Procedure B. Prepare an approximately $0.05M$ solution of oxalic acid by dissolving about 1.6 g of the compound and making up to 250 mL in a graduated flask. Standardise the solution with standard ($0.02M$) potassium permanganate solution using the procedure described in Section 10.94 (Method B).

Weigh out accurately 0.3–0.4 g potassium persulphate into a 500 mL conical flask, add 50 mL of $0.05M$-oxalic acid, followed by 0.2 g of silver sulphate dissolved in 20 mL of 10 per cent sulphuric acid. Heat the mixture in a water bath until no more carbon dioxide is evolved (15–20 minutes), dilute the solution to about 100 mL with water at about 40 °C, and titrate the excess of oxalic acid with standard $0.02M$ potassium permanganate.

OXIDATIONS WITH POTASSIUM DICHROMATE

10.98 DISCUSSION

Potassium dichromate is not such a powerful oxidising agent as potassium permanganate (compare reduction potentials in Table 2.6 in Section 2.31), but it has several advantages over the latter substance. It can be obtained pure, it is stable up to its fusion point, and it is therefore an excellent primary standard. Standard solutions of exactly known concentration can be prepared by weighing out the pure dry salt and dissolving it in the proper volume of water. Furthermore, the aqueous solutions are stable indefinitely if adequately protected from evaporation. Potassium dichromate is used only in acid solution, and is reduced rapidly at the ordinary temperature to a green chromium(III) salt. It is not reduced by cold hydrochloric acid, provided the acid concentration does not exceed 1 or $2M$. Dichromate solutions are less easily reduced by organic matter than are those of permanganate and are also stable towards light. Potassium dichromate is therefore of particular value in the determination of iron in iron ores: the ore is usually dissolved in hydrochloric acid, the iron(III) reduced to iron(II), and the solution then titrated with standard dichromate solution:

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

In acid solution, the reduction of potassium dichromate may be represented as:

$$Cr_2O_7^{2-} + 14H^+ + 6e \rightleftharpoons 2Cr^{3+} + 7H_2O$$

The green colour due to the Cr^{3+} ions formed by the reduction of potassium dichromate makes it impossible to ascertain the end-point of a dichromate titration by simple visual inspection of the solution and so a redox indicator must be employed which gives a strong and unmistakable colour change; this procedure has rendered obsolete the external indicator method which was formerly widely used. Suitable indicators for use with dichromate titrations include *N*-phenylanthranilic acid (0.1 per cent solution in $0.005M$ NaOH) and sodium diphenylamine sulphonate (0.2 per cent aqueous solution); the latter must be used in presence of phosphoric(V) acid.

10.99 PREPARATION OF 0.02*M* POTASSIUM DICHROMATE

Analytical grade potassium dichromate has a purity of not less than 99.9 per cent and is satisfactory for most purposes.* Powder finely about 6 g of the analytical grade material in a glass or agate mortar, and heat for 30–60 minutes in an air oven at 140–150 °C. Allow to cool in a closed vessel in a desiccator. Weigh out accurately about 5.88 g of the dry potassium dichromate into a weighing bottle and transfer the salt quantitatively to a 1 L graduated flask, using a small funnel to avoid loss. Dissolve the salt in the flask in water and make up to the mark; shake well. Alternatively, place a little over 5.88 g of potassium dichromate in a weighing bottle, and weigh accurately. Empty the salt into a 1 L graduated flask, and weigh the bottle again. Dissolve the salt in water, and make up to the mark.

The molarity of the solution can be calculated directly from the weight of salt taken, but if the salt has only been weighed out approximately, then the solution must be standardised as described in the following section.

10.100 STANDARDISATION OF POTASSIUM DICHROMATE SOLUTION AGAINST IRON

With metallic iron. Use iron wire of 99.9 per cent assay value (Note 1). Insert a well-fitting rubber stopper provided with a bent delivery tube into a 500 mL conical flask and clamp the flask in a retort stand in an inclined position, the tube being so bent as to dip into a small beaker containing saturated sodium hydrogencarbonate solution or 20 per cent potassium hydrogencarbonate solution (prepared from the solids) (Fig. 10.16). Place 100 mL 1.5*M* sulphuric acid (from 92 mL water and 8 mL concentrated sulphuric acid) in the flask, and add 0.5–1 g sodium hydrogencarbonate in two portions; the carbon dioxide produced will drive out the air. Meanwhile, weigh out accurately about 0.2 g of iron wire, place it quickly into the flask, replace the stopper and bent tube, and warm gently until the iron has dissolved completely. Cool the flask rapidly

