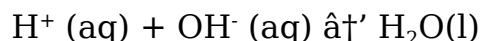


## 5. VOLUMETRIC ANALYSIS

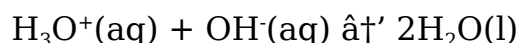
### 5.1 Introduction

Volumetric analysis is concerned with the measurement of volumes of solutions of different substances which react chemically. An indicator is often used to indicate when to stop the addition of one solution to a measured volume of another. For the determined volumes to be useful, the concentration of one of the reactant solutions should be known.

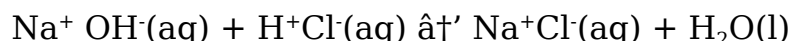
Neutralisation reactions involve essentially the reactions between hydrogen ions (or hydroxonium ions) and hydroxide ions, to form water.



or



The negative ion of the acid and the positive ion of the alkaline solution remain as ions in solution. They only combine to form a solid salt when the solution is evaporated.



### 5.2 Molar Concentration

The molar concentration,  $c$ , of a solution is the moles of solute in 1  $\text{dm}^3$  of solution. That is

$c = \frac{\text{Number of mole of solute}}{\text{Volume of solution (in dm}^3\text{)}}$
--

A solution containing one mole of sodium hydroxide, that is 40 NaOH, in 1  $\text{dm}^3$  of solution is 1 molar (1  $\text{mol dm}^{-3}$ ). If a solution contains 0.5 mole, that is 20g of sodium hydroxide in 1  $\text{dm}^3$ , it is 0.5  $\text{mol dm}^{-3}$ . Similarly, if the solution contains 1 mole that is 40g of NaOH in 2 $\text{dm}^3$ , it means that 1  $\text{dm}^3$  of that solution contains 0.5 or 20g of NaOH. That is, the solution is 0.5  $\text{mol dm}^{-3}$ . Notice that the **number of mole = molar concentration multiplied by volume (in  $\text{dm}^3$ )**.

### 5.3 Standard Solution

A standard solution is one whose concentration is known. The concentration is measured either in  $\text{g dm}^{-3}$  or  $\text{mol dm}^{-3}$

*Experiment 5.1: Preparation of a standard sodium trioxocarbonate(IV) solution.*

Formula:  $\text{Na}_2\text{CO}_3$

Molar mass =  $(23 \times 2) + 12 + (16 \times 3) \text{ g} = 106 \text{ g}$ .

106g made up to 1  $\text{dm}^3$  gives 1  $\text{mol dm}^{-3}$  solution.

10.6 g made up to 1  $\text{dm}^3$  gives 0.1  $\text{mol dm}^{-3}$  solution.

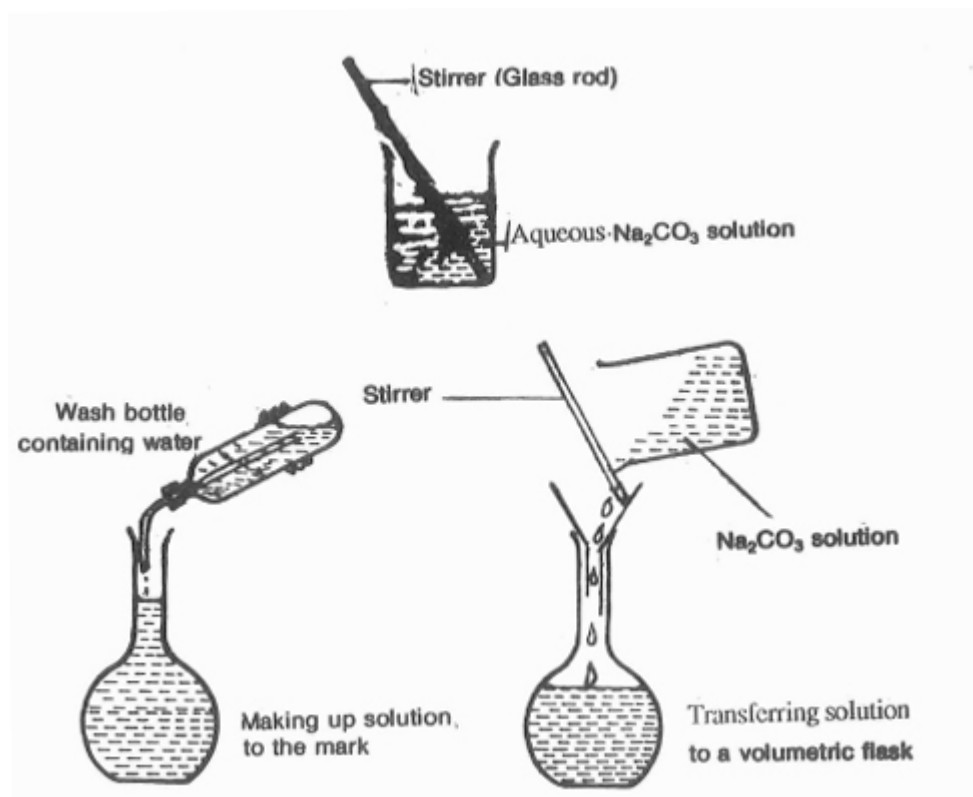
2.65g made up to 250  $\text{cm}^3$  gives 0.1  $\text{mol dm}^{-3}$  solution.

Weigh out accurately about 2.65 g of anhydrous sodium trioxocarbonate(IV). Dissolve this in water in a beaker. Rinse the weighing bottle several times with water and add the washings to the solution. Transfer the solution into a 250  $\text{cm}^3$  volumetric flask through a funnel. Rinse the funnel with water into the flask. Carefully add water from a wash bottle to bring the level to the mark. Stopper the flask and invert a couple of times to mix well.

