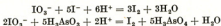
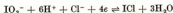


OXIDATIONS WITH POTASSIUM IODATE

III, 122. General discussion.—A glance at the table of standard reduction potentials (Table XVI, Section I, 46) reveals the fact that both potassium iodate and potassium bromate are stronger oxidising agents than iodine. The reaction between potassium iodate and reducing agents, such as potassium iodide or arsenious oxide, in fairly acidic solutions, say 0.1–2.0*M* hydrochloric acid, stops at the stage when the iodate is reduced to iodine:



L. W. Andrews (1903) showed that in the presence of a high concentration of hydrochloric acid (3–9*M*) iodate is reduced ultimately to iodine monochloride:



In hydrochloric acid solution, iodine monochloride forms a stable complex ion with chloride ion:

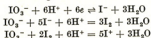


The overall half-cell reaction may therefore be written as:



the reduction potential is 1.23 volts, hence under these conditions potassium iodate acts as a very powerful oxidising agent. Furthermore, *under these particular conditions* the equivalent weight of potassium iodate is one-fourth the molecular weight $\text{KIO}_3/4$, and a 0.1*N* solution will contain $\text{KIO}_3/(4 \times 10)$, or $214.01/40 = 5.3503$ g. per litre.*

Oxidation by iodate ion in a strong hydrochloric acid medium (3–9*M*) proceeds through several stages:



In the initial stages of the reaction free iodine is liberated: as more titrant is added, oxidation proceeds to iodine monochloride, and the dark colour of the solution gradually disappears. The overall reaction may be written as:



The reaction has been used for the determination of many reducing agents by G. S. Jamieson (1926) and others. An important factor is the rate of reaction near the equivalence point. The optimum acidity for reasonably rapid reaction varies from one reductant to another within the range 2.5–9*M* hydrochloric acid: in many cases the concentration of acid is not critical, but for Sb(III) it is 2.5–3.5*M*.

* The same result can be deduced from the hypothetical equation:



Detection of end point. Starch cannot be used, because the characteristic blue colour of the starch-iodine complex is not formed at high acid concentrations. A few ml. of an immiscible solvent, such as carbon tetrachloride or chloroform, may be added to the aqueous test solution contained in a glass-stoppered bottle or conical flask. The end point is marked by the disappearance of the last trace of violet colour, due to iodine, from the solvent: iodine monochloride is not extracted and imparts a pale yellowish colour to the aqueous phase. The extraction end point is very sharp. The main disadvantage is the inconvenience of vigorous shaking with the extraction solvent in a stoppered vessel after each addition of the reagent near the end point.

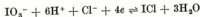
The immiscible solvent may be replaced by certain dyes, e.g., Amaranth (B.C.I. No. 184), Brilliant Ponceau 5R (B.C.I. No. 185), and Naphthol Blue Black (B.C.I. No. 246); the first two dyestuffs are generally preferred. The indicators are used as 0.2 per cent aqueous solutions and about 0.5 ml. per titration is added near the end point. The dyes are destroyed by the first excess of iodate, and hence the indicator action is irreversible. The indicator blank is equivalent to 0.05 ml. of 0.1N-potassium iodate per 1.0 ml. of indicator solution, and is therefore virtually negligible. The colour changes are: Amaranth, red to colourless; Brilliant Ponceau 5R, orange to colourless; Naphthol Blue Black, green to faint pink.

p-Ethoxychrysoidine is a moderately satisfactory reversible indicator. It is used as a 0.1 per cent solution in ethanol (about 12 drops per titration), and the colour change is from red to orange; the colour is red-purple just before the end point. The indicator is added after the colour of the iodine commences to fade. A blank determination should be made for each new batch of indicator.

Potassium iodate, as already pointed out in Section III, 102A, is available commercially in a high state of purity, is anhydrous, can be dried at 120° C., and is stable in solution. The A.R. product has an assay value of better than 99.9 per cent. Iodate titrations can be performed in the presence of filter paper, alcohol, formaldehyde, saturated organic acids, as well as many other kinds of organic matter.

III, 123. Preparation of 0.1N (0.025M)-potassium iodate.—Dry some A.R. potassium iodate at 120° C. for 1 hour and allow it to cool in a covered vessel in a desiccator. Weigh out exactly 5.350 g. of the finely powdered potassium iodate on a watch glass, and transfer it by means of a clean camel-hair brush directly into a dry 1-litre volumetric flask. Add about 400–500 ml. of water, and gently rotate the flask until the salt is completely dissolved. Make up to the mark with distilled water. Shake well. The solution will keep indefinitely.

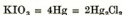
It must be emphasised again that the solution is 0.1N only for the reaction:



iodate solution under the usual conditions in accordance with the equation :



Thus



and 1 ml. 0.025*M*-KIO₃ = 0.02006 g. Hg = 0.02361 g. Hg₂Cl₂

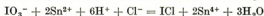
For practice, the student may determine the percentage of mercury in mercuric chloride, preferably of A.R. quality.

Procedure. Weigh out accurately about 2.5 g. of finely powdered mercuric chloride,* and dissolve it in 100 ml. of water in a volumetric flask. Shake well. Transfer 25.0 ml. of the solution to a conical flask, add 25 ml. of water, 2 ml. of *N*-hydrochloric acid, and excess of 50 per cent phosphorous acid solution. Stir thoroughly and allow to stand for 12 hours or more. Filter the precipitated mercurous chloride through a quantitative filter paper or through a Gooch crucible with asbestos, and wash the precipitate moderately with cold water. Transfer the precipitate with the filter paper or asbestos quantitatively to a 250-ml. reagent bottle, add 30 ml. of concentrated hydrochloric acid, 20 ml. of water, and 5 ml. of carbon tetrachloride or chloroform. Titrate the mixture with standard 0.1*N*-potassium iodate in the usual manner (Section III, 124).

Calculate the percentage of mercury in the sample.



III, 128. Determination of tin.—*Discussion.* Potassium iodate solution reacts quantitatively with stannous tin Sn(II) in the presence of concentrated hydrochloric acid in accordance with the equation :



Thus KIO₃ = 2Sn, or 1 ml. 0.025*M*-KIO₃ = 0.005935 g. Sn

This method possesses several advantages. The end point is very sharp. Extreme precautions need not be taken to prevent atmospheric oxidation if the bulk of the iodate solution is added rapidly at first; the titration can then be completed at leisure. The method cannot be applied in the presence of antimony, cuprous and ferrous salts, or precipitated metals; these interfering substances can, however, be simply removed.

For practice, the student may determine the percentage of tin in hydrated stannous chloride, preferably of A.R. grade.

Procedure. Weigh out accurately about 1.5 g. of crystallised stannous chloride SnCl₂·2H₂O, dissolve it in a small volume of concentrated hydrochloric acid, and make up to 250 ml. in a volumetric flask. Shake thoroughly. Remove 25 ml. of the solution to a 250-ml. reagent bottle, add 30 ml. of concentrated hydrochloric acid, 20 ml. of water, and 5 ml. of carbon tetrachloride or chloroform. Add standard 0.1*N*-potassium iodate rapidly at first, whilst shaking the bottle to give the contents a gentle rotary motion, until the iodine colour, which gradually appears, has increased to the maximum intensity, then insert the stopper, and shake the solution thoroughly. Continue the titration slowly, shaking

* Alternatively, use about 2.5 g. of mercurous nitrate, accurately weighed; the addition of phosphorous acid is, of course, unnecessary.

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after each addition, until the organic layer is no longer violet. Repeat the titration with two other 25-ml. portions of the solution.

Calculate the percentage of tin in the sample.