745. *An Electrometric Study of the Reaction between* (i) *Bromine and Iodide Ions in the Absence and in the Presence of Acid*; (ii) *Bromate and Bromide Ions in Acid Solution.*

By H. T. S. BRITTON and H. GREENSLADE BRITTON.

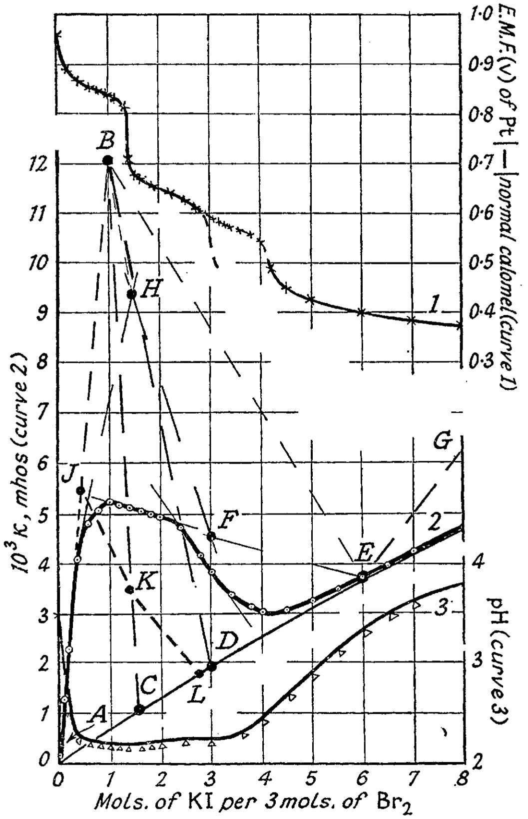
(1) Redox titrations of potassium iodide with bromine give inflections indicating the liberation of iodine and its conversion into iodine bromide. Bromine in acid solution, saturated with potassium bromide, may be titrated with potassium iodide to a good inflection corresponding to the formation of iodine bromide. When potassium bromide is absent, the bromine partially oxidises the iodide to iodate, the extent depending on the time allowed, and the iodide then reduces the iodate to iodine bromide and thence to iodine. Premature inflections denote the reduction to iodine bromide and iodine. When bromine-water is added to potassium iodide solution the oxidation to iodate involves the production of hydrobromic acid, the presence of which is shown by a rapid increase in conductivity and a decrease in pH.

(ii) Potassium bromate in presence of sulphuric (but not hydrochloric) acid can be titrated with potassium bromide.

INSTEAD of the simple replacement reaction $Br_2 + 2KI \longrightarrow 2KBr + I_2$ when a solution of potassium iodide is gradually added to one of bromine or *vice versa,* a succession of reactions occurs. The reason for this is that bromine is a powerful oxidising agent, the standard redox potential of the bromine–bromide couple being 1·087 volt on the hydrogen scale, and that iodide ions are relatively powerful reducing agents, the standard redox potential of the iodide–iodine couple being 0·535 volt; hence, when iodide ions are slowly added to a solution of bromine they may first suffer oxidation to valency states higher than that of iodine, whereas in the reverse method of addition it would be expected that the iodide ions would be oxidised first to free iodine and ultimately to higher valency states. In the ordinary volumetric determination of bromine the oxidation of potassium iodide beyond the stage of free iodine is prevented by keeping the salt in large excess.

The objects of this work were (i) to study electrometrically the mechanism of the reactions taking place between bromine and iodide ions under various conditions, and (ii) to ascertain whether potentiometric titrations could be applied to the estimation of either bromine or iodide ions. Some of the work was performed on bromine liberated by interaction of potassium bromate and potassium bromide in acid solution, and it was found that in the presence of sulphuric acid the quantitative reduction of bromate to bromine could be followed potentiometrically, the inflection indicating that only the reaction $KBrO_3 + 5KBr + 3H_2SO_4 \longrightarrow 3K_2SO_4 + 3Br_2 + 3H_2O$ had taken place. The potentiometric titration curves obtained when hydrochloric acid was present reveal that the reduction of the bromic acid passes through an intermediate stage and they fail to indicate its complete reduction to bromine. The positions of the two inflections in the redox potentiometric curves obtained by titrating the bromine so liberated with potassium iodide depended largely on the concentration of potassium bromide in the original bromine solution: the greater this concentration the more rapid was the reaction.

