ferroin or *N*-phenylanthranilic acid as indicator. Repeat the titration with two further portions of the nitrite solution. Standardise the iron solution by titrating 25 mL of it with the cerium(IV) solution in the presence of dilute sulphuric acid.

Determine the volume of the standard cerium(IV) sulphate solution which has reacted with the nitrite solution, and therefrom calculate the purity of the sodium nitrite employed.

Note. Cerium(IV) sulphate may also be used for the following analyses.

Hydrogen peroxide. The diluted solution, which may contain nitric or hydrochloric acid in any concentration between 0.5 and 3*M* or sulphuric acid in the concentration range 0.25 to 1.5*M*, is titrated directly with standard cerium(IV) sulphate solution, using ferroin or *N*-phenylanthranilic acid as indicator. The reaction is:

$$2Ce^{4+} + H_2O_2 = 2Ce^{3+} + O_2 + 2H^+$$

Persulphate (peroxydisulphate). Persulphate cannot be determined directly by reduction with iron(II) because the reaction is too slow:

$$S_2O_8^{2-} + 2Fe^{2+} = 2SO_4^{2-} + 2Fe^{3+}$$

An excess of a standard solution of iron(II) must therefore be added and the excess back-titrated with standard cerium(IV) sulphate solution. Erratic results are obtained, depending upon the exact experimental conditions, because of induced reactions leading to oxidation by air of iron(II) ion or to decomposition of the persulphate; these induced reactions are inhibited by bromide ion in concentrations not exceeding 1*M* and, under these conditions, the determination may be carried out in the presence of organic matter.

To 25.0 mL of 0.01–0.015*M* persulphate solution in a 150 mL conical flask, add 7 mL of 5*M* sodium bromide solution and 2 mL of 3*M* sulphuric acid. Stopper the flask. Swirl the contents, then add excess of 0.05*M* ammonium iron(II) sulphate (15.0 mL), and allow to stand for 20 minutes. Add 1 mL of 0.001*M* ferroin indicator, and titrate the excess of Fe^{2+} ion with 0.02*M* cerium(IV) sulphate in 0.5*M* sulphuric acid to the *first* colour change from orange to yellow.

Oxalates. Oxalates can be determined by means of the indirect method described in Section 10.106.

Hexacyanoferrate(II). This can be determined by titration in 1*M* H_2SO_4 using *N*-phenylanthranilic acid.

OXIDATION AND REDUCTION PROCESSES INVOLVING IODINE: IODOMETRIC TITRATIONS

10.110 GENERAL DISCUSSION

The direct iodometric titration method (sometimes termed **iodimetry**) refers to titrations with a standard solution of iodine. The indirect iodometric titration method (sometimes termed **iodometry**) deals with the titration of iodine liberated in chemical reactions. The normal reduction potential of the reversible system:

$$I_2 \text{ (solid)} + 2e \rightleftharpoons 2I^-$$

is 0.5345 volt. The above equation refers to a saturated aqueous solution in the presence of solid iodine; this half-cell reaction will occur, for example, towards the end of a titration of iodide with an oxidising agent such as potassium permanganate, when the iodide ion concentration becomes relatively low. Near the beginning, or in most iodometric titrations, when an excess of iodide ion is

present, the tri-iodide ion is formed

$$I_2\,(aq.) + I^- \rightleftharpoons I_3^-$$

since iodine is readily soluble in a solution of iodide. The half-cell reaction is better written:

$$I_3^- + 2e \rightleftharpoons 3I^-$$

and the standard reduction potential is 0.5355 volt. Iodine or the tri-iodide ion is therefore a much weaker oxidising agent than potassium permanganate, potassium dichromate, and cerium(IV) sulphate.

In most direct titrations with iodine (iodimetry) a solution of iodine in potassium iodide is employed, and the reactive species is therefore the tri-iodide ion I_3^-. Strictly speaking, all equations involving reactions of iodine should be written with I_3^- rather than with I_2, e.g.

$$I_3^- + 2S_2O_3^{2-} = 3I^- + S_4O_6^{2-}$$

is more accurate than

$$I_2 + 2S_2O_3^{2-} = 2I^- + S_4O_6^{2-}$$

For the sake of simplicity, however, the equations in this book will usually be written in terms of molecular iodine rather than the tri-iodide ion.

Strong reducing agents (substances with a much lower reduction potential), such as tin(II) chloride, sulphurous acid, hydrogen sulphide, and sodium thiosulphate, react completely and rapidly with iodine even in acid solution. With somewhat weaker reducing agents, e.g. arsenic(III), or antimony(III), complete reaction occurs only when the solution is kept neutral or very faintly acid; under these conditions the reduction potential of the reducing agent is a minimum, or its reducing power is a maximum.

If a strong oxidising agent is treated in neutral or (more usually) acid solution with a large excess of iodide ion, the latter reacts as a reducing agent and the oxidant will be quantitatively reduced. In such cases, an equivalent amount of iodine is liberated, and is then titrated with a standard solution of a reducing agent, which is usually sodium thiosulphate.