This is a standard solution of sodium trioxocarbonate(IV), of strength 0.1  $\text{mol dm}^{-3}$

Hygroscopic, deliquescent and efflorescent substances cannot be used to prepare standard solutions because accurate masses of such substances cannot be weighed out. Hence we cannot prepare a standard solution of sodium hydroxide because it is deliquescent. Similarly we cannot prepare a standard solution of tetraoxosulphate(VI) acid because it is hygroscopic. Substances to be used in preparing standard solutions must

- (i) be obtainable in a pure state;
- (ii) not decompose on standing;
- (iii) not be affected by the atmosphere. Sodium trioxocarbonate(IV) qualifies in these respects.



**Figure 5.1 Preparation of standard solution**

### Dilution of Solution

To dilute a solution the solvent (usually water) is added to a measured volume of the concentrated solution until a predetermined volume is reached. The relationship that exists between the molar concentration of the concentrated solution,  $c_1$ , the volume of it measured out,  $V_1$ , and the molar concentration of the dilute solution,  $c_2$ , the volume it is diluted to,  $V_2$  is

Molar concentration  $\times$  Volume = a constant, i.e.

**Molar concentration of original solution multiplied by its volume = molar concentration of diluted solution multiplied by its volume.**

$$\text{i.e. } c_1 V_1 = c_2 V_2$$

### WORKED EXAMPLES

1. What volume of distilled water will be added to  $1\text{ dm}^3$  of  $5\text{ mol/dm}^3$  solution to make it  $2\text{ mol dm}^{-3}$ ?

**SOLUTION** Using the relationship  $c \times V = \text{constant}$

$$5 \times 1 = 2 \times V$$

$$V = 2.5$$

That is, the new volume is  $2.5\text{ dm}^3$

$\therefore$  Volume of water added to  $1\text{ dm}^3$  of the solution to make it  $2.5\text{ dm}^3$

$$= 1.5 \text{ dm}^3.$$

2. What volume of commercial concentrated tetraoxosulphate(VI) acid will be diluted to  $1 \text{ dm}^3$  to get a  $1.0 \text{ mol dm}^{-3}$  solution?

(The specific gravity of the commercial acid is  $1.84 \text{ g dm}^{-3}$ )

### SOLUTION

Formula of the acid is  $\text{H}_2\text{SO}_4$

$$\begin{aligned}\text{Molar mass} &= (2 \times 1) + 32 + (16 \times 4) \\ &= 98 \text{ g.}\end{aligned}$$

$\therefore$  98 g of pure  $\text{H}_2\text{SO}_4$  made up to  $1 \text{ dm}^3$  is  $1.0 \text{ mol dm}^{-3}$ . That is 98 g of the pure acid is needed.

$$\begin{aligned}\frac{\text{Mass}}{\text{Volume}} &= 1.84 \text{ g cm}^{-3} \\ \therefore \frac{98}{\text{Volume}} &= 1.84 \text{ g cm}^{-3} \\ \therefore \text{Volume needed} &= \frac{98}{1.84} \text{ cm}^3 = 53.26 \text{ cm}^3.\end{aligned}$$

### EXERCISE 5A

- (1) What masses of the named substances are needed to prepare the solutions indicated?
  - (a)  $1 \text{ dm}^3$  of  $0.5 \text{ mol dm}^{-3}$  sodium trioxocarbonate(IV),
  - (b)  $200 \text{ cm}^3$  of  $1 \text{ mol dm}^{-3}$  sodium hydroxide,
  - (c)  $500 \text{ cm}^3$  of  $0.25 \text{ mol dm}^{-3}$  sodium hydrogen trioxocarbonate(IV),
  - (d)  $750 \text{ cm}^3$  of  $0.1 \text{ mol dm}^{-3}$  tetraoxosulphate(VI) acid,
  - (e)  $250 \text{ cm}^3$  of  $0.25 \text{ mol dm}^{-3}$  hydrogen chloride acid (hydrochloric acid).
- (2) What volume of water is needed for diluting  $1 \text{ dm}^3$  of the following solutions?
  - (a)  $3.6 \text{ mol dm}^{-3}$  hydrogen chloride acid (hydrochloric acid) to  $1 \text{ mol dm}^{-3}$
  - (b)  $18 \text{ mol dm}^{-3}$  tetraoxosulphate(VI) acid to  $2 \text{ mol dm}^{-3}$ ,
  - (c)  $0.5 \text{ mol dm}^{-3}$  sodium hydroxide solution to  $0.1 \text{ mol dm}^{-3}$

## 5.4 Titration

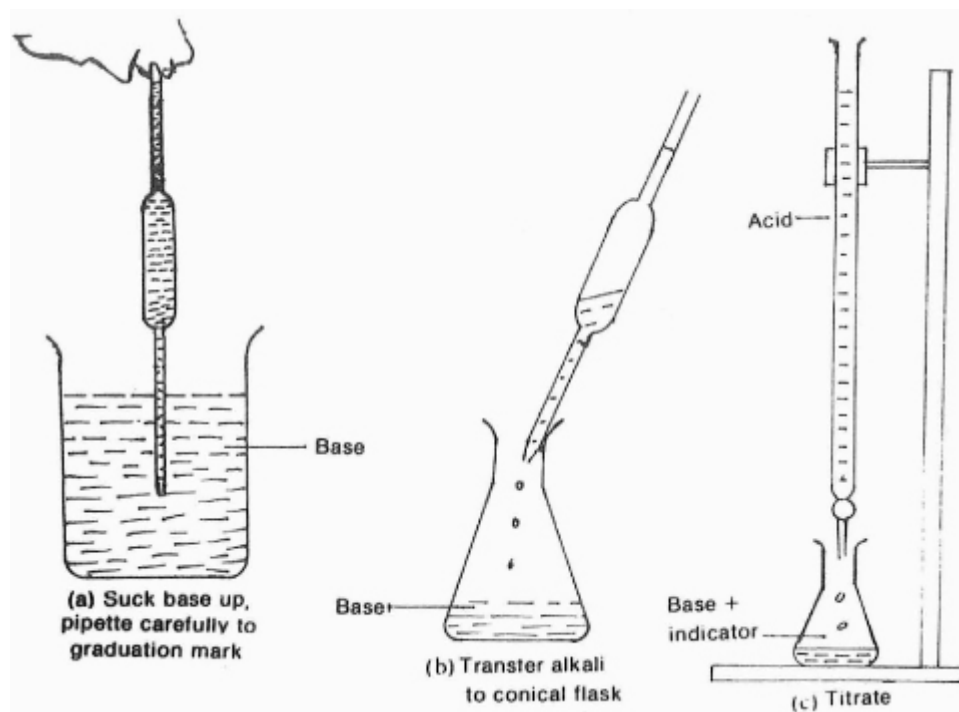
Titration involves the addition of one solution, from a burette, to a known volume of another, in a conical flask, to determine the equivalent volumes for their complete reaction. In acid-base titrations the acid is usually poured into a burette, and the alkali is transferred into the conical flask with the aid of a pipette. One of these solutions

