744. *The Potentiometric Titration of Iodic Acid with Potassium Iodide in Sulphuric and Hydrochloric Acid Solutions.*

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Iodic acid can be accurately titrated potentiometrically with potassium iodide in sulphuric acid or very dilute hydrochloric acid solutions, the reduction proceeding directly to iodine. In hydrochloric acid of higher concentrations (1—2N), two inflections in the titration curve show that iodic acid is first reduced quantitatively to iodine monochloride, and this, in turn, to iodine. In hydrochloric acid of still higher concentration ($\gg$5N), these two inflections appear before the correct amounts of titrant have been added, the amounts depending on the time taken for titration.

MÜLLER and JUNCK (*Z. Elektrochem.*, 1925, **31**, 200) showed that potassium iodate can be titrated potentiometrically by potassium iodide in solutions containing hydrochloric acid, but they did not investigate solutions in which the concentration of acid exceeded 2N. In the present work a much wider range of concentrations has been studied, and it has also been shown that accurate titrations can be carried out in solutions containing sulphuric acid up to 6N.

EXPERIMENTAL

(i) *Titration in hydrochloric acid solution.* In Fig. 1 are given typical curves of the titration by N-potassium iodide of 100 c.c. of 0·005M-potassium iodate in the presence of the following concentrations: *A*, 0·1; *B*, 0·2; *C*, 0·25; *D*, 0·35; *E*, 1·0; *F*, 2·0; *G*, 5·0; *H*, 7·5N. The titrations were carried out at 19°, separate E.M.F.s being measured between the saturated Calomel Electrode and two independent bright platinum electrodes (1 cm. × 1 cm.) immersed in the solution. Both of these electrodes reached the same potential within 2—3 minutes, provided that the solution was thoroughly stirred after each addition of potassium iodide solution.

In titration *A* the solution became red on the addition of the first drops of potassium iodide solution and remained red even when stirred, but in titrations *B*—*H*, although a red colour was similarly produced at first, this became pale yellow when the solutions were stirred thoroughly. The pale yellow colour changed abruptly to red again at the points indicated by the first inflections. In all titrations, except *G* and *H*, iodine was ultimately precipitated.

(ii) *Titration in sulphuric acid solution.* Fig. 2 refers to similar titrations in sulphuric acid of concentrations 0·7, 1·7, 3·3, and 6·0N (curves *A*, *B*, *C*, *D*, respectively). The low potentials set up at the beginning of the titrations must have been caused by the lack of adequate "poise" in the iodate solutions. The solutions were red, and some iodine was precipitated as the titrations proceeded. At all four concentrations of sulphuric acid, the end-point inflections occurred with the addition of exactly 5 mols. of iodide as required by $KIO_3 + 5KI + 3H_2SO_4 \longrightarrow 3K_2SO_4 + 3H_2O + 3I_2$, and, unlike the titrations in hydrochloric acid solutions, the final inflections become more satisfactory the greater the concentration of sulphuric acid.

DISCUSSION

Titration with hydrochloric acid. The indefinite inflections produced in the early part of curves *C* and *D* are attributed to the slowness of the first stage of the reduction in 0·25—0·35N-hydrochloric acid. The broken lines illustrate the effect of allowing longer times (5 minutes of vigorous stirring) after each addition of titrant before measuring the E.M.F.s. The titration curves so obtained ultimately became coincident with the original curves.

The first inflection of curves *E* and *F* and that of the broken curve *D* occur with 2 mols. of potassium iodide and thus correspond with the completion of the first stage of the reduction:

$$2KI + KIO_3 + 6HCl \longrightarrow 3ICl + 3KCl + 3H_2O \quad . \quad . \quad . \quad . \quad (1)$$

whence it appears that the pale yellow colour was that of iodine monochloride. The inflection of the broken curve *C*, with 1 mol. of potassium iodide, is ascribed to insufficient time having been allowed.

The E_h at the mid-point of the first section of curve *E* (*i.e.*, with 1 mol. of potassium iodide) is 1·10 volt, which is also the normal redox potential of $IO_3' + 6H^{\cdot} + Cl' \longrightarrow$

$ICl + 3H_2O + 4F$. The higher potentials set up in the first section of curve *F* show the effect of the greater hydrogen-ion activity.