The normal reduction potential of the iodine–iodide system is independent of the pH of the solution so long as the latter is less than about 8; at higher values iodine reacts with hydroxide ions to form iodide and the extremely unstable hypoiodite, the latter being transformed rapidly into iodate and iodide by self-oxidation and reduction:

$$I_2 + 2OH^- = I^- + IO^- + H_2O$$

$$3IO^- = 2I^- + IO_3^-$$

The reduction potentials of certain substances increase considerably with increasing hydrogen ion concentration of the solution. This is the case with systems containing permanganate, dichromate, arsenate, antimonate, bromate, etc., i.e. with anions which contain oxygen and therefore require hydrogen for complete reduction. Many weak oxidising anions are completely reduced by iodide ions if their reduction potentials are raised considerably by the presence in solution of a large amount of acid.

By suitable control of the pH of the solution, it is sometimes possible to

titrate the reduced form of a substance with iodine, and the oxidised form, after the addition of iodide, with sodium thiosulphate. Thus with the arsenite–arsenate system:

$$H_3AsO_3 + I_2 + H_2O \rightleftharpoons H_3AsO_4 + 2H^+ + 2I^-$$

the reaction is completely reversible. At pH values between 4 and 9, arsenite can be titrated with iodine solution. In strongly acid solutions, however, arsenate is reduced to arsenite and iodine is liberated. Upon titration with sodium thiosulphate solution, the iodine is removed and the reaction proceeds from right to left.

Two important **sources of error in titrations involving iodine** are: (*a*) loss of iodine owing to its appreciable volatility; and (*b*) acid solutions of iodide are oxidised by oxygen from the air:

$$4I^- + O_2 + 4H^+ = 2I_2 + 2H_2O$$

In the presence of excess of iodide, the volatility is decreased markedly through the formation of the tri-iodide ion; at room temperature the loss of iodine by volatilisation from a solution containing at least 4 per cent of potassium iodide is negligible provided the titration is not prolonged unduly. Titrations should be performed in cold solutions in conical flasks and not in open beakers. If a solution is to stand it should be kept in a glass-stoppered vessel. The atmospheric oxidation of iodide is negligible in neutral solution in the absence of catalysts, but the rate of oxidation increases rapidly with decreasing pH. The reaction is catalysed by certain metal ions of variable charge value (particularly copper), by nitrite ion, and also by strong light. For this reason titrations should not be performed in direct sunlight, and solutions containing iodide should be stored in amber glass bottles. Furthermore, the air oxidation of iodide ion may be induced by the reaction between iodide and the oxidising agent, especially when the main reaction is slow. Solutions containing an excess of iodide and acid must therefore not be allowed to stand longer than necessary before titration of the iodine. If prolonged standing is necessary (as in the titration of vanadate or Fe^{3+} ions) the solution should be free from air before the addition of iodide and the air displaced from the titration vessel by carbon dioxide [e.g. by adding small portions (0.2–0.5 g) of pure sodium hydrogencarbonate to the acid solution, or a little solid carbon dioxide, dry ice]; potassium iodide is then introduced and the glass stopper replaced immediately.

It seems appropriate to refer at this point to the uses of a standard solution containing **potassium iodide and potassium iodate**. This solution is quite stable and yields iodine when treated with acid:

$$IO_3^- + 5I^- + 6H^+ = 3I_2 + 3H_2O$$

The standard solution is prepared by dissolving a weighed amount of pure potassium iodate in a solution containing a slight excess of pure potassium iodide, and diluting to a definite volume. This solution has two important uses. The first is as a source of a known quantity of iodine in titrations [compare Section 10.115(A)]; it must be added to a solution containing strong acid; it cannot be employed in a medium which is neutral or possesses a low acidity.

The second use is in the determination of the acid content of solutions iodometrically or in the **standardisation of solutions of strong acids**. It is evident from the above equation that the amount of iodine liberated is equivalent to

the acid content of the solution. Thus if, say, 25 mL of an approximately 0.1 *M* solution of a strong acid is treated with a slight excess of potassium iodate (say, 25 mL of 0.02 *M* potassium iodate solution, Section 10.126) and a slight excess of potassium iodide solution (say, 10 mL of a 10 per cent solution), and the liberated iodine titrated with standard 0.1 *M* sodium thiosulphate with the aid of starch as an indicator, the concentration of the acid may be readily evaluated.

10.111 DETECTION OF THE END POINT

A solution of iodine in aqueous iodide has an intense yellow to brown colour. One drop of 0.05 *M* iodine solution imparts a perceptible pale yellow colour to 100 mL of water, so that in otherwise colourless solutions iodine can serve as its own indicator. The test is made much more sensitive by the use of a solution of starch as indicator. Starch reacts with iodine in the presence of iodide to form an intensely blue-coloured complex, which is visible at very low concentrations of iodine. The sensitivity of the colour reaction is such that a blue colour is visible when the iodine concentration is $2 \times 10^{-5} M$ and the iodide concentration is greater than $4 \times 10^{-4} M$ at 20 °C. The colour sensitivity decreases with increasing temperature of the solution; thus at 50 °C it is about ten times less sensitive than at 25 °C. The sensitivity decreases upon the addition of solvents, such as ethanol: no colour is obtained in solutions containing 50 per cent ethanol or more. It cannot be used in a strongly acid medium because hydrolysis of the starch occurs.