should be a standard solution for the titration result to be useful. An indicator is required to indicate the point when enough acid from the burette has been added.

*Experiment 5.2: Titration of a standard sodium trioxocarbonate(IV) solution against an approximately 0.2 mol dm<sup>-3</sup> hydrogen chloride acid (hydrochloric acid) solution.*

Rinse a burette with a little of an approximately 0.2 mol dm<sup>-3</sup> hydrogen chloride acid (hydrochloric acid) solution, then fill it with the acid. Rinse a pipette with a little of 0.1 mol dm<sup>-3</sup> solution of sodium trioxocarbonate(IV). Pipette 25 cm<sup>3</sup> of this standard solution into a clean conical flask. Add two drops of methyl orange indicator to it, then place it on a white tile under the clamped burette. Record the initial burette reading to two places of decimal.

Run in the acid from the burette, swirling the solution in the conical flask continuously. After some time, a pink colour is observed to persist for a short time at the spot where the acid contacts the base. At this point, adjust the burette to deliver the acid in drops. At the end point, the yellow solution of methyl orange in alkali turns to orange colour. Stop the titration then. Record the final burette reading. Refill the burette with the acid and repeat the titration two more times.



**Figure 5.2 Titration**

## **SPECIMEN RESULTS**

Burette readings (cm<sup>3</sup>)

Titration	Rough	1	2
Final	25.90	36.10	26.30
Initial	0.00	10.50	0.60
Vol. of acid	25.90	25.60	25.70

$$\text{Average} = \frac{25.60 + 25.70}{2} \text{ cm}^3$$

$$= 25.65 \text{ cm}^3$$

Volume of alkali = 25 cm<sup>3</sup>.

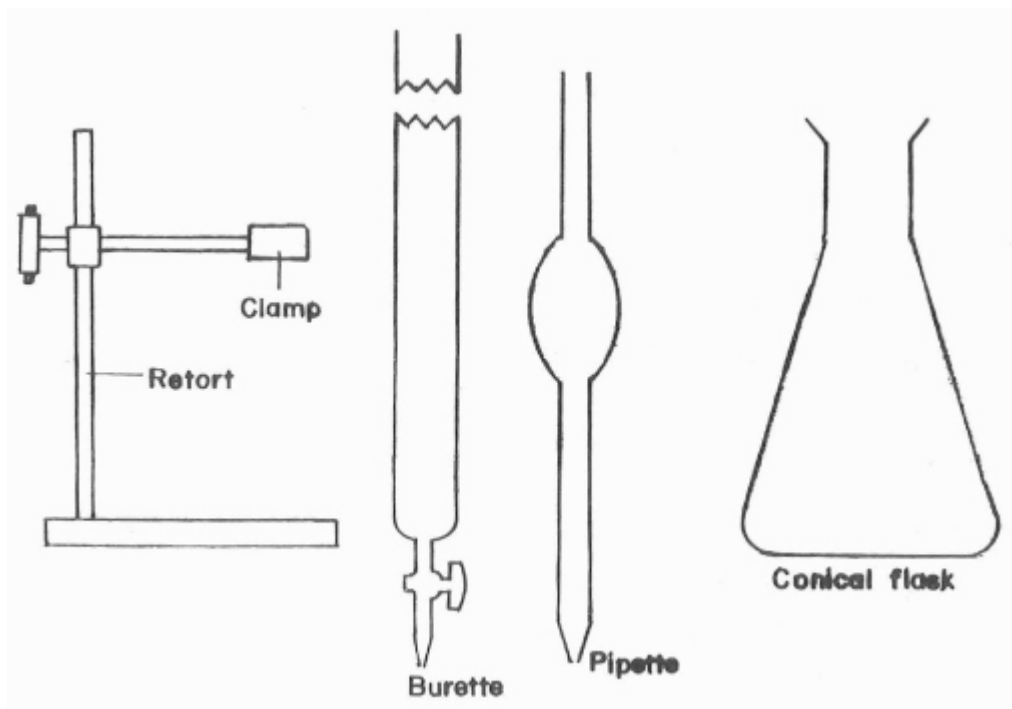
The first reading is usually a rough one and may be ignored. Two other accurate readings are chosen and averaged. The difference between any two readings averaged should not be more than 0.2 cm<sup>3</sup>.

### EXERCISE 5B

In a titration experiment, a student records the following readings:

Burette readings (cm <sup>3</sup> ).				
	Titration	Rough	1	2
Volume of alkali = 25 cm <sup>3</sup>	Final	23.50	46.80	33.55
	Initial	0.00	23.50	10.20

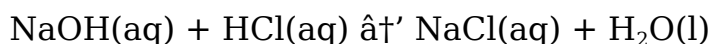
What average titre should be recorded?



**Figure 5.3 Titration equipments**

## 5.5 Calculating Molar Concentration of a Solution from the Results of Titration

First, we need a balanced equation to determine the mole ratios of reactants. For example, in the reaction



1 mole NaOH reacts with 1 mole HCl.

That is, the mole ratio of the reactants is 1 : 1 .