Curves *G* and *H* show that the first stage of the reduction was completed in 5N- and 7·5N-hydrochloric acid when 1·5 mol. of potassium iodide had been added. If in these concentrated acid solutions reduction is strictly stepwise, the first product would be either iodous acid, HIO_2, or the equivalent iodide trichloride, which would require 0·5 mol. of potassium iodide, and subsequent reduction of either of these to iodine monochloride would require a further 1·5 mols. of potassium iodide. The appearance of inflections in *G* and *H* with 1·5 mols. of potassium iodide may be connected with the formation of some iodine trichloride. Owing to the proximity of the redox potentials of the systems involving iodine trichloride and iodine monochloride no inflection would occur marking the formation of the former.

FIG. 1.

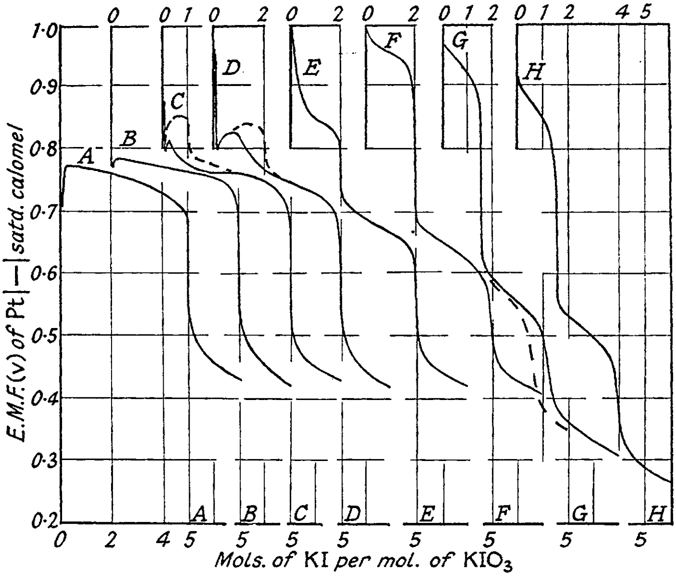
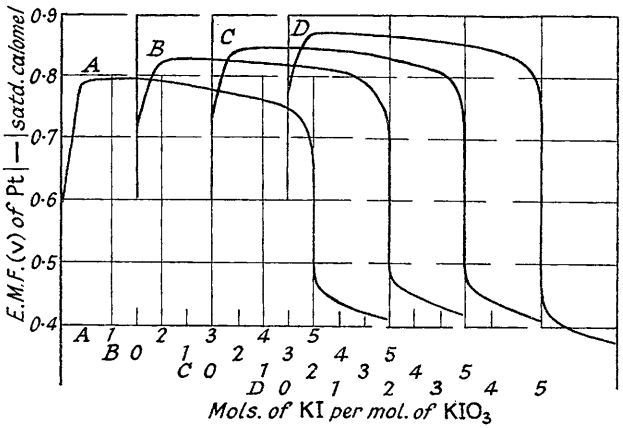


FIG. 2.



The final inflections of curves *A*—*F*, occurring with the addition of exactly 5 mols. of potassium iodide, correspond with the equation

$$KIO_3 + 5KI + 6HCl \longrightarrow 6KCl + 3I_2 + 3H_2O \quad . \quad . \quad . \quad . \quad (2)$$

but this can represent the mechanism of the reduction process only in titrations *A* and *B*. In the other titrations some iodine monochloride was produced, and curves *D*, *E*, and *F* reveal that, given sufficient time, 1 mol. of iodic acid is first quantitatively reduced according to equation (1), so that the subsequent reduction of the 3 mols. of iodine monochloride to iodine requires 3 mols. of potassium iodide :

$$3ICl + 3KI \longrightarrow 3KCl + 3I_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

In titration *C*, therefore, a certain amount of iodic acid must have been directly reduced to iodine according to (2), the remainder undergoing stepwise reduction according to (1) and (3).

The appearance of the final inflections in curves *G* and *H* with 4·2 and 4·0 mols. of potassium iodide, respectively, must be attributed to the higher concentration of acid. Their precise location depends to some extent on the time taken over the titration as shown, *e.g.*, by the broken line at 3·8 mols. in *G*.

Consideration of Fig. 1 shows that for accurate results the concentration of hydrochloric acid should preferably be 0·1—0·35N (curves *A*—*D*) and should certainly not exceed 2N.

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