Starches can be separated into two major components, amylose and amylopectin, which exist in different proportions in various plants. Amylose, which is a straight-chain compound and is abundant in potato starch, gives a blue colour with iodine and the chain assumes a spiral form. Amylopectin, which has a branched-chain structure, forms a red–purple product, probably by adsorption.

The great merit of starch is that it is inexpensive. It possesses the following disadvantages: (1) insolubility in cold water; (2) instability of suspensions in water; (3) it gives a water-insoluble complex with iodine, the formation of which precludes the addition of the indicator early in the titration (for this reason, in titrations of iodine, the starch solution should not be added until just prior to the end point when the colour begins to fade); and (4) there is sometimes a 'drift' end point, which is marked when the solutions are dilute.

Most of the shortcomings of starch as an indicator are absent in **sodium starch glycollate**. This is a white, non-hygroscopic powder, readily soluble in hot water to give a faintly opalescent solution, which is stable for many months; it does not form a water-insoluble complex with iodine, and hence the indicator may be added at any stage of the reaction. With excess of iodine (e.g. at the beginning of a titration with sodium thiosulphate) the colour of the solution containing 1 mL of the indicator (0.1 per cent aqueous solution) is green; as the iodine concentration diminishes the colour changes to blue, which becomes intense just before the end point is reached. The end point is very sharp and reproducible and there is no 'drift' in dilute solution.

Carbon tetrachloride has been used in certain reactions instead of starch solution. One litre of water at 25 °C will dissolve 0.335 g of iodine, but the same volume of carbon tetrachloride will dissolve about 28.5 g. Iodine is therefore about 85 times as soluble in carbon tetrachloride as it is in water, and the carbon

tetrachloride solution is highly coloured. When a little carbon tetrachloride is added to an aqueous solution containing iodine and the solution well shaken, the great part of the iodine will dissolve in the carbon tetrachloride; the latter will fall to the bottom since it is immiscible with water, and the colour of the organic layer will be much deeper than that of the original aqueous solution. The reddish-violet colour of iodine in carbon tetrachloride is visible in very low concentrations of iodine; thus on shaking 10 mL of carbon tetrachloride with 50 mL of 10^{-5} *M* iodine, a distinct violet coloration is produced in the organic layer. This enables many iodometric determinations to be carried out with comparative ease. The titrations are performed in 250 mL glass-stoppered bottles or flasks with accurately ground stoppers. After adding the excess of potassium iodide solution and 5–10 mL of carbon tetrachloride to the reaction mixture, the titration with sodium thiosulphate is commenced. At first the presence of iodine in the aqueous solution will be apparent, and gentle rotation of the liquid causes sufficient mixing. Towards the end of the titration the bottle or flask is stoppered and shaken after each addition of sodium thiosulphate solution; the end point is reached when the carbon tetrachloride just becomes colourless. Equally satisfactory results can be obtained with chloroform.

Preparation and use of starch solution. Make a paste of 0.1 g of soluble starch with a little water, and pour the paste, with constant stirring, into 100 mL of boiling water, and boil for 1 minute. Allow the solution to cool and add 2–3 g of potassium iodide. Keep the solution in a stoppered bottle.

Only freshly prepared starch solution should be used. Two millilitres of a 1 per cent solution per 100 mL of the solution to be titrated is a satisfactory amount; the same volume of starch solution should always be added in a titration. In the titration of iodine, starch must not be added until just before the end point is reached. Apart from the fact that the fading of the iodine colour is a good indication of the approach at the end point, if the starch solution is added when the iodine concentration is high, some iodine may remain adsorbed even at the end point. The indicator blank is negligibly small in iodimetric and iodometric titrations of 0.05 *M* solutions; with more dilute solutions, it must be determined in a liquid having the same composition as the solution titrated has at the end point.

A solid solution of starch in urea may also be employed. Reflux 1 g of soluble starch and 19 g of urea with xylene. At the boiling point of the organic solvent the urea melts with little decomposition, and the starch dissolves in the molten urea. Allow to cool, then remove the solid mass and powder it; store the product in a stoppered bottle. A few milligrams of this solid added to an aqueous solution containing iodine then behaves like the usual starch indicator.

Preparation and use of sodium starch glycollate indicator. Sodium starch glycollate, prepared as described below, dissolves slowly in cold but rapidly in hot water. It is best dissolved by mixing, say, 5.0 g of the finely powdered solid with 1–2 mL ethanol, adding 100 mL cold water, and boiling for a few minutes with vigorous stirring: a faintly opalescent solution results. This 5 per cent stock solution is diluted to 1 per cent concentration as required. The most convenient concentration for use as an indicator is 0.1 mg mL^{-1}, i.e. 1 mL of the 1 per cent aqueous solution is added to 100 mL of the solution being titrated.