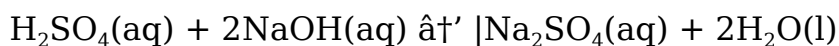
Since molar concentration  $\times$  volume is equal to number of mole.

$$\frac{c_A V_A}{c_B V_B} = \frac{1}{1}$$

$$\text{or } c_A V_A = c_B V_B$$

Where  $c_A$  and  $V_A$  are molar concentration and volume of acid, and  $c_B V_B$  molar concentration and volume of alkali respectively.

For the reaction

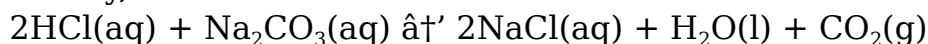


1 mole of acid neutralises 2 mole of alkali.

$$\text{That is, } \frac{c_A V_A}{c_B V_B} = \frac{1}{2}$$

$$\text{or } 2c_A V_A = c_B V_B$$

Similarly, for the reaction:



2 mole of acid neutralises 1 mole of alkali.

$$\therefore \frac{c_A V_A}{c_B V_B} = \frac{2}{1}$$
$$\text{or } c_A V_A = 2c_B V_B$$

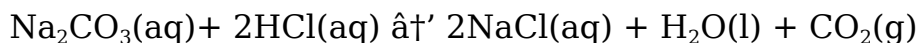
With these relationships we can calculate the unknown molar concentration of a solution used in a titration.

### WORKED EXAMPLES

1.25 cm of 0.1 mol dm<sup>-3</sup> sodium trioxocarbonate(IV) solution is neutralised by 25.65 cm<sup>3</sup> hydrogen chloride acid (hydrochloric acid) of unknown mol dm of the acid. What is the molar concentration?

### SOLUTION

The equation of the reaction is:



i.e. 1 mole of base is neutralised by 2 mole of acid,

$$\text{or } \frac{c_A V_A}{c_B V_B} = \frac{2}{1}$$

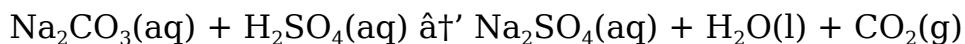
Substitute in this equation.

$$\therefore \frac{c_A \times 25.65}{0.1 \times 25} = \frac{2}{1}$$
$$\therefore c_A = \frac{2 \times 0.1 \times 25}{25.65} = 0.195 \text{ mol dm}^{-3}$$

Thus the accurate molar concentration of the acid is 0.195 mol dm<sup>-3</sup>.

2. If the acid used in the experiment were tetraoxosulphate(VI) acid, and if exactly the same results were got, (that is 25.0 cm<sup>3</sup> of Na<sub>2</sub>CO<sub>3</sub> is neutralised by 25.65 cm<sup>3</sup> of acid), what is the molar concentration of the acid solution?

### SOLUTION



Mole ratio: 1 : 1



$$\therefore \frac{c_A V_A}{c_B V_B} = \frac{1}{1}$$

$$\therefore \frac{c_A \times 25.65}{0.1 \times 25} = \frac{1}{1}$$

$$\therefore c_A \times 25.65 = 0.1 \times 25$$

$$\therefore c_A = \frac{0.1 \times 25}{25.65}$$

$$= 0.097 \text{ mol dm}^{-3}$$

The concentration of a solution in  $\text{g dm}^{-3}$  may be obtained from the expression:

$$\text{Concentration (g dm}^{-3}\text{)} = \text{molar concentration} \times \text{molar mass}$$

3. Consider the result of this titration:

	Rough	1	2
Final burette reading ( $\text{cm}^3$ )	23.60	46.80	33.55
Initial " " "	0.00	23.50	10.20
Volume of acid used in $\text{cm}^3$	23.60	23.30	23.35 $\text{cm}^3$

$$\text{Volume of alkali} = 25 \text{ cm}^3$$

If the acid solution is  $0.097 \text{ mol dm}^{-3}$  tetraoxosulphate(VI) acid, and the alkali is sodium trioxocarbonate(IV) decahydrate, calculate the concentration of the crystals of the hydrated salt in  $\text{g dm}^{-3}$ .

### SOLUTION

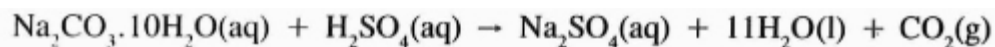
Subtracting the initial burette readings from the final burette readings, the volumes of acid for titrations 1, 2, and 3 are :

1	2	3
23.60 $\text{cm}^3$	23.30 $\text{cm}^3$	23.35 $\text{cm}^3$

$$\text{The average titre is } \frac{23.30 + 23.35}{2} \text{ cm}^3$$

$$= 23.325 \text{ cm}^3$$

Equation of reaction



1 mole

1 Mole

$$\frac{c_A V_A}{c_B V_B} = \frac{1}{1}$$

$$\therefore \frac{0.097 \times 23.325}{c_B \times 25} = \frac{1}{1}$$

$$\therefore c_B = \frac{0.097 \times 23.325}{25} = 0.0905 \text{ mol dm}^{-3}$$

$$\begin{aligned} \text{Molar mass of Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O} &= [(23 \times 2) + 12 + (16 \times 3) + (10 \times 18)]\text{g} \\ &= 286\text{g} \end{aligned}$$

$$\begin{aligned} \text{Concentration in g dm}^{-3} &= \text{Mol dm}^{-3} \times \text{Molar mass} \\ &= 0.0905 \times 286 \text{ g dm}^{-3} \\ &= 25.88 \text{ g dm}^{-3} \end{aligned}$$

*Experiment 5.3: To determine the percentage purity of a sample of impure sodium trioxocarbonate(IV).*

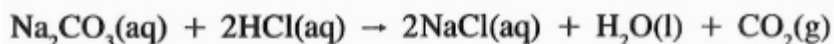
Weigh out about 2 g of the impure sample of sodium trioxocarbonate(IV). Dissolve it in water. If any solid impurity remains undissolved, filter it off and wash the residue with distilled water, adding the washings to the salt solution contained in a 250 cm<sup>3</sup> volumetric flask. Make up the solution to the mark as described in Experiment 5.1.

