TITRATIONS WITH POTASSIUM IODATE

Potassium iodate is a fairly strong oxidizing agent that may be used in the assay of a number of pharmaceutical substances, for instance : benzalkonium chloride, cetrimide, hydralazine hydrochloride, potassium iodide, phenylhydrazine hydrochloride, semicarbazide hydrochloride and the like. Under appropriate experimental parameters the iodate reacts quantitatively with both iodides and iodine. It is, however, interesting to observe here that the iodate titrations may be carried out effectively in the presence of saturated organic acids, alcohol and a host of other organic substances.

The oxidation-reduction methods with potassium iodate invariably based on the formation of iodine monochloride (ICl) in a medium of strong hydrochloric acid solution.

Preparation of 0.05 M Potassium Iodate

Potassium iodate is dried to a constant weight at 110°C to make it completely free from moisture and then brought to room temperature in a desiccator. It is pertinent to mention here that KIO_3 is a very stable salt and may be obtained in a very pure form. Therefore, it is possible to prepare the standard solutions of KIO_3 by dissolving the calculated weight of the salt in water and diluting the same to an approximate volume.
Since, the normality of iodate solution varies significantly depending on the nature of the reaction, therefore, in usual practice standard iodate solutions of known molarity are used.

The reduction of potassium iodate to iodide is usually not feasible in a direct titrimetric method (unlike the reduction of potassium bromate to bromide) and hence, has no viable application in the official procedures

$$IO_3^- + 6e + 6H^+ \longrightarrow I^- + 3H_2O \qquad \text{..........................(a)}$$
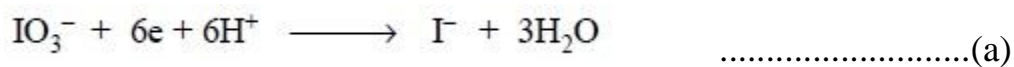
In this type of reaction, 1 mol of KIO_3 is 6 equivalent and a 0.05 M solution would be 0.3 N.

In a situation, whereby excess of potassium iodate is employed, any I^- formed [Eq. (*a*)] is readily oxidized to iodine, and subsequently the excess iodate and the iodine are estimated by the iodometric proce-dure. Thus, the reduction of the iodate to iodine may be expressed as shown below :

$$2IO_3^- + 10e + 12H^+ \longrightarrow I_2 + 6H_2O \qquad \text{..........................(b)}$$
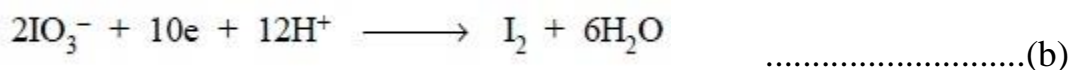
In such a reaction, 1 mol of iodate is 5 equivalent and a 0.05 M solution would be 0.25 N. This reaction of iodate is never used in the offcial assay methods.

Interestingly, at higher concentrations of hydrochloric acid, both the iodide and iodine obtained as reduction products of iodate [Eqs. (*a*) and (*b*)] are quantitatively converted to I^+. It forms the basis of official procedures for iodate titrations.

The iodine produced intially by the reduction of iodate [Eq. (*b*)] undergoes solvolysis in a polar solvent as expressed in the following reaction :

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

The iodine cation forms iodine monochloride (ICl) in a medium having sufficiently high concentration of HCl and the latter is subsequently stabilized by complex ion formation. Thus, we have :

$$I^+ + HCl \rightleftharpoons ICl + H^+ \qquad \qquad \qquad ...(c)$$
$$ICl + HCl \rightleftharpoons ICl_2^- + H^+ \qquad \qquad \qquad ...(d)$$
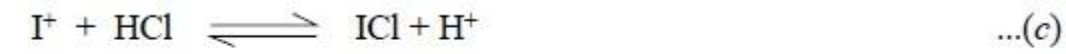
Adding Equations (c) and (d), we may have :

$$I^+ + 2HCl \rightleftharpoons ICl_2^- + 2H^+$$

In actual practice, either carbon tetrachloride or chloroform is usually added so as to make the end-point distinctly visible. Iodine is liberated at the initial stages of the titration which renders the chloroform layer coloured. At that material point when all the reducing agent under estimation has been duly oxidized, the iodate completes the oxidation of iodine and iodide to I^+, and hence the colour from the chloroform layer disappears.

ASSAY OF POTASSIUM IODIDE

PRINCIPLE

The iodine monochloride method employing standard potassium iodate is the basis for the official assay of potassium iodide. Vigorous shaking is a prime requirement, as the end-point is approached in this assay, because of the fact that both iodine and iodate in different phases attribute a heterogeneous medium. However, the reaction involving the oxidation of KI by iodate may be designated as shown below :
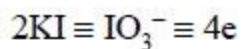
$$\underset{2(166.0)}{2KI} + KIO_3 + 6HCl \longrightarrow 3ICl + KCI + 3H_2O$$

The reduction of KIO_3 may be expressed as :

$$IO_3^+ + 4e + 6H^+ \longrightarrow I^+ + 3H_2O$$

Hence, from the above equation we have, 1 mol of KIO_3 is 4 equivalent and a 0.05 M solution would be 0.2 N.

Thus, we have :

$$2KI \equiv IO_3^- \equiv 4e$$

or $\qquad$ $166 \text{ g } KI \equiv 2e \equiv 2000 \text{ ml } N$

or $\qquad$ $83 \text{ g } KI \equiv 1000 \text{ ml } N$

or $\qquad$ $16.60 \text{ g } KI \equiv 1000 \text{ ml } 0.2 \text{ N} \equiv 1000 \text{ ml } 0.05 \text{ M}$

or $\qquad$ $0.01660 \text{ g } KI \equiv 1 \text{ ml } 0.05 \text{ M } KIO_3$

Procedure :

Weigh accurately 0.5 g of potassium iodide and dissolve it in about 10 ml of DW. Add to it 35 ml of hydrochloric acid and 5 ml of chloroform. Titrate with 0.05 M potassium iodate till the purple colour of iodine disappears from the chloroform layer. Add the last portion of the iodate solution carefully and dropwise while shaking the contents of the flask vigorously and continuously. Allow to stand for 5 minutes. In case any colour still develops in the chloroform layer continue the titration.

Each ml of 0.05 M potassium iodate is equivalent to 0.0166 g of potassium iodide.