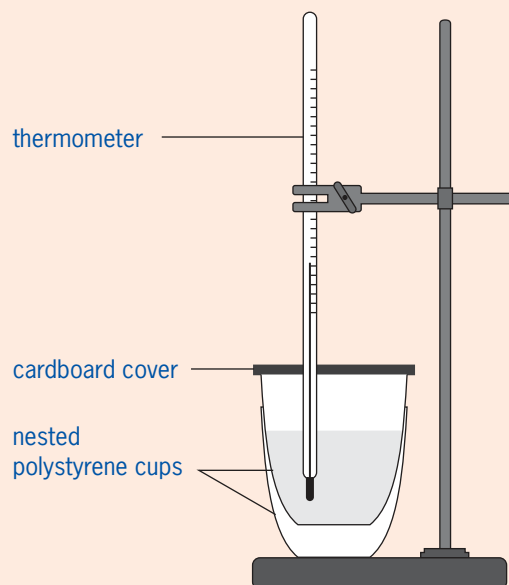


Figure 1.2 Experimental setup of calorimeter

Questions:

1. Calculate the average initial temperature of the acid and base.
2. Calculate the change in temperature $\Delta T = T_{\text{final}} - T_{\text{initial}}$
3. Calculate the heat evolved using:
 Energy transferred = mass × specific heat capacity × ΔT (for dilute solutions, specific heat capacity approximately equals that of H_2O , i.e. $4.18 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$).
4. Calculate the number of moles of water produced.
5. Calculate the heat evolved per mole of water.
6. What is the value of ΔH (neutralisation)?
7. Comment on the ΔH values determined in both cases.

Bomb calorimeter

The bomb calorimeter is a device that is used to measure the heat of reaction with a high level of accuracy. This type of calorimeter is commonly used for reactions that involve gases, especially for combustion that takes place at high

temperature and forms gaseous substances. It consists of a sealed container, like a bomb, where the chemical reaction takes place.

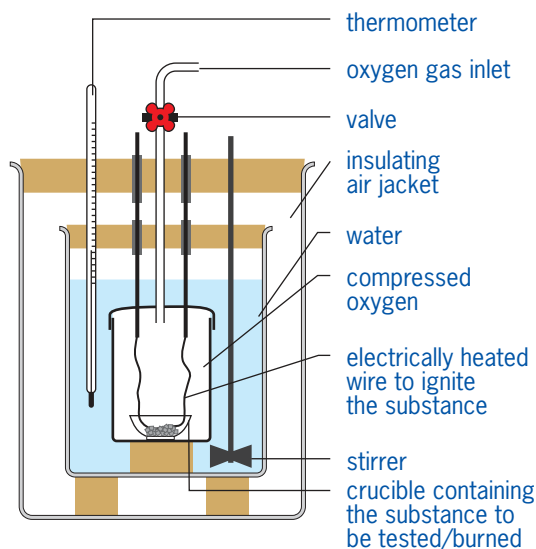


Figure 1.3 Bomb calorimeter

Titration to determine water of crystallisation

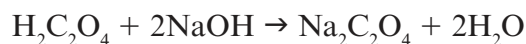
Water of crystallisation is water which is found as part of the structure of a crystalline substance. Some ionic crystals trap water molecules between their ions when they form, and are called hydrated salts. The water of crystallisation is generally represented in the chemical equations of such compounds at the end of the formula, for example, $\text{Na}_2\text{CO}_3 \cdot x\text{H}_2\text{O}$. The 'x' is a number which represents the number of water molecules in the crystal. The ratio of water molecules to the ions is a fixed number.

Hydrated substances are sometimes used in volumetric analysis. During the titration process, it is only the anhydrous part of the substance that is actually neutralised and the water of crystallisation remains in the solution, just like impurities.

Worked example: Determine water of crystallisation

3.5 g of hydrated oxalic acid ($\text{H}_2\text{C}_2\text{O}_4 \cdot x\text{H}_2\text{O}$) was made up to 250 cm³ of solution. 25.0 cm³ of this solution required 22.2 cm³ of 0.25 mol·dm⁻³ NaOH solution for complete neutralisation. Calculate the value of 'x' to the nearest whole number.