Rinse a burette with a 0.12 mol dm<sup>-3</sup> hydrogen chloride acid (hydrochloric acid) solution, then fill it with the acid. Pipette 25 cm<sup>3</sup> of the sodium trioxocarbonate(IV) solution into a conical flask. Add two drops of methyl orange (or screened methyl orange) to it. Titrate the solution against the acid from the burette. Perform two more titrations to get two concordant readings.

### SPECIMEN RESULTS AND CALCULATIONS

	Burette readings (cm <sup>3</sup> )		
	1	2	3
Final	25.00	24.85	24.75
Initial	0.00	0.00	0.00
	25.00	24.85	24.75

Average volume of acid = 24.80 cm<sup>3</sup>



$$\frac{c_A V_A}{c_B V_B} = \frac{2}{1}$$

$$\therefore \frac{0.12 \times 24.8}{c_B \times 25} = \frac{2}{1}$$

$$\therefore c_B = \frac{0.12 \times 24.8}{2 \times 25} = 0.05952 \text{ mol dm}^{-3}$$

Molar mass of Na<sub>2</sub>CO<sub>3</sub> = 106g.

$$\therefore \text{Concentration} = 106 \times 0.05952 \text{ g dm}^{-3} \\ = 6.309 \text{ g dm}^{-3}$$

$$\therefore \text{Mass in 250 cm}^3 \text{ of solution} = \frac{6.309 \text{ g}}{4} = 1.577 \text{ g.}$$

$$\therefore \% \text{ purity} = \frac{1.577}{2} \times 100\% \\ = 78.9\%$$

*Experiment 5.4 : To find the number of mole of water of crystallization per mole of sodium trioxocarbonate(IV) crystals.*

Weigh out accurately about 7.8 g of hydrated sodium trioxocarbonate(IV). Dissolve this in water, and make up to 500 cm<sup>3</sup> in a standard flask. Pipette 25 cm<sup>3</sup> of the solution each time for titrations against 0.09 mol dm<sup>-3</sup> hydrogen chloride acid (hydrochloric acid) solution.

### **SPECIMEN RESULTS AND CALCULATIONS**

25 cm<sup>3</sup> of the sodium trioxocarbonate(IV) solution required 31.00 cm<sup>3</sup> of 0.09 mol dm<sup>-3</sup> hydrogen chloride acid (hydrochloric acid) for neutralisation.



$$\frac{c_A V_A}{c_B V_B} = \frac{2}{1}$$

$$\therefore \frac{0.09 \times 31.00}{25 \times c_B} = \frac{2}{1}$$

$$\therefore c_B = \frac{0.09 \times 31.00}{25 \times 2} = 0.0558 \text{ mol dm}^{-3}$$

$$\text{Molar mass} = (106 + 18x)\text{g}.$$

$$\text{Concentration} = (7.8 \times 2)\text{g dm}^{-3}$$

$$\therefore (106 + 18x) \times 0.0558 = 7.8 \times 2$$

$$\therefore 5.92 + 1.004x = 15.6$$

$$\therefore 1.004x = 9.68$$

$$\therefore x = \frac{9.68}{1.004} = 9.64.$$

But x must be a whole number,

$$\therefore x = 10.$$

But x must be a whole number,

$$\hat{\wedge} \text{ } x = 10.$$

### WORKED EXAMPLES

(1) Calculate the volume of  $0.5 \text{ mol dm}^{-3} \text{H}_2\text{SO}_4$  which will be needed to react completely with 0.8 g of copper(II) oxide.

#### SOLUTION



(63.5 + 16) g of CuO reacts with 1 dm<sup>3</sup> of 1 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>

i.e. 79.5 g    "    "    "    "    1 dm<sup>3</sup>    "    "

$\therefore$  79.5 g    "    "    "    "    2 dm<sup>3</sup> of 0.5 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>

$\therefore$  0.8 g    "    "    "    "     $\frac{2000 \times 0.8}{79.5} \text{ cm}^3$   
 $= 20.13 \text{ cm}^3$

(2) 5.3 g of Na<sub>2</sub>CO<sub>3</sub> was made up to 250 cm<sup>3</sup> of solution with distilled water and 25 cm<sup>3</sup> of the solution required 20.0 cm<sup>3</sup> of HCl for neutralisation. Calculate

- the molar concentration of the alkaline solution,
- the molar concentration of the acid solution,
- the concentration of the acid solution in g dm<sup>-3</sup>

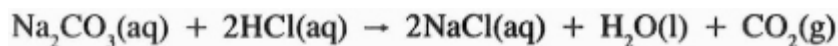
## SOLUTION

250 cm<sup>3</sup> of solution contains 5.3 g Na<sub>2</sub>CO<sub>3</sub>

∴ 1 dm<sup>3</sup> of solution contains (5.3 ÷ 0.25) g Na<sub>2</sub>CO<sub>3</sub> = 21.2 g.

Molar mass of Na<sub>2</sub>CO<sub>3</sub> = 106g.

∴ Molar concentration of the solution =  $\frac{21.2}{106} = 0.2 \text{ mol dm}^{-3}$



1 mole : 2 mole

$$\therefore \frac{c_A V_A}{c_B V_B} = \frac{2}{1}$$

$$\therefore \frac{20 \times c_A}{25 \times 0.2} = \frac{2}{1}$$

$$\therefore c_A = \frac{2 \times 25 \times 0.2}{20} = 0.5 \text{ mol dm}^{-3}$$

i.e. Molar concentration of the acid solution is 0.5 mol dm<sup>-3</sup> Molar mass of HCl = (1 + 35.5)g = 36.5g.

