

ART. XX.—*The Estimation of Iodine and Bromine in Haloid Salts by Means of Telluric Acid*; by HARRIET ISABELLE COLE.

[Contributions from the Kent Chemical Laboratory of Yale University—cclxi.]

It has been shown in a previous paper* from this laboratory that telluric acid may be used as an oxidizing agent to liberate bromine from hydrobromic acid and that the method may be relied upon to determine with accuracy amounts of bromine up to 0.3 grm. associated with 0.25 grm. of chlorine combined in the form of chloride. The present paper is the account of an attempt to extend this process to the estimation of iodine by finding the conditions under which telluric acid will react, first, with hydriodic acid to liberate the iodine quantitatively without a similar liberation of bromine, and second, with hydrobromic acid in such a way as to bring the reaction to completion without setting free chlorine from the hydrochloric acid formed in the reaction.

Telluric acid is not capable alone of bringing to completion the reaction with iodides to form hydriodic acid and then free iodine in solution, at such dilution that it will not also liberate some bromine from the bromide. The function of liberating the hydriodic acid so that the telluric acid may act as oxidizer has been performed by a very dilute solution of sulphuric acid, which after the removal of the iodine is then increased in order that the bromine of the hydrobromic acid may be similarly set free.

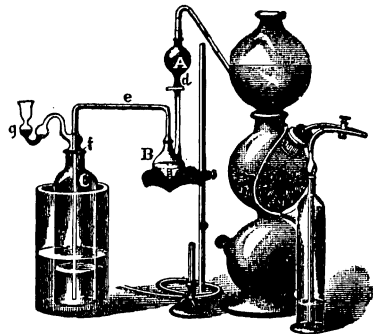
In the work to be described the telluric acid was prepared directly from the dioxide by precipitating tellurous acid from a hot solution of tetrachloride by means of water, and oxidizing with chlorine to telluric acid. Selenium present in the material may be removed by evaporating the telluric acid solution on a water bath. A slight reduction takes place in the presence of strong hydrochloric acid at this temperature and the selenium is first thrown out, the reduction being hastened by the presence of metallic tellurium. The filtered solution is re-chlorinated and evaporated in a current of air at room temperature. The telluric acid is washed with strong alcohol to remove traces of hydrochloric acid and recrystallized two or more times from water solution. In this way a very pure product may be readily prepared in considerable quantity.

The potassium bromide used was made by ignition and thorough fusion of potassium bromate specially prepared from purified bromine and potassium hydroxide. The potassium chloride was made by recrystallizing five times and thoroughly igniting pure potassium chlorate. The potassium iodide was prepared with great care, by acting with re-sublimed iodine upon iron wire, three-fourths of the iodine being

* Gooch and Cole, this Journal (4), xxxvii, 219, 1914.

added to an excess of iron covered with distilled water, decanting the solution from the excess of iron when the color of iodine had vanished, adding the remainder of the iodine, pouring the filtered solution slowly into boiling water, to which the exact amount of acid potassium carbonate necessary to combine with the iodine had been added, and filtering off the magnetic oxide of iron thus precipitated. The solution of potassium iodide thus made, very faintly alkaline and entirely free from chlorine and bromine, was evaporated and recrystallized and the resulting salt carefully

FIG. 1.



ground in a mortar to insure a homogeneous product. This preparation gave by the arsenate method in three determinations, 0.4994 grm.; 0.4994 grm.; 0.4993 grm. of potassium iodide in 0.5000 grm. of salt weighed out.

The sulphuric acid used in the determinations was absolutely free from nitrous fumes, as an exceedingly slight trace will greatly increase the dilution at which chlorine is liberated.

Solutions of iodine and sodium thiosulphate of approximately N/10 strength were carefully standardized, the iodine against N/10 arsenite and the thiosulphate against the iodine with the use of starch as indicator. The halogen salts were kept over sulphuric acid in a desiccator and were weighed directly for each determination.

The form of apparatus used for the distillation and absorption of liberated bromine in the earlier work, and shown in the accompanying figure (fig. 1), was again used in the iodine and bromine determination, the smaller Voit flask being replaced therein, by an ether wash-bottle having the larger capacity of 200^{cm}³. All joints in the apparatus were of glass. The ether wash-bottle which served as the distillation flask was graduated with etched lines at 10^{cm}³ intervals. A thick platinum wire so bent as to rest upon the bottom of the flask with the two ends upright was used as an aid in indicating the final volumes of 70^{cm}³ and 18^{cm}³. The Drechsel bottle, which served as the receiver of the

distillate, was kept cool by immersion in ice-water. A Kipp generator for the delivery of washed carbon dioxide was connected, as needed, with the separating funnel.