Fig. 1.



Experimental

(1) *Reaction between Bromine-water and Potassium Iodide.*—The curves in Fig. 1 refer to the gradual addition of N-potassium iodide to 100 c.c. of 0·030N-bromine-water at 20°. In the bromine-water were two bright platinum electrodes (1 cm. × 1 cm.), and a saturated potassium chloride salt bridge connected the solution undergoing titration to the normal calomel electrode; the solution also carried a conductivity cell of the dip-type, the tube of a glass electrode, a stirrer, a tube for the introduction of nitrogen above the bromine-water, and a very fine tube for introduction of the potassium iodide solution from a microburette. As the vessel was fitted with an ebonite cap, loss of bromine or iodine through volatilisation was negligible.

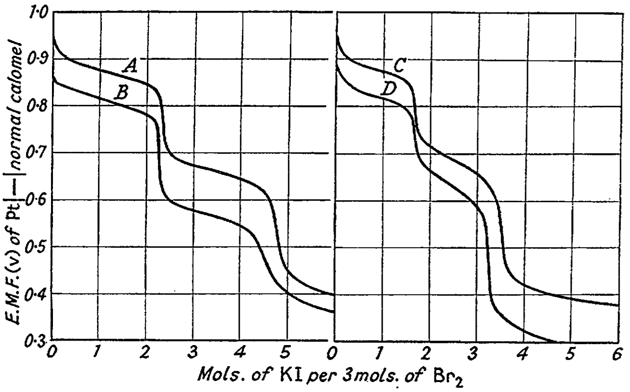
The reaction is illustrated by Fig. 1 in which curve 1 gives the change in redox potentials, curve 2 the specific conductivities, and curve 3 the pH values. The abscissæ represent mols. of potassium iodide per 3 mols. of bromine (2 horizontal divisions = 1 c.c. of N-potassium iodide).

The various measurements were sensibly steady for 5—10 minutes, except the redox potentials indicated by the broken line in curve 1, at which stage iodine was being precipitated and the potentials were drifting slowly to the higher values shown by the continuous curve. The broken line refers to the potentials that were set up after each fresh addition of titrant.

In curve 1 the first inflection appears with 1·35 mols. of potassium iodide and up to this point the colour of the solution was that of bromine, but here it suddenly changed to the orange colour of iodine and increased in intensity until iodine began to be precipitated. The final inflection occurred with 4·2 mols. of iodide and not with the stoicheiometrical amount, 6 mols. Curve 2 shows a remarkable initial increase in specific conductivity as the first 0·4 mol. of iodide was added, and since the pH correspondingly fell from 3·49 to 2·2 (curve 3), a strong acid was being produced. Curve 3 also shows that this acidity persisted until 4 mols. of iodide had been added, and then gradually decreased.

The curve *ACDE* gives the specific conductivities observed when 1·0N-potassium bromide was added to 100 c.c. of water at 20°, and these would have been the values observed during the addition of 6 mols. of iodide to 3 mols. of bromine had the reaction been simply $Br_2 + 2KI \longrightarrow 2KBr + I_2$, the contribution by the iodine being negligible. Thereafter, continued addition of potassium iodide would have caused curve 2 to follow the line *EG*; the complicated nature of the reactions concerned is demonstrated by the fact that the observed titration graph bears no resemblance to *AEG*.

FIG. 2.



(2) *Action of Potassium Iodide on Bromine in Aqueous Acids.*—The redox titration curves in Fig. 2 bring out clearly the important effect which acid has on the reaction between bromine and iodide ions. They refer to the titrations by N-potassium iodide of 100 c.c. of bromine solution containing either hydrochloric or sulphuric acid at the concentrations given in Table 1, which also records the number of mols. of iodide (per 3 mols. of bromine) required to produce the first and the second inflection of each curve. The E.M.F.s after each addition of iodide were measured as before; identical E.M.F.s were rapidly set up at the two electrodes after each addition of titrant and were stable for at least 5 minutes.