10.112 PREPARATION OF 0.05*M* IODINE SOLUTION

Discussion. In addition to a small solubility (0.335 g of iodine dissolves in 1 L of water at 25 °C), aqueous solutions of iodine have an appreciable vapour pressure of iodine, and therefore decrease slightly in concentration on account of volatilisation when handled. Both difficulties are overcome by dissolving the iodine in an aqueous solution of potassium iodide. Iodine dissolves readily in aqueous potassium iodide: the more concentrated the solution, the greater is the solubility of the iodine. The increased solubility is due to the formation of a tri-iodide ion:

$$I_2 + I^- \rightleftharpoons I_3^-$$

The resulting solution has a much lower vapour pressure than a solution of iodine in pure water, and consequently the loss by volatilisation is considerably diminished. Nevertheless, the vapour pressure is still appreciable so that **precautions should always be taken to keep vessels containing iodine closed except during the actual titrations.** When an iodide solution of iodine is titrated with a reductant, the free iodine reacts with the reducing agent, this displaces the equilibrium to the left, and eventually all the tri-iodide is decomposed; the solution therefore behaves as though it were a solution of free iodine.

For the preparation of standard iodine solutions, resublimed iodine and iodate-free potassium iodide should be employed. The solution may be standardised against pure arsenic(III) oxide or with a sodium thiosulphate solution which has been recently standardised against potassium iodate.

The equation for the ionic reaction is:

$$I_2 + 2e \rightleftharpoons 2I^-$$

Procedure: Preparation of 0.05*M* iodine. Dissolve 20 g of iodate-free potassium iodide in 30–40 mL of water in a glass-stoppered 1 L graduated flask. Weigh out about 12.7 g of resublimed iodine on a watchglass on a rough balance (never on an analytical balance on account of the iodine vapour), and transfer it by means of a small dry funnel into the concentrated potassium iodide solution. Insert the glass stopper into the flask, and shake in the cold until all the iodine has dissolved. Allow the solution to acquire room temperature, and make up to the mark with distilled water.

The iodine solution is best preserved in small glass-stoppered bottles. These should be filled completely and kept in a cool, dark place.

10.113 STANDARDISATION OF IODINE SOLUTIONS

(A) With arsenic(III) oxide: Discussion. As already indicated (Section 10.94), arsenic(III) oxide which has been dried at 105–110 °C for two hours is an excellent primary standard. The reaction between this substance and iodine is a reversible one:

$$H_3AsO_3 + I_2 + H_2O \rightleftharpoons H_3AsO_4 + 2H^+ + 2I^-$$

and only proceeds quantitatively from left to right if the hydrogen iodide is removed from the solution as fast as it is formed. This may be done by the addition of sodium hydrogencarbonate: sodium carbonate and sodium hydroxide cannot be used, since they react with the iodine, forming iodide,

hypoiodite, and iodate. Actually it has been shown that complete oxidation of the arsenite occurs when the pH of the solution lies between 4 and 9, the best value being 6.5, which is very close to the neutral point. Buffer solutions are employed to maintain the correct pH. A 0.12 *M* solution of sodium hydrogencarbonate saturated with carbon dioxide has a pH of 7; a solution saturated with both sodium tetraborate and boric acid has a pH of about 6.2, whilst a Na_2HPO_4–NaH_2PO_4 solution is almost neutral. Any of these three buffer solutions is suitable, but as already stated the first-named is generally employed.

Procedure. Weigh out accurately about 2.5 g of finely powdered arsenic(III) oxide, transfer to a 500 mL beaker, and dissolve it in a concentrated solution of sodium hydroxide, prepared from 2 g of iron-free sodium hydroxide and 20 mL of water. Dilute to about 200 mL, and neutralise the solution with 1*M* hydrochloric acid, using a pH meter. When the solution is faintly acid transfer the contents of the beaker quantitatively to a 500 mL graduated flask, add 2 g of pure sodium hydrogencarbonate, and, when all the salt has dissolved, dilute to the mark and shake well.

Using a burette or a pipette with a safety pump (this is necessary owing to the poisonous properties of the solution) measure out 25.0 mL of the arsenite solution into a 250 mL conical flask, add 25–50 mL of water, 5 g of sodium hydrogencarbonate, and 2 mL of starch solution. Swirl the solution carefully until the hydrogencarbonate has dissolved. Then titrate slowly with the iodine solution, contained in a burette, to the first blue colour.

Alternatively, the arsenite solution may be placed in the burette, and titrated against 25.0 mL of the iodine solution contained in a conical flask. When the solution has a pale yellow colour, add 2 mL of starch solution, and continue the titration slowly until the blue colour is just destroyed.

If it is desired to base the standardisation directly upon arsenic(III) oxide, proceed as follows. Weigh out accurately about 0.20 g of pure arsenic(III) oxide into a conical flask, dissolve it in 10 mL of 1*M* sodium hydroxide, and add a small excess of dilute sulphuric acid (say, 12–15 mL of 0.5*M* acid). Mix thoroughly and cautiously. Then add carefully a solution of 2 g of sodium hydrogencarbonate in 50 mL of water, followed by 2 mL of starch solution. Titrate slowly with the iodine solution to the first blue colour. Repeat with two other similar quantities of the oxide.

(B) With standard sodium thiosulphate solution. Sodium thiosulphate solution, which has been recently standardised, preferably against pure potassium iodate, is employed. Transfer 25 mL of the iodine solution to a 250 mL conical flask, dilute to 100 mL and add the standard thiosulphate solution from a burette until the solution has a pale yellow colour. Add 2 mL of starch solution, and continue the addition of the thiosulphate solution slowly until the solution is just colourless.