Solution:



$$n(\text{NaOH}) = cV = (0.25)(0.0222)$$

$$= 0.00555 \text{ mol (or } 555 \times 10^{-3} \text{ mol)}$$

2 moles of NaOH require 1 mole of $\text{H}_2\text{C}_2\text{O}_4$

5.55×10^{-3} mol of NaOH requires

$$\frac{1}{2}(5.55 \times 10^{-3} \text{ mol}) = 2.78 \times 10^{-3} \text{ mol } \text{H}_2\text{C}_2\text{O}_4$$

$$c(\text{H}_2\text{C}_2\text{O}_4) = \frac{n}{V} = \frac{2.78 \times 10^{-3} \text{ mol}}{25 \times 10^{-3} \text{ dm}^3}$$

$$= 0.111 \text{ mol} \cdot \text{dm}^{-3}$$

To find the value of 'x':

Mass concentration of hydrated acid in 3.5 g in 250 cm³:

i.e. 250 cm³ contains 3.5 g of hydrated acid

$$1 \text{ 000 cm}^3 \text{ contains } 3.5 \text{ g } \left(\frac{1 \text{ 000}}{250}\right) = 3.5 \times 4$$

$$= 14.0 \text{ g} \cdot \text{dm}^{-3}$$

molar mass of hydrated acid =

$$\frac{\text{mass concentration}}{\text{molar concentration}} = \frac{14 \text{ g} \cdot \text{dm}^{-3}}{0.111 \text{ mol} \cdot \text{dm}^{-3}}$$

$$= 126.1 \text{ g} \cdot \text{mol}^{-1}$$

Relative molar mass of $\text{H}_2\text{C}_2\text{O}_4 \cdot x\text{H}_2\text{O}$

$$= 126.1$$

$$2(1) + 2(12) + 4(16) + 18x = 126.1$$

$$18x = 36.1$$

$$x = 2$$

Experiment 1.3 Percentage water of crystallisation

Aim: To determine the percentage of water of crystallisation in hydrated sodium carbonate (washing soda) by titration

Materials/apparatus:

- watch glass
- mass meter
- sodium carbonate
- 250 ml volumetric flask
- 25 ml pipette
- conical flask
- methyl orange
- burette

Method:

1. Weigh 5.0 g of sodium carbonate on a watch glass.
2. Make up a standard solution of sodium carbonate by using a 250 ml volumetric flask filled up to the mark with water.
3. Using a pipette, add 25 ml of the solution to a conical flask.
4. Add a few drops of methyl orange to the solution in the conical flask.
5. Place the 0.2 mol·dm⁻³ HCl in the burette.
6. Titrate until the yellow colour is replaced by a permanent pink colour, which indicates the endpoint of the titration.
7. Record the volume of acid required to reach the endpoint and repeat the experiment several times.

Results:

Record the results in a table with headings such as the one shown at the top of the next column.

Trial	Volume of sodium carbonate (ml)	Volume of hydrochloric acid (ml)
1		
2		
3		
Average volume		

Questions:

1. Calculate the concentration of sodium carbonate.
2. Calculate the percentage of water of crystallisation in sodium carbonate.
3. Calculate the number of water molecules 'x' in Na₂CO₃·xH₂O.

Activity 1.1 Acid-base titrations

Work on your own.

1. Students were asked to determine the amount of inert impurities in a contaminated sample of anhydrous oxalic acid (H₂C₂O₄). They prepared a standard solution of sodium hydroxide by diluting 50 cm³ of a 1.63 mol·dm⁻³ solution in a 1.0 dm³ volumetric flask. They then prepared a solution of contaminated oxalic acid by dissolving 0.25 g of oxalic acid in 75 cm³ of water. The acid solution was then titrated against the NaOH solution. The titration required 40 cm³ of the NaOH solution to reach the equivalence point. The equation for the reaction is:

$$2\text{NaOH} + \text{H}_2\text{C}_2\text{O}_4 \rightarrow \text{Na}_2\text{C}_2\text{O}_4 + \text{H}_2\text{O}$$

- a) What is meant by the equivalence point?
- b) Suggest a suitable indicator for the titration.

- c) Use the information that the learners obtained and calculate the percentage purity of the oxalic acid sample.

2. 150 cm³ of 1.0 mol·dm⁻³ hydrochloric acid was placed in a polystyrene cup and its temperature was recorded. 50 cm³ of 1.0 mol·dm⁻³ sodium hydroxide (at the same temperature) was added to the acid in the cup. The reaction mixture was stirred with the thermometer and the highest temperature was recorded. The following results were obtained:

	Temperature (°C)
NaOH solution	26.5
HCl solution	26.0
Average initial temperature	26.25
Final temperature	27.0
Change in temperature	0.75

Answer the following questions:

- a) Calculate the number of moles of NaOH in 50 cm³ of 1.0 mol·dm⁻³ NaOH solution.
- b) Calculate the number of moles of HCl in 50 cm³ of 1.0 mol·dm⁻³ HCl solution.
- c) Calculate the energy transferred from the experiment.
- d) What is the enthalpy change of the reaction?
3. Washing soda was titrated against hydrochloric acid. 0.352 g of hydrated sodium carbonate crystals (Na₂CO₃·xH₂O) was titrated with 0.1 mol·dm⁻³ standard hydrochloric acid solution. If the titrated value was 24.65 cm³, calculate the number of moles of Na₂CO₃ titrated and determine the value of 'x' (the number of molecules of water of crystallisation) in washing soda crystals.