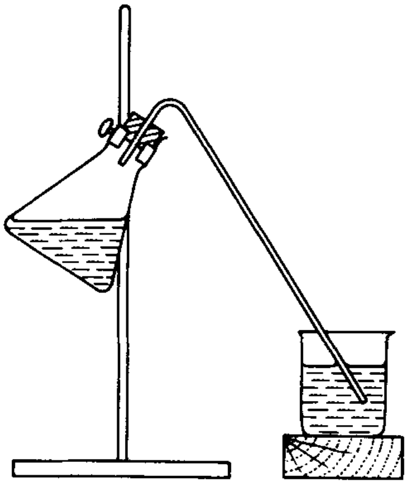

Fig. 10.16

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* If only a 'pure' grade (as distinct from analytical grade) of commercial salt is available, or if there is some doubt as to the purity of the salt, the following method of purification should be used. A concentrated solution of the salt in hot water is prepared and filtered. The crystals which separate on cooling are filtered on a sintered-glass filter funnel and sucked dry. The resultant crystals are recrystallised again. The purified crystals are then dried at 180–200 °C, ground to a fine powder in a glass or agate mortar, and again dried at 140–150 °C to constant weight.

under a stream of cold water, with the delivery tube still dipping into the solution in the beaker (Note 2).

Titrate the cooled solution immediately with the dichromate solution, using either sodium diphenylamine sulphonate or *N*-phenylanthranilic acid as indicator. If the former is selected, add 6–8 drops of the indicator, followed by 5 mL of syrupy phosphoric(V) acid: titrate slowly with the dichromate solution, stirring well, until the pure green colour changes to a grey–green. Then add the dichromate solution dropwise until the first tinge of blue–violet, which remains permanent on shaking, appears. If the latter indicator is selected, add 200 mL of 1*M* sulphuric acid, then 0.5 mL of the indicator; add the dichromate solution, with shaking until the colour changes from green to violet–red (Note 3).

1 mole $K_2Cr_2O_7 \equiv 6$ moles Fe

Notes. (1) Iron wire of 99.9 per cent purity is available commercially and is a suitable analytical standard. If the wire exhibits any sign of rust, it should be drawn between two pieces of fine emery cloth, and then wiped with a clean, dry cloth before use. The general reaction which occurs has been given in Section 10.92.

(2) As the flask cools, the hydrogencarbonate solution is automatically drawn in until the pressure of the carbon dioxide inside the flask is equal to the atmospheric pressure.

(3) The standardisation may also be effected with ethylenediammonium iron(II) sulphate.

10.101 DETERMINATION OF CHROMIUM IN A CHROMIUM(III) SALT

Discussion. Chromium(III) salts are oxidised to dichromate by boiling with excess of a persulphate solution in the presence of a little silver nitrate (catalyst). The excess of persulphate remaining after the oxidation is complete is destroyed by boiling the solution for a short time. The dichromate content of the resultant solution is determined by the addition of excess of a standard iron(II) solution and titration of the excess of the latter with standard 0.02*M* potassium dichromate.

$$2Cr^{3+} + 3S_2O_8^{2-} + 7H_2O \xrightarrow{(AgNO_3)} Cr_2O_7^{2-} + 6HSO_4^- + 8H^+$$

$$2S_2O_8^{2-} + 2H_2O = O_2\uparrow + 4HSO_4^-$$

Procedure. Weigh out accurately an amount of the salt which will contain about 0.25 g of chromium, and dissolve it in 50 mL distilled water. Add 20 mL of *ca* 0.1*M* silver nitrate solution, followed by 50 mL of a 10 per cent solution of ammonium or potassium persulphate. Boil the liquid gently for 20 minutes. Cool, and dilute to 250 mL in a graduated flask. Remove 50 mL of the solution with a pipette, add 50 mL of a 0.1*M* ammonium iron(II) sulphate solution (Section 10.97, Procedure A), 200 mL of 1*M* sulphuric acid, and 0.5 mL of *N*-phenylanthranilic acid indicator. Titrate the excess of the iron(II) salt with standard 0.02*M* potassium dichromate until the colour changes from green to violet–red.

Standardise the ammonium iron(II) sulphate solution against the 0.02*M* potassium dichromate, using *N*-phenylanthranilic acid as indicator. Calculate the volume of the iron(II) solution which was oxidised by the dichromate originating from the chromium salt, and from this the percentage of chromium in the sample.

Note. Lead or barium can be determined by precipitating the sparingly soluble chromate, dissolving the washed precipitate in dilute sulphuric acid, adding a known excess of ammonium iron(II) sulphate solution, and titrating the excess of Fe^{2+} ion with $0.02M$ potassium dichromate in the usual way.

$$2PbCrO_4 + 2H^+ = 2Pb^{2+} + Cr_2O_7^{2-} + H_2O$$

10.102 DETERMINATION OF CHLORATE

Discussion. Chlorate ion is reduced by warming with excess of iron(II) in the presence of a relatively high concentration of sulphuric acid:

$$ClO_3^- + 6Fe^{2+} + 6H^+ = Cl^- + 6Fe^{3+} + 3H_2O$$

The excess Fe^{2+} ion is determined by titration with standard dichromate solution in the usual way.