TABLE 1.

Curve	Acid	Concn., N	KI, mols. 1st Infln.	KI, mols. 2nd Infln.	*f* *	Curve	Acid	Concn., N	KI, mols. 1st Infln.	KI, mols. 2nd Infln.	*f* *
A	HCl	0·2	2·35	4·70	0·78	*C*	H_2SO_4	0·7	1·68	3·50	0·56
B	HCl	2·0	2·30	4·58	0·77	*D*	H_2SO_4	7·0	1·73	3·34	0·58

* See p. 3886.

The sequence of visible changes was as described in (1). The amounts of potassium iodide needed to produce the second inflections of curves *A* and *B* were double those required to give the respective first inflections, but in titrations *C* and *D* this is only approximately true.

(3) *Addition of Bromine-water to Aqueous Solutions of Potassium Iodide.*—Fig. 3 gives the redox curves of titrations with 0·1168N-bromine-water of 100 c.c. of: (*A*) 0·025M-KI, (*B*) 0·025M-KI + 0·7N-H_2SO_4, (*C*) 0·025M-KI + 0·2N-HCl, and (*D*) 0·025M-KI + 2N-HCl. The observed E.M.F.s set up at the platinum electrodes when referred to the normal calomel

electrode are plotted against the equivalents of bromine added per equivalent of potassium iodide. In titrations *A*, *B*, and *C*, iodine was precipitated when rather more than $\frac{1}{2}$ equiv. of bromine had been added, but it redissolved when just under 2 equivs. had been added; no precipitation occurred in titration *D*.

The first section of each curve refers to the simple displacement reaction $2KI + Br_2 \longrightarrow 2KBr + I_2$, the end of which is indicated by a well-defined inflection. The second section, terminated by an inflection which in the absence of acid is only just perceptible, corresponds to the oxidation of the iodine to iodine bromide in *A* and *B*, $I_2 + Br_2 \longrightarrow 2IBr$, and probably to iodine chloride in *C* and *D*: $I_2 + 2HCl + Br_2 \longrightarrow 2ICl + 2HBr$.

The bromine solutions used in the foregoing titrations were prepared directly from bromine and estimated volumetrically by normal procedure. As it was considered desirable that acidified bromine solutions of known concentration should also be prepared by some other method, we investigated the reaction between potassium bromate and potassium bromide in acid solution.

4. *Potentiometric Investigation of the Action of Potassium Bromide on Potassium Bromate in Acid Solution.*—Curve *A* in Fig. 4 is the redox titration curve of 100 c.c. of 0·005M-potassium bromate in 4N-sulphuric acid with 0·1M-potassium bromide and is typical of those in which the concentration of sulphuric acid lies between 3 and 6N. Bromine was liberated by the first drop of potassium bromide, and during most of the titration steady potentials were immediately set up, but towards the end they were obtained only after 5—10 minutes.

FIG. 3.

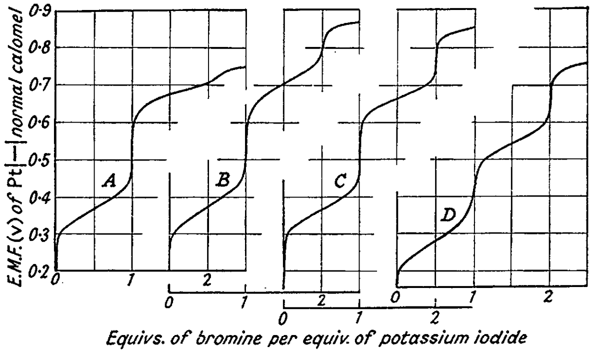
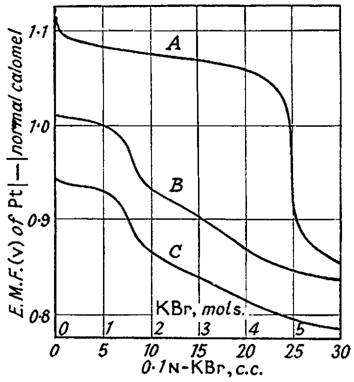


FIG. 4.