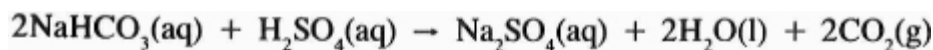
∴ Concentration of the acid solution in g/dm<sup>-3</sup>

$$= 0.5 \times 36.5 \text{ g dm}^{-3}$$

$$= 18.25 \text{ g dm}^{-3}$$

(3) 10g of sodium hydrogen trioxocarbonate(IV) was shaken up with 100 cm<sup>3</sup> of water and the solution allowed to stand for several hours, for undissolved solid to settle. 25 cm<sup>3</sup> of the clear solution was carefully pipetted into a 250 cm<sup>3</sup> standard flask and the solution made up to the mark with, distilled water, and thoroughly shaken. 25 cm<sup>3</sup> of this solution required 23.5 cm<sup>3</sup> of 0.1 mol dm<sup>-3</sup> tetraoxosulphate(VI) acid for neutralisation. Calculate the solubility of sodium hydrogen trioxocarbonate(IV) in moles dm<sup>-3</sup>, at the temperature of the experiment.

## SOLUTION



i.e. 2 mole<sup>-</sup> NaHCO<sub>3</sub> requires 1 mole of H<sub>2</sub>SO<sub>4</sub>.

$$\therefore \frac{c_B V_B}{c_A V_A} = \frac{2}{1}$$

$$\therefore 2c_A V_A = c_B V_B$$

$$\therefore 2 \times 23.5 \times 0.1 = 25 C_B$$

$$\therefore c_B = \frac{2 \times 23.5 \times 0.1}{25} = 0.188 \text{ mol dm}^{-3}$$

Molar mass of  $\text{NaHCO}_3 = [23 + 1 + 12 + (16 \times 3)]\text{g} = 84\text{g}$ .

Concentration of the  $\text{NaHCO}_3$  solution used for titration in  $\text{g/dm}^3$   
 $= (0.188 \times 84) \text{ g dm}^{-3} = 15.79 \text{ g dm}^{-3}$

But the  $\text{NaHCO}_3$  solution for titration was made by diluting the saturated solution 10 times. that is  $25 \text{ cm}^3$  made up to  $250 \text{ cm}^3$ .

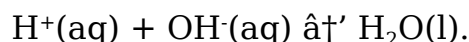
$$\therefore \text{Concentration of the saturated solution} = 10 \times 15.79 \text{ g dm}^{-3} \\ = 157.9 \text{ g dm}^{-3}$$

$$\therefore \text{Solubility of NaHCO}_3 = \frac{157.9}{84} \text{ mol dm}^{-3} \\ = 1.88 \text{ mol dm}^{-3}$$

$$\therefore \text{Solubility of NaHCO}_3 \text{ at the temperature of the experiment} \\ = 1.88 \text{ mol dm}^{-3}$$

## 5.6 Heat of Neutralization

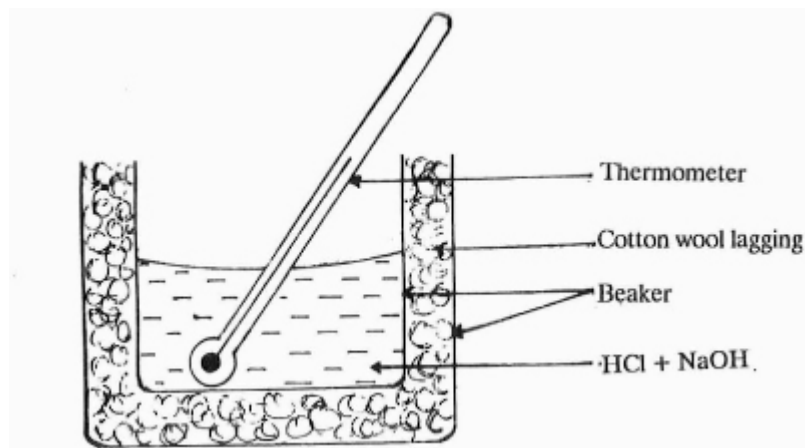
We started our discussions on volumetric analysis by stating that neutralization reactions involve



No matter what acid yields the  $\text{H}^+$ , or what alkali yields the  $\text{OH}^-$  ions, this same basic reaction is involved. Since strong acids and strong alkalis are completely ionised in water, all neutralization reactions involving them are expected to be the same. Are they the same in all respects?

*Experiment 5.5: Investigating the heat of neutralization of a strong acid by a strong base.*

Put  $50 \text{ cm}^3$  of  $2 \text{ mol dm}^{-3}$  hydrogen chloride acid (hydrochloric acid), into a  $250 \text{ cm}^3$  beaker. Measure the temperature of this solution. Put the  $250 \text{ cm}^3$  beaker into a larger beaker ( $400 \text{ cm}^3$  capacity) with cotton wool lagging to avoid loss of heat. Measure  $50 \text{ cm}^3$  of  $2 \text{ mol dm}^{-3}$  sodium hydroxide solution into another  $250 \text{ cm}^3$  flask and again take its temperature. Pour the  $50 \text{ cm}^3$  sodium hydroxide solution into the  $50 \text{ cm}^3$  hydrogen chloride acid (hydrochloric acid) solution and stir with the thermometer. Record the highest temperature attained by the mixture.



**Figure 5.4 Determining the heat of neutralization**

Repeat the experiment with various combinations of strong acids and equivalent amounts of strong alkalis such as

$50 \text{ cm}^3 \text{ } 2 \text{ mol dm}^{-3} \text{ HNO}_3 + 50 \text{ cm}^3 \text{ } 2 \text{ mol dm}^{-3} \text{ KOH}$ ,  
 $50 \text{ cm}^3 \text{ } 1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4 + 50 \text{ cm}^3 \text{ } 2 \text{ mol dm}^{-3} \text{ NaOH}$ ,  
 $50 \text{ cm}^3 \text{ } 2 \text{ mol dm}^{-3} \text{ HCl} + 50 \text{ cm}^3 \text{ } 2 \text{ mol dm}^{-3} \text{ KOH}$ .