10.114 PREPARATION OF 0.1*M* SODIUM THIOSULPHATE

Discussion. Sodium thiosulphate ($Na_2S_2O_3,5H_2O$) is readily obtainable in a state of high purity, but there is always some uncertainty as to the exact water content because of the efflorescent nature of the salt and for other reasons. The substance is therefore unsuitable as a primary standard. It is a reducing agent

by virtue of the half-cell reaction:

$$2S_2O_3^{2-} \rightleftharpoons S_4O_6^{2-} + 2e$$

An approximately 0.1*M* solution is prepared by dissolving about 25 g crystallised sodium thiosulphate in 1 L of water in a graduated flask. The solution is standardised by any of the methods described below.

Before dealing with these, it is necessary to refer briefly to the stability of thiosulphate solutions. Solutions prepared with conductivity (equilibrium) water are perfectly stable. However, ordinary distilled water usually contains an excess of carbon dioxide; this may cause a slow decomposition to take place with the formation of sulphur:

$$S_2O_3^{2-} + H^+ = HSO_3^- + S$$

Moreover, decomposition may also be caused by bacterial action (e.g. *Thiobacillus thioparus*), particularly if the solution has been standing for some time. For these reasons, the following recommendations are made:

1. Prepare the solution with recently boiled distilled water.
2. Add 3 drops of chloroform or 10 mg L^{-1} of mercury(II) iodide; these compounds improve the keeping qualities of the solution.

   Bacterial activity is least when the pH lies between 9 and 10. The addition of a *small* amount, 0.1 g L^{-1}, of sodium carbonate is advantageous to ensure the correct pH. In general, alkali hydroxides, sodium carbonate (>0.1 g L^{-1}), and sodium tetraborate should not be added, since they tend to accelerate the decomposition:

   $$S_2O_3^{2-} + 2O_2 + H_2O \rightleftharpoons 2SO_4^{2-} + 2H^+$$

3. Avoid exposure to light, as this tends to hasten the decomposition.

The standardisation of thiosulphate solutions may be effected with potassium iodate, potassium dichromate, copper and iodine as primary standards, or with potassium permanganate or cerium(IV) sulphate as secondary standards. Owing to the volatility of iodine and the difficulty of preparation of perfectly pure iodine, this method is not a suitable one for beginners. If, however, a standard solution of iodine (see Sections 10.112 and 10.113) is available, this may be used for the standardisation of thiosulphate solutions.

Procedure. Weigh out 25 g of sodium thiosulphate crystals ($Na_2S_2O_3,5H_2O$), dissolve in boiled-out distilled water, and make up to 1 L in a graduated flask with boiled-out water. If the solution is to be kept for more than a few days, add 0.1 g sodium carbonate or three drops of chloroform.

10.115 STANDARDISATION OF SODIUM THIOSULPHATE SOLUTIONS

(A) With potassium iodate. Potassium iodate has a purity of at least 99.9 per cent: it can be dried at 120 °C. This reacts with potassium iodide in acid solution to liberate iodine:

$$IO_3^- + 5I^- + 6H^+ = 3I_2 + 3H_2O$$

Its relative molecular mass is 214.00; a 0.02*M* solution therefore contains 4.28 g of potassium iodate per litre.

Weigh out accurately 0.14–0.15 g of pure dry potassium iodate, dissolve it in 25 mL of cold, boiled-out distilled water, add 2 g of iodate-free potassium iodide (Note 1) and 5 mL of 1*M* sulphuric acid (Note 2). Titrate the liberated iodine with the thiosulphate solution with constant shaking. When the colour of the liquid has become a pale yellow, dilute to *ca* 200 mL with distilled water, add 2 mL of starch solution, and continue the titration until the colour changes from blue to colourless. Repeat with two other similar portions of potassium iodate.

Notes. (1) The absence of iodate is indicated by adding dilute sulphuric acid when no immediate yellow coloration should be obtained. If starch is added, no immediate blue coloration should be produced.

(2) Only a small amount of potassium iodate is needed so that the error in weighing 0.14–0.15 g may be appreciable. In this case it is better to weigh out accurately 4.28 g of the salt (if a slightly different weight is used, the exact molarity is calculated), dissolve it in water, and make up to 1 L in a graduated flask. Twenty-five millilitres of this solution are treated with excess of pure potassium iodide (1 g of the solid or 10 mL of 10 per cent solution), followed by 3 mL of 1*M* sulphuric acid, and the liberated iodine is titrated as detailed above.

(B) With potassium dichromate. Potassium dichromate is reduced by an acid solution of potassium iodide, and iodine is set free:

$$Cr_2O_7^{2-} + 6I^- + 14H^+ = 2Cr^{3+} + 3I_2 + 7H_2O$$

This reaction is subject to a number of errors: (1) the hydriodic acid (from excess of iodide and acid) is readily oxidised by air, especially in the presence of chromium(III) salts, and (2) it is not instantaneous. It is accordingly best to pass a current of carbon dioxide through the reaction flask before and during the titration (a more convenient but less efficient method is to add some solid sodium hydrogencarbonate to the acid solution, and to keep the flask covered as much as possible), and to allow 5 minutes for its completion.