The position of the inflection in curve *A* corresponds exactly with the completion of the reaction given on p. 3880, the potentials before the inflection being those of the redox system $BrO_3' + 6H^{\bullet} \rightleftharpoons \frac{1}{2}Br_2 + 3H_2O + 5F$, and those after to $Br_2 \rightleftharpoons 2Br' + 2F$.

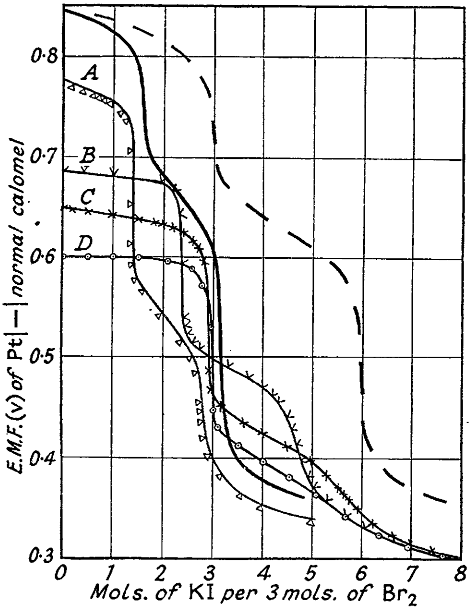
Curves *B* and *C* (Fig. 4) are those of similar titrations at 20° but in presence of 2N- and 5N-hydrochloric acid, respectively. Although bromine was liberated from the beginning of each of these two titrations, the fact that inflections occur with approximately 1·5 mols. of bromide per mol. of bromate indicates that some reaction must have occurred other than that which took place in titration *A*. Reduction to bromous acid would have required 0·5 mol. of potassium bromide, and to hypobromous acid, 2·0 mols. The inflection at an intermediate point may indicate simultaneous production of bromous acid and bromine, although the possibility of the formation of hypobromous acid cannot be excluded. That such titration curves should only be obtained with hydrochloric acid present suggests the production of bromine chloride in the course of the progressive reduction of bromic acid to bromine.

(5) *Effect of Bromide Ions on the Reduction of Bromine with Iodide Ions in Acid Solution.*—The "heavy" curve in Fig. 5 illustrates an immediate redox titration with N-potassium iodide of a solution prepared by adding 30 c.c. of 0·1M-potassium bromide to 100 c.c. of 0·005M-bromate + 4N-sulphuric acid, thereby yielding 130 c.c. of 0·0231N-bromine + 0·00385M-KBr + 3N-H_2SO_4. The two inflections occur at 1·58 and 2 × 1·58 (*i.e.*, 3·16) mols., respectively, of iodide per 3 mols. of bromine. As the stoicheiometric amount is 6 mols., it was suspected that one of the reactions involved in the reduction of bromine with bromide ions is slow and that in this titration insufficient time had been allowed for its completion. To ascertain whether this was the case, a number of solutions were taken, identical with that used before, but different quantities of N-potassium iodide were added. These solutions were kept in stoppered bottles,

with intermittent shaking, for 24 hours, and titrations were then continued with N-potassium iodide. In this time further reaction took place, so that the graph of total titration against potential was as shown by the broken line, the two inflections being at 3·0 and 6·0 mols. of iodide per 3 mols. of bromine.