### SPECIMEN RESULTS AND CALCULATIONS

Temperature of acid before mixing =  $28^\circ\text{C}$   
 Temperature of base before mixing =  $28^\circ\text{C}$   
 Average of initial temperature =  $28^\circ\text{C}$   
 Highest temperature of mixture =  $42.0^\circ\text{C}$   
 $\Delta$  Rise in temperature =  $14^\circ\text{C}$

Assuming that the solutions have the same density and specific heat as water.

Mass of mixture = 100g.

Specific heat of water =  $4.2 \text{ Joule g}^{-1} ^\circ\text{C}^{-1}$

$\Delta$  Heat evolved by the neutralization reaction =

specific heat  $\times$  mass  $\times$  temp rise =  $4.2 \times 100 \times 14 \text{ Joule}$

$50 \text{ cm}^3$  of  $2 \text{ mol dm}^{-3} \text{ NaOH}$  and  $50 \text{ cm}^3 \text{ } 2 \text{ mol dm}^{-3} \text{ HCl}$  contain 0.1 mole of base and acid.

$\Delta$  Heat evolved when 1 mole of each react

$$= 100 \times 14 \times 4.2 \times 10 = 58800 \text{ Joules mol}^{-1}$$

That is, the heat of neutralization of sodium hydroxide by hydrogen chloride/acid (hydrochloric acid) is  $58.8 \text{ KJ mol}^{-1}$

The heat of neutralization of all other strong acids by strong alkalis are of this same value. But the heat of neutralization of weak acids by strong alkalis, strong acids by weak bases, or weak acids by weak bases, are different. The difference lies in the fact that the energy for

the complete ionisation of such weak acids and bases before neutralization of the weak electrolytes is drawn from the solution.

## Chapter Summary

1. Titration experiments give the equivalent volumes of reactants in solution. The concentration of one of the reactants must be known for a calculation of the reacting masses to be feasible.
2. The following relationships are useful in the calculations.
  - (a) Molar Concentration,  $c$ , = number of mole of solute per  $\text{dm}^3$  of solution.
  - (b) For diluting a solution,  $cV = \text{a constant}$ .
  - (c) For the generalised reaction

$$\begin{array}{l} aA + bB \rightarrow \text{products;} \\ \text{if } V_1 = \text{volume of A and } c_1 \text{ molar concentration of A,} \\ \quad V_2 = \text{volume of B and } c_2 \text{ molar concentration of B,} \\ \text{Then, } \frac{c_1 V_1}{c_2 V_2} = \frac{a}{b} \end{array}$$

- (d) Concentration in  $\text{mol dm}^{-3} = \text{molar concentration } \tilde{A} - \text{molar mass}$ .
3. Neutralization reactions involve the reaction between hydroxonium ions and hydroxide ions to form water.
$$\text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l})$$

The heat of neutralization of a strong acid by a strong base is therefore constant.

## Assessment

1.
  - (a) What mass of sodium hydroxide is needed to make
    - (i)  $250 \text{ cm}^3$  of  $0.1 \text{ mol dm}^{-3}$  solution,
    - (ii)  $500 \text{ cm}^3$  of  $0.25 \text{ mol dm}^{-3}$  solution?
  - (b) What is the molar concentration of a solution containing
    - (i)  $9.8 \text{ g}$  tetraoxosulphate(VI) acid in  $500 \text{ cm}^3$  of solution,
    - (ii)  $31.4 \text{ g}$  of calcium chloride dihydrate in  $1 \text{ dm}^3$  of solution?
2.
  - (a) What new molar concentration is obtained if
    - (i)  $56 \text{ cm}^3$  of concentrated hydrogen chloride acid (hydrochloric acid),  $16 \text{ mol dm}^{-3}$ , is diluted to  $1 \text{ dm}^3$
    - (ii)  $200 \text{ cm}^3$  of  $5 \text{ mol dm}^{-3}$  sodium hydroxide solution is diluted to  $600 \text{ cm}^3$  of solution?
  - (b) What volume of water should be added to
    - (i)  $1 \text{ dm}^3$  of  $2 \text{ mol dm}^{-3}$  solution of sodium trioxocarbonate(IV) to make it  $0.5 \text{ mol dm}^{-3}$ ?



- (ii) 200 cm<sup>3</sup> of concentrated hydrogen chloride acid (hydrochloric acid) that is 16 mol dm<sup>-3</sup> to make it 2 mol dm<sup>-3</sup>?
3. (a) Calculate the concentration in g dm<sup>-3</sup> of the following solutions:
- 1.02 mol dm<sup>-3</sup> sodium chloride
  - 0.5 mol dm<sup>-3</sup> sodium trioxocarbonate(IV)
  - 5 mol dm<sup>-3</sup> sodium hydroxide solution.
- (b) What volume of 0.2 mol dm<sup>-3</sup> tetraoxosulphate(VI) acid is required to neutralise 25 cm<sup>3</sup> of 0.1 mol dm<sup>-3</sup> sodium hydroxide solution?
4. Calculate the molar concentration of a sodium hydroxide solution if 25 cm<sup>3</sup> of it requires 20.5 cm<sup>3</sup> of 0.103 mol dm<sup>-3</sup> solution of tetraoxosulphate(VI) acid for neutralization. What is the concentration of the alkaline solution in g dm<sup>-3</sup>?
5. The following results were got in a titration of sodium trioxocarbonate(IV) solution against 0.12 mol dm<sup>-3</sup> tetraoxosulphate(VI) acid solution: Volume of alkaline solution = 25 cm<sup>3</sup>.