Procedure. To obtain experience in the method, the purity of analytical-grade potassium chlorate may be determined. Prepare a $0.02M$ potassium chlorate solution. Into a 250 mL conical flask, place 25.0 mL of the potassium chlorate solution, 25.0 mL of $0.2M$ ammonium iron(II) sulphate solution in $2M$ sulphuric acid and add **cautiously** 12 mL concentrated sulphuric acid. Heat the mixture to boiling (in order to ensure completion of the reduction), and cool to room temperature by placing the flask in running tap water. Add 20 mL 1:1 water/phosphoric(V) acid, followed by 0.5 mL sodium diphenyl-amine-sulphonate indicator. Titrate the excess Fe^{2+} ion with standard $0.02M$ potassium dichromate to a first tinge of purple coloration which remains on stirring.

Standardise the ammonium iron(II) sulphate solution by repeating the procedure but using 25 mL distilled water in place of the chlorate solution. The difference in titres is equivalent to the amount of potassium chlorate added.

10.103 DETERMINATION OF CHEMICAL OXYGEN DEMAND

Discussion. One very important application of potassium dichromate is in a back-titration for the environmental determination[16] of the amount of oxygen required to oxidise all the organic material in a sample of impure water, such as sewage effluent. This is known as the chemical oxygen demand (C.O.D.) and is expressed in terms of milligrams of oxygen required per litre of water, mg L^{-1}. The analysis of the impure water sample is carried out in parallel with a blank determination on pure, double-distilled water.

Procedure. Place a 50 mL volume of the water sample in a 250 mL conical flask with a ground-glass neck which can be fitted with a water condenser for refluxing. Add 1 g of mercury(II) sulphate, followed by 80 mL of a silver sulphate/sulphuric acid solution (Note 1). Then add 10 mL of approximately $0.00833M$ standard potassium dichromate solution (Note 2), fit the flask with the reflux condenser and boil the mixture for 15 minutes. On cooling rinse the inside of the condenser with 50 mL of water into the flask contents. Add either diphenylamine indicator (1 mL) or ferroin indicator and titrate with $0.025M$ ammonium iron(II) sulphate solution (Note 3). Diphenylamine gives a colour change from blue to green at the end-point, whilst that for ferroin is blue–green to red–brown. Call this titration A mL. Repeat the back-titration for the blank (titration B mL). The difference between the two values is the amount of potassium dichromate used up in the oxidation. The C.O.D. is calculated from the relationship:

$$\text{C.O.D.} = (A - B) \times 0.2 \times 20\,\text{mg L}^{-1}$$

as a 1 mL difference between the titrations corresponds to 0.2 mg of oxygen required by the 50 mL sample (a correction must, of course, be made if solutions of slightly different molarities are employed); see Note 4.

Notes. (1) This solution is prepared by dissolving 5 g of silver sulphate in 500 mL of concentrated sulphuric acid.

(2) The required concentration is obtained by weighing out 1.225 g of potassium dichromate and diluting to 500 mL with de-ionised water in a graduated flask.

(3) Dissolve 4.9 g of ammonium iron(II) sulphate heptahydrate in 150 mL of water and add 2.5 mL of concentrated sulphuric acid. Dilute the solution to 500 mL in a graduated flask.

(4) This method gives high results with samples possessing a high chloride content due to reaction between the mercury(II) sulphate and the chloride ions. In these cases the problem can be overcome by following a procedure using chromium(III) potassium sulphate, $Cr(III)K(SO_4)_2,12H_2O$.[17]

OXIDATIONS WITH CERIUM(IV) SULPHATE SOLUTION

10.104 GENERAL DISCUSSION

Cerium(IV) sulphate is a powerful oxidising agent; its reduction potential in 0.5–4.0M sulphuric acid at 25 °C is 1.43 ±0.05 volts. It can be used only in acid solution, best in 0.5M or higher concentrations: as the solution is neutralised, cerium(IV) hydroxide [hydrated cerium(IV) oxide] or basic salts precipitate. The solution has an intense yellow colour, and in hot solutions which are not too dilute the end point may be detected without an indicator; this procedure, however, necessitates the application of a blank correction, and it is therefore preferable to add a suitable indicator.

The advantages of cerium(IV) sulphate as a standard oxidising agent are:

1. Cerium(IV) sulphate solutions are remarkably stable over prolonged periods. They need not be protected from light, and may even be boiled for a short time without appreciable change in concentration. The stability of sulphuric acid solutions covers the wide range of 10–40 mL of concentrated sulphuric acid per litre. It is evident, therefore, that an acid solution of cerium(IV) sulphate surpasses a permanganate solution in stability.
2. Cerium(IV) sulphate may be employed in the determination of reducing agents in the presence of a high concentration of hydrochloric acid (contrast potassium permanganate, Section 10.92).
3. Cerium(IV) solutions in 0.1 M solution are not too highly coloured to obstruct vision when reading the meniscus in burettes and other titrimetric apparatus.
4. In the reaction of cerium(IV) salts in acid solution with reducing agents, the simple change

   $$Ce^{4+} + e \rightleftharpoons Ce^{3+}$$

   is assumed to take place. With permanganate, of course, a number of reduction products are produced according to the experimental conditions.