Although the curves *B* and *C* in Fig. 4 do not reveal that in hydrochloric acid solution bromine is quantitatively liberated on addition of an excess of potassium bromide to potassium bromate, it is feasible to assume that this must ultimately be the case, and the following redox titrations were performed to ascertain the effect of (1) hydrochloric acid or (2) potassium bromide concentration on the manner in which bromine is reduced by iodide ions. In Fig. 5, curve *A* is that of the titration with 0·1N-potassium iodide of 150 c.c. of 0·00333M-potassium bromate containing hydrochloric acid (3·33N) and potassium bromide (0·033M). Curves *B*, *C*, and *D* refer to the titration by 0·1N-potassium iodide of 100 c.c. of 0·005M-potassium bromate, containing hydrochloric acid equivalent to 5N, which were (*B*) 0·192M; (*C*) 1·275M-, with respect to, and (*D*) saturated with, potassium bromide. The curves refer to the immediate measurements of the E.M.F.s.

FIG. 5.



The depressing effect of the increasing concentrations of bromide ions on the potentials prevailing during the first and second sections of these titrations is apparent in Fig. 5. Referred to the arbitrary standard hydrogen electrode as of zero potential, the initial potentials indicated by curves *A*, *B*, *C*, and *D* are 1·058, 0·971, 0·940, and 0·883 v, respectively, and when these are compared with 1·085, the standard redox potential of the iodate–iodide couple, it appears unlikely that any appreciable concentration of iodide ions was oxidised initially to iodate ions in titrations *C* and *D*, although such oxidation is possible in *A* and perhaps to a small extent in *B*. Table 2 summarises the details of the concentrations of bromine and potassium bromide in the above solutions and of the inflections produced.

TABLE 2.

Curve	Bromine, N	KBr, N	KI, mols., at 1st Infln.	KI, mols., at 2nd Infln.	Curve	Bromine, N	KBr, N	KI, mols., at 1st Infln.	KI, mols., at 2nd Infln.
A	0·020	0·0167	1·40	2·82	*C*	0·030	1·25	2·90	5·80
B	0·030	0·167	2·40	4·80	*D*	0·030	Sat.	3·00	6·00

It is significant that the effect of increasing the concentration of potassium bromide is the elimination of the " slow " reaction, for the initial and final inflections are immediately produced with 3 and 6 mols. of iodide (per 3 mols. of bromine). The curves in Fig. 5 also confirm the view that bromine is quantitatively liberated when an excess of potassium bromide reacts with potassium bromate in hydrochloric acid solution (see, however, curves *B* and *C* in Fig. 4).

Other redox titrations performed in solutions which contained either hydrochloric acid ranging from 0·2 to 5N or sulphuric acid ranging from 0·7 to 7N immediately produced curves that were inflected at 3 and 6-mols. of iodide provided that the solutions had been saturated with potassium bromide. Increase of acid concentration lowered the potentials set up at the platinum electrodes throughout the entire titrations by as much as 0·1 v, the extent depending on the concentration.

DISCUSSION

Fig. 3 shows that, on addition of bromine to potassium iodide solution in equivalent amounts, iodine is liberated which, on addition of another equivalent, is immediately converted into iodine bromide. If therefore, these reactions take place in the reverse order when potassium iodide is added to a solution of bromine, the first reaction would be

$$KI + Br_2 \longrightarrow KBr + IBr \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and the second

$$KI + IBr \longrightarrow KBr + I_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

the completion of each reaction being indicated by an inflection when 3 mols. and 6 mols. of potassium iodide per 3 mols. of bromine respectively had been added. Although the redox curves in Figs. 1, 2, and 5 each have two inflections, yet it was only when (i) a very considerable time was taken, particularly over the first half of the titration (broken line, Fig. 5) and (ii) the concentration of bromide ions was very large (curve *D*, Fig. 5) that the inflections appeared with these amounts. As will be shown later, however, it is only under the latter conditions that the reactions are those shown by (1) and (2).