Place 100 mL of cold, recently boiled distilled water in a 500 mL conical, preferably glass-stoppered, flask, add 3 g of iodate-free potassium iodide and 2 g of pure sodium hydrogencarbonate, and shake until the salts dissolve. Add 6 mL of concentrated hydrochloric acid slowly while gently rotating the flask in order to mix the liquids; run in 25.0 mL of standard 0.017*M* potassium dichromate (see Note), mix the solutions well, and wash the sides of the flask with a little boiled-out water from the wash bottle. Stopper the flask (or cover it with a small watchglass), and allow to stand in the dark for 5 minutes in order to complete the reaction. Rinse the stopper or watchglass, and dilute the solution with 300 mL of cold, boiled-out water. Titrate the liberated iodine with the sodium thiosulphate solution contained in a burette, while constantly rotating the liquid so as to mix the solutions thoroughly. When most of the iodine has reacted as indicated by the solution acquiring a yellowish-green colour, add 2 mL of starch solution and rinse down the sides of the flask; the colour should change to blue. Continue the addition of the thiosulphate solution dropwise, and swirling the liquid constantly, until one drop changes the colour from greenish-blue to light green. The end-point is sharp, and is readily observed in a good light against a white background. Carry out a blank determination, substituting distilled water for the potassium dichromate solution; if the potassium iodide is iodate-free, this should be negligible.

Note. If preferred, about 0.20 g of potassium dichromate may be accurately weighed out, dissolved in 50 mL of cold, boiled-out water, and the titration carried out as detailed above.

Alternative procedure. The following method utilises a trace of copper sulphate as a catalyst to increase the speed of the reaction; in consequence, a weaker acid (acetic acid) may be employed and the extent of atmospheric oxidation of hydriodic acid reduced. Place 25.0 mL of 0.017*M* potassium dichromate in a 250 mL conical flask, add 5.0 mL of glacial acetic acid, 5 mL of 0.001*M* copper sulphate, and wash the sides of the flask with distilled water. Add 30 mL of 10 per cent potassium iodide solution, and titrate the iodine as liberated with the approximately 0.1*M* thiosulphate solution, introducing a little starch indicator towards the end. The titration may be completed in 3–4 minutes after the addition of the potassium iodide solution. Subtract 0.05 mL to allow for the iodine liberated by the copper sulphate catalyst.

(C) With a standard solution of iodine. If a standard solution of iodine is available (see Section 10.112), this may be used to standardise the thiosulphate solution. Measure a 25.0 mL portion of the standard iodine solution into a 250 mL conical flask, add about 150 mL distilled water and titrate with the thiosulphate solution, adding 2 mL of starch solution when the liquid is pale yellow in colour.

When thiosulphate solution is added to a solution containing iodine the overall reaction, which occurs rapidly and stoichiometrically under the usual experimental conditions (pH < 5), is:

$$2S_2O_3^{2-} + I_2 = S_4O_6^{2-} + 2I^-$$

or

$$2S_2O_3^{2-} + I_3^- = S_4O_6^{2-} + 3I^-$$

It has been shown that the colourless intermediate $S_2O_3I^-$ is formed by a rapid reversible reaction:

$$S_2O_3^{2-} + I_2 \rightleftharpoons S_2O_3I^- + I^-$$

The intermediate reacts with thiosulphate ion to provide the main course of the overall reaction:

$$S_2O_3I^- + S_2O_3^{2-} = S_4O_6^{2-} + I^-$$

The intermediate also reacts with iodide ion:

$$2S_2O_3I^- + I^- = S_4O_6^{2-} + I_3^-;$$

This explains the reappearance of iodine after the end point in the titration of very dilute iodine solutions by thiosulphate.

10.116 DETERMINATION OF COPPER IN CRYSTALLISED COPPER SULPHATE

Procedure. Weigh out accurately about 3.0 g of the salt, dissolve it in water, and make up to 250 mL in a graduated flask. Shake well. Pipette 50.0 mL of this solution into a 250 mL conical flask, add 1 g potassium iodide (or 10 mL of a 10 per cent solution) (Note 1), and titrate the liberated iodine with standard

0.1*M* sodium thiosulphate (Note 2). Repeat the titration with two other 50 mL portions of the copper sulphate solution.

The reaction, written in molecular form, is:

$$2CuSO_4 + 4KI = 2CuI + I_2 + 2K_2SO_4$$

from which it follows that:

$$2CuSO_4 \equiv I_2 \equiv 2Na_2S_2O_3$$

Notes. (1) If in a similar determination, free mineral acid is present, a few drops of dilute sodium carbonate solution must be added until a *faint* permanent precipitate remains, and this is removed by means of a drop or two of acetic acid. The potassium iodide is then added and the titration continued. For accurate results, the solution should have a pH of 4–5.5.

(2) After the addition of the potassium iodide solution, run in standard 0.1*M* sodium thiosulphate until the brown colour of the iodine fades, then add 2 mL of starch solution, and continue the addition of the thiosulphate solution until the blue colour commences to fade. Then add about 1 g of potassium thiocyanate or ammonium thiocyanate, preferably as a 10 per cent aqueous solution: the blue colour will instantly become more intense. Complete the titration as quickly as possible. The precipitate possesses a pale pink colour, and a distinct permanent end point is readily obtained.