	1	2	3
Final burette reading (cm <sup>3</sup> )	26.70	28.00	27.60
Initial " reading (cm <sup>3</sup> )	0.00	1.30	0.80

- Calculate (a) the average titre,
- the molar concentration of the alkaline solution,
  - the concentration of the alkaline solution in g dm<sup>-3</sup>
6. Write down a balanced equation for the reaction between sodium trioxocarbonate(IV) and hydrogen chloride acid (hydrochloric acid). If 0.5 mole of sodium chloride is produced,
- how many grammes of anhydrous sodium trioxocarbonate(IV) should be used with excess hydrogen chloride acid (hydrochloric acid)?
  - What will be the volume in dm<sup>3</sup> of the gaseous products at s.t.p? (G.M.V. = 22.4 dm<sup>3</sup> at s.t.p.)
7. 15.0 cm<sup>3</sup> of a solution of sodium chloride saturated at 20°C required 35.5 cm<sup>3</sup> of silver trioxonitrate(V) containing 240 g dm<sup>-3</sup> for complete precipitation. Calculate the solubility in mole per dm<sup>3</sup> of sodium chloride at 20°C.
8. (a) Calculate the volume of 0.5 mol dm<sup>-3</sup> tetraoxosulphate(VI) acid that will be needed to react completely with
- 0.8g of copper(II) oxide;
  - 10g of sodium hydrogen trioxocarbonate(IV).
- (b) Why would you rinse a burette with an acid before filling it,

but not rinse a conical flask with an alkali before pipetting 25 cm<sup>3</sup> of the solution into it?

## 5P EXPERIMENTAL PROJECT

### 5P.1 Titration Using Plant Extracts as Indicator

Collect samples of flowers and leaves from your compound (you may collect flowers and leaves of the hibiscus plant, flamboyant tree, etc. Wash each sample with clean water, then rinse it with distilled water. Grind each plant part separately in a mortar with pestle. While grinding each sample add about 5 cm<sup>3</sup> of propan-1-ol, then mix well with the pestle. Filter off the solid. Use the filtrate separately as indicator in the following titration experiment.

Prepare a standard sodium trioxocarbonate(IV) solution by weighing out 2.65 g of anhydrous salt and making it up to 250 cm<sup>3</sup> of solution with distilled water. This solution is 0.1 mol dm<sup>-3</sup>. Dilute bench hydrogen chloride acid (hydrochloric acid), which is about 2 mol dm<sup>-3</sup>, ten times by pipetting 25 cm<sup>3</sup> of it into a 250 cm<sup>3</sup> volumetric flask and making it up to the mark with distilled water. This solution is not a standard solution because the bench acid which is diluted is not a standard solution.

Determine the molar concentration of the diluted solution by titrating the standard sodium trioxocarbonate(IV) solution against it. Pipette 25 cm<sup>3</sup> of the alkali into a conical flask. Add about 0.5 cm<sup>3</sup> of your plant extract. Use the extracts one after the other for a number of titrations. Perform a rough titration first with each extract, to know the colour change expected, followed by one accurate titration. Since the indicators may not give sharp end points, a titre difference of up to 0.5 cm<sup>3</sup> is allowed. Calculate the average titre from the readings got for the different indicators. Use your average titre reading to calculate the molar concentration of the diluted acid solution, and hence, of the bench acid.

#### SPECIMEN RESULTS AND CALCULATIONS

Volume of alkali = 25 cm<sup>3</sup>

Burette readings (cm <sup>3</sup> )	Hibiscus flower	Hibiscus leaf	Flamboyant flower	Yellow bell flower
Final	23.30	23.40	23.70	23.40
Initial	0.00	0.00	0.50	0.30
Volume of acid added	23.30	23.40	23.20	23.10

$$\begin{aligned}\text{Average titre} &= \frac{23.30 + 23.40 + 23.20 + 23.10}{4} \text{ cm}^3 \\ &= 23.25 \text{ cm}^3 \\ \text{Na}_2\text{CO}_3(\text{aq}) + 2\text{HCl}(\text{aq}) &\rightarrow 2\text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g}) \\ 1 \text{ mole} &: 2 \text{ mole} \\ \therefore \frac{c_A V_A}{c_B V_B} &= \frac{2}{1} \\ \therefore \frac{23.25 \times c_A}{25 \times 0.1} &= \frac{2}{1} \\ \therefore c_A &= \frac{2 \times 25 \times 0.1}{23.25} = 0.215 \text{ mol dm}^{-3}\end{aligned}$$

But the bench acid was diluted ten times.

∧' Molar concentration of the bench acid =  $0.215 \times 10 = 2.15 \text{ mol dm}^{-3}$

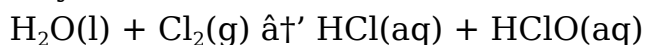
## 5P.2 Titration Using Water from Different Sources

Use tap water, rain water, stream water and water from any other source to prepare standard sodium trioxocarbonate(IV) solutions as described earlier. Titrate each solution against the hydrogen chloride acid (hydrochloric acid) from 5P. 1 above, using methyl orange as indicator. Record your results in a table thus:

Burette readings (cm <sup>3</sup> )	Distilled water	Tap water	Stream water	Rain water
Final				
Initial				
Vol. of Acid				

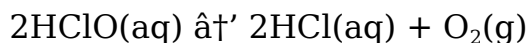
Compare the titre values for the different water samples. Sources of error introduced by the water samples include:

- Carbon(IV) oxide which dissolves in rain water forming trioxocarbonate(IV) acid. However, carbon(IV) oxide is only sparingly soluble in water and trioxocarbonate(IV) acid is a weak acid. Therefore the error introduced by rain water is minimal.
- Chlorine gas which is added to tap water forms hydrogen chloride acid (hydrochloric acid) and oxochlorate(I) acid.



The oxochlorate(I) acid soon decomposes, yielding oxygen and

hydrogen chloride acid (hydrochloric acid). This makes tap water acidic.



Other impurities could be present in tap water depending on the locality. Water in limestone areas will contain dissolved calcium hydrogen trioxocarbonate(IV), and little calcium/magnesium trioxocarbonate(IV). All these introduce errors to the titre value.

- (iii) Stream water may contain hydrogen trioxocarbonates(IV) and trioxocarbonate(IV) salts in addition to some other impurities. If the stream has an industry near it, industrial effluents may also be present. They affect the pH of the water and hence the titre value.

If your titre value for a given sample of water is higher than the titre value for distilled water, then the water sample contains basic impurities. If it is lower than the titre value for distilled water, then the water sample contains acidic impurities. Try to find the source of each type of impurity.