The redox curves in Figs. 1 and 2, show that the potentials at the beginning of the titrations varied from +0·85 to +0·97 v, *i.e.*, $E_h = 1{\cdot}13$—$1{\cdot}25$. The highest potential was set up in bromine-water itself and the potentials became smaller as the concentration of acid became larger. In the early part of these titrations the redox system was $Br_2 \rightleftharpoons 2Br'$, for which the standard electrode potential is 1·08 v, and since the bromide-ion concentration was derived entirely from the equilibrium $Br_2 + H_2O \rightleftharpoons H^{\bullet} + Br' + HBrO$, it is clear why the values of E_h were high and depended on the hydrogen-ion concentration. When these E_h values are compared with the standard redox potential, 1·085 v, of the system $IO_3' + 6H^{\bullet} \rightleftharpoons 3H_2O + I' + 6F$, for which

$$E_h = 1{\cdot}085 - (0{\cdot}058/6) \log_{10} [I']/[IO_3'][H^{\bullet}]^6$$

it appears that bromine should be able to oxidise some iodide to iodate ions, but owing to the lowering of E_h, which occurs as the oxidation proceeds through the change in the ratio [Red/[Ox], it is unlikely that the oxidation reaction

$$3Br_2 + 3H_2O + I' \rightleftharpoons 6H^{\bullet} + IO_3' + Br' \quad . \quad . \quad . \quad . \quad . \quad (3)$$

will proceed to completion, *i.e.*, with 1 mol. of iodide (to 3 mols. of bromine). None of the redox curves in Figs. 1, 2, and 5 is inflected at this point, however. If iodate ions were first formed, the absence of an inflection would indicate that the E_h range within which the next reduction process occurred could not have been very much lower than that previously set up by the bromine–bromide couple.

The conductometric curve (2) in Fig. 1 shows that the addition of the first 0·3 mol. of potassium iodide to bromine-water resulted in a sharp increase in conductivity, whereas the pH curve (3) reveals a corresponding fall in pH. Hence an appreciable concentration of a strong acid must have been produced. If iodide had been oxidised to iodate (3), then the increase in specific conductivity would have followed the line *AB*. That the increasing conductivity should have followed *AB* nearly to the point *J*, shows that a substantial fraction of 1 mol. of iodide ions had been so oxidised, but the less rapid increase in specific conductivity occurring during the addition of the remainder of the 1 mol. of potassium iodide suggests that some other reaction was then taking place.

If the reduction of iodate ions takes place in a stepwise manner on the progressive addition of potassium iodide, then if iodous acid, HIO_2, or its derivative, IBr_3, is formed, the first step might be expected to follow either

$$KIO_3 + 1\tfrac{1}{2}HBr + \tfrac{1}{2}KI \longrightarrow 1\tfrac{1}{2}HIO_2 + 1\tfrac{1}{2}KBr \quad . \quad . \quad . \quad . \quad (4a)$$

or

$$KIO_3 + 6HBr + \tfrac{1}{2}KI \longrightarrow 1\tfrac{1}{2}IBr_3 + 1\tfrac{1}{2}KBr + 3H_2O \quad . \quad . \quad (4b)$$

Had the first mol. of iodide reacted entirely in accordance with (3), the change in specific conductivity would have been given by *AB*, and if this had been followed by reaction (4*a*) the subsequent change in conductivity would have been that indicated by *BC*, either reaction being complete when $1\frac{1}{2}$ mols. of iodide had been added. Had iodine tribromide been formed and it underwent no hydrolysis, the pH curve (3) would have been inflected with $1\frac{1}{2}$ mols. of iodide. It might be thought that as the redox curve (1) is inflected with 1·35 mols. of iodide, some iodous acid or iodine tribromide might have been formed, and that the slightly premature appearance of the inflection might have been caused by one or other of the reactions involved having been incomplete. The failure of the conductometric graph (2) to follow either course *ABH* or *ABC* renders such a supposition highly improbable. If iodous acid or iodine tribromide had then been reduced either to hypoiodous acid or to the corresponding iodine monobromide, another $1\frac{1}{2}$ mols. of iodide would have been required, making a total of 3 mols., and the respective section of the conductometric graph would have been *HF* or *CD*. It seems highly improbable, therefore, that reduction of iodate ions proceeds through the valency state of iodine of +3 to that of + 1.