10.117 DETERMINATION OF CHLORATES

Discussion. One procedure is based upon the reaction between chlorate and iodide in the presence of concentrated hydrochloric acid:

$$ClO_3^- + 6I^- + 6H^+ = Cl^- + 3I_2 + 3H_2O$$

The liberated iodine is titrated with standard sodium thiosulphate solution.

In another method the chlorate is reduced with bromide in the presence of *ca* 8*M* hydrochloric acid, and and the bromine liberated is determined iodimetrically:

$$ClO_3^- + 6Br^- + 6H^+ = Cl^- + 3Br_2 + 3H_2O$$

Procedure. (*a*) Place 25 mL of the chlorate solution (approx. 0.02*M*) in a glass-stoppered conical flask and add 3 mL of concentrated hydrochloric acid followed by two portions of about 0.3 g each of pure sodium hydrogencarbonate to remove air. Add immediately about 1.0 g of iodate-free potassium iodide and 22 mL of concentrated hydrochloric acid. Stopper the flask, shake the contents, and allow it to stand for 5–10 minutes. Titrate the solution with standard 0.1*M* sodium thiosulphate in the usual manner.

(*b*) Place 10.0 mL of the chlorate solution in a glass-stoppered flask, add *ca* 1.0 g potassium bromide and 20 mL concentrated hydrochloric acid (the final concentration of acid should be about 8*M*). Stopper the flask, shake well, and allow to stand for 5–10 minutes. Add 100 mL of 1 per cent potassium iodide solution, and titrate the liberated iodine with standard 0.1*M* sodium thiosulphate.

10.118 ANALYSIS OF HYDROGEN PEROXIDE

Discussion. Hydrogen peroxide reacts with iodide in acid solution in accordance with the equation:

$$H_2O_2 + 2H^+ + 2I^- = I_2 + 2H_2O$$

The reaction velocity is comparatively slow, but increases with increasing concentration of acid. The addition of three drops of a neutral 20 per cent ammonium molybdate solution renders the reaction almost instantaneous, but as it also accelerates the atmospheric oxidation of the hydriodic acid, the titration is best conducted in an inert atmosphere (nitrogen or carbon dioxide).

The iodometric method has the advantage over the permanganate method (Section 10.95) that it is less affected by stabilisers which are sometimes added to commercial hydrogen peroxide solutions. These preservatives are often boric acid, salicylic acid, and glycerol, and render the results obtained by the permanganate procedure less accurate.

Procedure. Dilute the hydrogen peroxide solution to *ca* 0.3 per cent H_2O_2. Thus, if a '20-volume' hydrogen peroxide is used, transfer 10.0 mL by means of a burette or pipette to a 250 mL graduated flask, and make up to the mark. Shake well. Remove 25.0 mL of this diluted solution, and add it gradually and with constant stirring to a solution of 1 g of pure potassium iodide in 100 mL of 1*M* sulphuric acid (1:20) contained in a stoppered bottle. Allow the mixture to stand for 15 minutes, and titrate the liberated iodine with standard 0.1*M* sodium thiosulphate, adding 2 mL starch solution when the colour of the iodine has been nearly discharged. Run a blank determination at the same time.

Better results are obtained by transferring 25.0 mL of the diluted hydrogen peroxide solution to a conical flask, and adding 100 mL 1*M*(1:20) sulphuric acid. Pass a slow stream of carbon dioxide or nitrogen through the flask, add 10 mL of 10 per cent potassium iodide solution, followed by three drops of 3 per cent ammonium molybdate solution. Titrate the liberated iodine immediately with standard 0.1*M* sodium thiosulphate in the usual way.

Note. The above method may also be used for all per-salts.

10.119 DETERMINATION OF DISSOLVED OXYGEN

Discussion. One of the most useful titrations involving iodine is that originally developed by Winkler[18] to determine the amount of oxygen in samples of water. The dissolved oxygen content is not only important with respect to the species of aquatic life which can survive in the water, but is also a measure of its ability to oxidise organic impurities in the water (see also Section 10.103). Despite the advent of the oxygen-selective electrode (Section 16.36) direct titrations on water samples are still used extensively.[19]

In order to avoid loss of oxygen from the water sample it is 'fixed' by its reaction with manganese(II) hydroxide which is converted rapidly and quantitatively to manganese(III) hydroxide:

$$4Mn(OH)_2 + O_2 + 2H_2O \rightarrow 4Mn(OH)_3$$

The brown precipitate obtained dissolves on acidification and oxidises iodide ions to iodine:

$$Mn(OH)_3 + I^- + 3H^+ \rightarrow Mn^{2+} + \tfrac{1}{2}I_2 + 3H_2O$$

The free iodine may then be determined by titration with sodium thiosulphate (Section 10.113).

$$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$$

This means that 4 moles of thiosulphate correspond to 1 mole of dissolved oxygen.

The main interference in this process is due to the presence of nitrites (especially in waters from sewage treatment). This is overcome by treating the original water sample with sodium azide, which destroys any nitrite when the sample is acidified:

$$HNO_2 + HN_3 \rightarrow N_2 + N_2O + H_2O$$

Procedure. The water sample should be collected by carefully filling a 200–250 mL bottle to the very top and stoppering it while it is below the water surface. This should eliminate any further dissolution of atmospheric oxygen. By using a dropping pipette placed below the surface of the water sample, add 1 mL of a 50 per cent manganese(II) solution (Note 1) and in a similar way add 1 mL of alkaline iodide–azide solution (Note 2). Re-stopper the water sample and shake the mixture well. The manganese(III) hydroxide forms as a brown precipitate. Allow the precipitate to settle completely for 15 minutes and add 2 mL of concentrated phosphoric(V) acid (85 per cent). Replace the stopper and turn the bottle upside-down two or three times in order to mix the contents. The brown precipitate will dissolve and release iodine in the solution (Note 3).