Redox titrations involving KMnO₄, Fe²⁺, C₂O₄²⁻, I₂, KI, S₂O₃²⁻

A redox reaction is a chemical reaction that involves a transfer of electrons. Electrons lost by one substance are gained by another. Reduction and oxidation always happen at the same time. A change in the oxidation number of an atom during a reaction means that the atom has either lost or gained electrons. The substance that gains electrons is the oxidising agent (oxidant) and the substance that loses electrons is the reducing agent (reductant).

Redox titrations involve the chemical reaction between the oxidising agent and reducing agent in aqueous solutions under suitable conditions. For redox titrations, one solution must be the standard solution. For some reactions, for example those involving the permanganate ion (MnO₄⁻), the endpoint will be indicated by a colour change in the reacting solutions, whereas for others an indicator must be added in order to detect the endpoint.

Volumetric analysis involving redox reactions can be used to determine the composition of many substances. When a solution of an oxidising agent is titrated against a solution of a reducing agent, the amounts of the oxidising agent and that of the reducing agent titrated are in the same ratio as in the stoichiometry in the balanced equation at the endpoint. We can use stoichiometric calculations, for example, to determine the composition of substances by using the following equation:

$$\frac{c_{\text{OA}} V_{\text{OA}}}{c_{\text{RA}} V_{\text{RA}}} = \frac{n_{\text{OA}}}{n_{\text{RA}}}$$

where:

c_{OA} is the concentration of the oxidising agent
 c_{RA} is the concentration of the reducing agent

A solution containing 0.161 g of sodium oxalate ($\text{Na}_2(\text{COO})_2$) reacted with 26.7 ml of a potassium permanganate solution. Determine the concentration of this solution.

Solution:

$$n_{\text{RA}} = \frac{m}{M} = \frac{0.161 \text{ g}}{134 \text{ g}\cdot\text{mol}^{-1}} = 0.0012 \text{ mol}$$

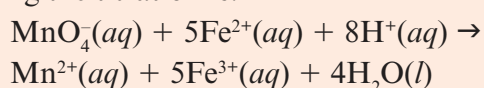
From the equation:

$$\begin{aligned} n(\text{MnO}_4^-) &= \frac{2}{5}n((\text{COO})_2^{2-}) \\ &= \frac{2}{5} \times 0.0012 \text{ mol} = 0.000481 \text{ mol} \\ c(\text{MnO}_4^-) &= \frac{n}{V} = \frac{0.000481 \text{ mol}}{0.0267 \text{ dm}^{-3}} \\ &= 0.0180 \text{ M} \end{aligned}$$

Experiment 1.4 Redox titration with potassium permanganate

Aim: To standardise an iron(II) solution using a standard solution of potassium permanganate

The equation of the reaction taking place during the titration is:



Materials/apparatus:

- burette
- conical flask
- burette stand
- pipette
- measuring cylinder
- standardised KMnO_4
- iron(II) solution of unknown concentration
- dilute H_2SO_4 solution

Method:

1. Fill the burette with KMnO_4 and record the initial reading.
2. Rinse the pipette with iron(II) solution, then transfer 25 cm^3 into a clean conical flask and add 10 cm^3 dilute H_2SO_4 .
3. Titrate the iron(II) solution with the KMnO_4 while swirling the conical flask until the solution just retains a permanent pink colour.
4. Repeat the titration twice using fresh samples each time.
5. Record your reading in a table and calculate the average volume of KMnO_4 used.

Questions:

1. From your results, calculate the amount of iron(II) in 25 cm^3 of iron(II) solution.
2. Calculate the concentration (in $\text{mol}\cdot\text{dm}^{-3}$) of the iron(II) solution.

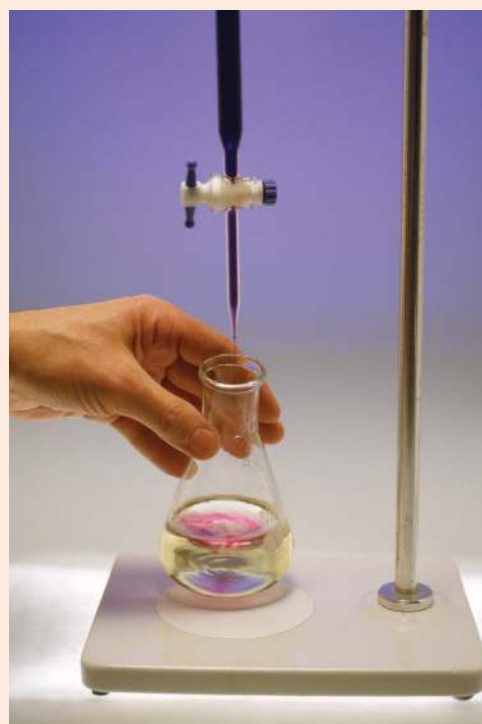


Figure 1.5 Redox titration with potassium permanganate