It is much more likely that the reduction of iodate originally formed proceeded directly thus:

$$KIO_3 + 3HBr + 2HI \longrightarrow 3HIO + 3KBr \quad . \quad . \quad . \quad . \quad . \quad (5a)$$

or

$$KIO_3 + 6HBr + 2KI \longrightarrow 3IBr + 3KBr + 3H_2O \quad . \quad . \quad . \quad (5b)$$

If reduction had proceeded according to (5*a*) then the conductometric graph (2) would have been *ABF*, but if according to (5*b*) then it would have been *ABD*, and the pH curve (3) would have been inflected with 3 mols. of iodide. If, however, the iodate is reduced directly to iodine, thus

$$KIO_3 + 6HBr + 5KI \longrightarrow 3I_2 + 6KBr + 3H_2O \quad . \quad . \quad . \quad . \quad (6)$$

the conductometric graph would have been *ABEG* and inflection in the pH curve would have occurred with 6 mols. of iodide. Had reduction to either hypoiodous acid or iodine bromide taken place, the next 3 mols. of iodide would react in either of the following ways:

$$3HIO + 3HBr + 3KI \longrightarrow 3I_2 + 3KBr + 3H_2O \quad . \quad . \quad . \quad (7a)$$

$$3IBr + 3KI \longrightarrow 3I_2 + 3KBr \quad . \quad . \quad . \quad . \quad . \quad . \quad (7b)$$

so that the remaining part of the conductometric graph would have been either *FEG* or *DEG*, and if the former reaction had occurred an inflection in the pH curve would have appeared with 6 mols. of iodide.

Evidence has been advanced for the belief that hypoiodous acid or iodine bromide is formed in the course of the reduction of bromine with iodide ions. The potentials during the first section of curves *A*, *B*, *C*, and *D* in Fig. 5 show that in 5N-hydrochloric acid solution the increasing bromide-ion concentration depresses the redox potential. Associated with this lowering in E_h is the experimental fact that oxidation of the iodide ions proceeds rapidly to the valency state of +1, as shown by the inflection in *D* (Fig. 5) with 3 mols. of iodide. The depression of the initial redox potential to +0·60 v, *i.e.*, $E_h = +0{\cdot}88$ in this case below that of the iodate–iodide couple thereby renders impossible the oxidation of iodide to iodate ions. Hence in the absence of a large concentration of bromide ions the oxidation to iodate and/or the reduction of iodate to the +1 valency state are/is low. Owing to the close proximity of the standard redox potentials of the bromine–bromide and the iodate–iodide couples it is improbable that reaction (3) would proceed to completion. As shown in the preceding paper, the reduction of iodate with iodide in dilute acid solution is not unduly slow, whence it would appear that the slow reaction is that represented by equation (3). It was also shown in the preceding paper that in the presence of sulphuric acid there is no evidence of the reduction of iodate ions to the intermediate +1 valency state of iodine. The curves in Figs. 2 (*C* and *D*) and 5 that refer to titrations in sulphuric acid solution are, however, inflected at points which correspond with the reduction to the +1 valency state, *i.e.*, to formation of either hypoiodous acid or iodine monobromide. In the case of the titrations depicted by Fig. 2 (*C* and *D*) the only hydrobromic acid available is that which was formed during the oxidation of iodide to iodate ions in an amount which was twice that required to convert the hypoiodous acid into iodine monobromide. For the reaction of potassium iodide with bromine-water the hydrobromic acid so produced is just sufficient, as shown by equations (3) and (5*b*), for the intermediate formation of iodine monobromide.

Hence, in the presence of a very large concentration of bromide ions, bromine is progressively reduced with iodide ions according to equations (1) and (2), but in the presence of a low concentration of bromide ions or in their absence some iodate is produced according to equation (3), and on addition of more potassium iodide the iodate is reduced by the successive reactions :

$$IO_3' + 3Hal' + 6H^{\cdot} + 2I' \longrightarrow 3H_2O + 3IHal \quad . \quad . \quad . \quad (5c)$$

$$3IHal + 3I' \longrightarrow 3I_2 + 3Hal \quad . \quad . \quad . \quad . \quad (2a)$$

In the last two equations Hal′ signifies either a Br′ or a Cl′ ion, for the latter ions are involved in hydrochloric acid solutions. There is little doubt that the first inflection of the redox titration occurs when the reactions (3) and (5*c*) have proceeded as far as possible in the available time. The second section terminating with the final inflection the reaction corresponds to equation (2*a*).