Measure out a 100 mL portion of the solution with a pipette and titrate the iodine with approximately $M/80$ standard sodium thiosulphate solution adding 2 mL of starch solution as indicator as the titration proceeds and *after* the titration liquid has become pale yellow in colour.

Calculate the dissolved oxygen content and express it as mg L^{-1}; 1 mL of $M/80$ thiosulphate $\equiv$ 1 mg dissolved oxygen.

Notes. (1) Prepared by dissolving 50 g of manganese(II) sulphate pentahydrate in water and making up to 100 mL.

(2) Prepared from 40 g of sodium hydroxide, 20 g of potassium iodide and 0.5 g of sodium azide made up to 100 mL with water.

(3) If the brown precipitate has not completely dissolved then add a little more (a few drops) phosphoric(V) acid.

10.120 DETERMINATION OF THE AVAILABLE CHLORINE IN HYPOCHLORITES

Discussion. Most hypochlorites are normally obtained only in solution, but calcium hypochlorite exists in the solid form in commercial bleaching powder which consists essentially of a mixture of calcium hypochlorite $Ca(OCl)_2$ and the basic chloride $CaCl_2,Ca(OH)_2,H_2O$; some free slaked lime is usually present. The active constituent is the hypochlorite, which is responsible for the bleaching action. Upon treating bleaching powder with hydrochloric acid, chlorine is liberated:

$$OCl^- + Cl^- + 2H^+ = Cl_2 + H_2O$$

The **available chlorine** refers to the chlorine liberated by the action of dilute acids on the hypochlorite, and is expressed as the percentage by weight in the case of bleaching powder. Commercial bleaching powder contains 36–38 per cent of available chlorine.

Two methods are in common use for the determination of the available

chlorine. In the first, the hypochlorite solution or suspension is treated with an excess of a solution of potassium iodide, and strongly acidified with acetic acid:

$$OCl^- + 2I^- + 2H^+ \rightleftharpoons Cl^- + I_2 + H_2O$$

The liberated iodine is titrated with standard sodium thiosulphate solution. The solution should not be strongly acidified with hydrochloric acid, for the little calcium chlorate which is usually present, by virtue of the decomposition of the hypochlorite, will react slowly with the potassium iodide and liberate iodine:

$$ClO_3^- + 6I^- + 6H^+ = Cl^- + 3I_2 + 3H_2O$$

In the second method, the hypochlorite solution or suspension is titrated against standard sodium arsenite solution; this is best done by adding an excess of the arsenite solution and then back-titrating with standard iodine solution.

Procedure (iodometric method). Weigh out accurately about 5.0 g of the bleaching powder into a clean glass mortar. Add a little water, and rub the mixture to a smooth paste. Add a little more water, triturate with the pestle, allow the mixture to settle, and pour off the milky liquid into a 500 mL graduated flask. Grind the residue with a little more water, and repeat the operation until the whole of the sample has been transferred to the flask either in solution or in a state of very fine suspension, and the mortar washed quite clean. The flask is then filled to the mark with distilled water, well shaken, and 50.0 mL of the turbid liquid immediately withdrawn with a pipette. This is transferred to a 250 mL conical flask, 25 mL of water added, followed by 2 g of iodate-free potassium iodide (or 20 mL of a 10 per cent solution) and 10 mL of glacial acetic acid. Titrate the liberated iodine with standard 0.1*M* sodium thiosulphate.

10.121 DETERMINATION OF ARSENIC(V)

The reaction is the reverse of that employed in the standardisation of iodine with sodium arsenite solution (Section 10.113):

$$As_2O_5 + 4H^+ + 4I^- \rightleftharpoons As_2O_3 + 2I_2 + 2H_2O$$

or

$$H_3AsO_4 + 2H^+ + 2I^- \rightleftharpoons H_3AsO_3 + I_2 + H_2O$$

For good results, the following experimental conditions must be observed: (1) the hydrochloric acid concentration in the final solution should be at least 4*M*; (2) air should be displaced from the titration mixture by adding a little solid sodium hydrogencarbonate; (3) the solution must be allowed to stand for at least 5 minutes before the liberated iodine is titrated; and (4) constant stirring is essential during the titration to prevent decomposition of the thiosulphate in the strongly acid solution.

Treat the arsenate solution (say, 20.0 mL of *ca* 0.025*M*) in a glass-stoppered conical flask with concentrated hydrochloric acid to give a solution in 4*M* hydrochloric acid. Displace the air by introducing two 0.4 g portions of pure sodium hydrogencarbonate into the flask. Add 1.0 g of pure potassium iodide, replace the stopper, mix the solution, and allow to stand for at least 5 minutes. Titrate the solution, whilst stirring vigorously, with standard 0.1*M* sodium thiosulphate.