Attention has already been directed (p. 3881) to the fact that the amount of potassium iodide necessary to bring a redox curve to the first inflection was equal to that required further to produce the second inflection. An explanation is forthcoming if it be assumed that instead of 1 mol. of iodide ions reacting with 3 mols. of bromine according to equation (3), a fraction of 1 mol. of iodide ions, f, reacted in the time available to produce f mol. of iodate ions. Their reduction according to (5*c*) would require $2f$ mol. of iodide ions, thus making a total of $3f$ mol. of iodide ions to complete the first section of a redox curve. Equation (2*a*) would then demand another $3f$ mol. of iodide ions for the second section of the redox curve, *i.e.*, instead of 3 mols. of iodide ions being needed for each of the two sections of the reduction, $3f$ mols. would be used in each case. Hence in reaction of iodide ions with 3 mols. of bromine, $6f$ equiv. of iodine would at first be set free, the remainder, $6(1 - f)$, being very slowly liberated. In these considerations it has tacitly been assumed that the bromine which originally escaped reduction according to equation (3) did not begin to react with the iodide ions until reactions (5*c*) and (2*a*) had come to an end with the iodate ions first formed.

The column headed f in Table 1 gives the fraction of a mol. of iodide ions which had been oxidised to iodate in the different titrations. Table 1 shows that $f = 0{\cdot}77$—$0{\cdot}78$ for titrations carried out immediately in hydrochloric acid solution, whereas $f = 0{\cdot}56$—$0{\cdot}58$ for those in sulphuric acid solution. The broken-line curve in Fig. 5 shows that if adequate time be allowed f ultimately becomes unity.

By reasoning along these lines it is possible to give a more detailed explanation of the curves in Fig. 1. As the first inflection in the redox curve (1) occurs with 1·35 mols. of iodide, it follows that $f = 0{\cdot}45$, *i.e.*, 0·45 mol. of iodide reacts with bromine according to equation (3). In consequence, during the addition of this iodide the conductivity should increase along *AB* to the point *J*, and the pH should diminish correspondingly as shown by curves (2) and (3) in Fig. 1. If the remaining 0·90 mol. of iodide had reacted according to equation (5*a*), the conductivity would have fallen from *J* to *K*, whereas if the iodate had been converted into iodine bromide (equation 6*b*) the conductivity would have fallen from *J* to a point on *AC* immediately below *K*. If the subsequent reaction had been that indicated by equation (8*b*) the conductometric graph (2) would have followed the remaining part of *AE*, the pH curve (3) would have been inflected upwards with 1·35 mols. of iodide, and the redox curve (1) would have been inflected a second time with 2·70 mols. of iodide (cf. broken line). Unlike those in titrations of bromine in acid solutions, the potentials during the second section were very unsteady and tended to higher values, with the result that the final inflection did not appear until after 4 mols. of iodide had been added; the conductometric graph showed larger conductivities than expected, and the pH curve showed that the solution remained appreciably acidic. These facts suggest that the potassium iodide was continuing to react with the unattacked bromine according to equation (3). It is probable that the iodate thus formed was subsequently reduced to iodine by the added potassium iodide and the free hydrobromic acid according to equation (6). Even so, just over two-thirds of the stoicheiometric amount of iodine was immediately liberated when 6 mols. of iodide (per 3 atoms of bromine) had been added. Because of the tardy manner in which iodine is liberated when potassium iodide is added to bromine, it is essential that in volumetric analytical procedure the reverse order be adopted, and to avoid the possible formation of iodine monobromide (cf. Fig. 3) the bromine to be estimated should be added to a much larger excess of potassium iodide in solution.

WASHINGTON SINGER LABORATORIES,
UNIVERSITY COLLEGE, EXETER.

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