In the following preliminary tests the alkali halides and the telluric acid were introduced in solution into the distillation flask with 15^{cm}³ of sulphuric acid of sp. gr. 1.015 (measured from a burette and prepared by diluting 10^{cm}³ of concentrated acid to 1000^{cm}³) and the total volume was made up to 125^{cm}³ with water. The connection was made between the flask and the receiver charged with 200^{cm}³ of a 1.5 per cent solution of potassium iodide, carbon dioxide was passed slowly through the apparatus, and the liquid in the flask, heated gradually at first, was concentrated by boiling to the volume recorded.

TABLE I.
Preliminary tests upon mixtures of the Halogen Salts.
[Initial volume 125 cm³ : H₂TeO₄ 1 grm.]

KI taken	KBr taken	KCl taken	First final volume*	KI found	Error in terms of iodine	Second final volume†	KBr found	Error in terms of bromine
grm.	grm.	grm.	cm ³ .	grm.	grm.	cm ³ .	grm.	grm.
A								
0.5000	-----	--	75	0.4993	-0.0001			
0.5000	-----	--	72	0.4995	+0.0001			
-----	0.5000	--	50	{ Trace due to evolution of bromine				
-----	0.5000	--	50					
B								
0.2000	-----	0.2	65	0.1996	-0.0001			
0.2000	-----	0.2	50	0.1996	-0.0001			
C								
0.2000	0.2000	--	67	0.2009	+0.0008	17.5	0.1990	-0.0006
0.2000	0.2000	--	67+	0.1999	+0.0001	17.5	0.1995	-0.0003
0.2000	0.2000	--	67+	0.1996	-0.0001	17.0	0.2002	+0.0001
D								
0.1000	0.2000	0.2	67	0.1012	+0.0009	17.0	0.2030	+0.0018
0.1000	0.2000	0.2	67	0.1008	+0.0006	18.0	0.2004	+0.0002
0.1000	0.2000	0.2	67	0.0999	0.0000	20.0	0.2016	+0.0009
0.1000	0.2000	0.2	67	0.1009	+0.0007	19.5	0.2007	+0.0004
0.2000	0.2000	0.2	67	0.2009	+0.0008	20.5	0.1980	-0.0012
0.2000	0.2000	0.2	64	0.2017	+0.0014	19.5	0.1957	-0.0025
0.2000	0.2000	0.2	73	0.1996	-0.0001	16.5	0.2015	+0.0009
0.3000	0.2000	0.3	65	0.3005	+0.0008	20.0	0.1994	-0.0003
0.3000	0.2000	0.3	67	0.2992	-0.0002	17.5	0.2026	+0.0015
0.3000	0.2000	0.3	67	0.2996	0.0000	17.0	0.2026	+0.0015
0.3000	0.2000	0.3	67	0.2998	+0.0001	18.0	0.2018	+0.0010
0.0200	0.4000	0.3	67	0.0231	+0.0022	17.5	0.3995	-0.0003
0.0200	0.4000	0.3	65	0.0223	+0.0016	21.0	0.4002	+0.0001
0.4000	0.0200	0.3	63	0.3990	-0.0002	17.0	0.0207	+0.0004
0.4000	0.0200	0.3	63	0.3995	+0.0001	18.5	0.0203	+0.0001

* H₂SO₄ of lower concentration.

† H₂SO₄ of higher concentration.

The preliminary tests of Table I, A, show that the iodine is completely eliminated from 0.5 grm. of potassium iodide during the process of concentrating to 75^{cm³} the solution containing 1 grm. of telluric acid and 15^{cm³} of the dilute sulphuric acid, sp. gr. 1.015; and that no bromine is evolved from 0.5 grm. of potassium bromide similarly treated until the concentration of 50^{cm³} is reached. From the results given in B and C it appears that, while the presence of a chloride does not affect the determination of the iodine of the iodide, the presence of bromine tends to introduce slight errors of excess. On the other hand, in those determinations in which an excess of iodine is indicated the results show a slight deficiency in the bromine. This complementary relation of the errors of the iodine and the bromine points to an easier evolution of bromine if free iodine is present during concentration to a limit in the neighborhood of that at which the bromide by itself begins to evolve bromine. A similar phenomenon was noted in previous work* when the presence of free bromine had the effect of raising the limit at which chlorine began to be evolved from a chloride.

In these tests the iodine collected in the receiver after the concentration of the solution to a volume of 65^{cm³} to 70^{cm³} was estimated by titration with N/10 thiosulphate, the receiver was recharged with 200^{cm³} of a 1.5 per cent solution of potassium iodide and connected with the distilling flask, 10^{cm³} of sulphuric acid [1 : 1] was then added through the separating funnel to the reaction mixture, and the solution concentrated as before to a volume between 17^{cm³}–18^{cm³}. The bromine was estimated by titrating with N/10 thiosulphate the iodine set free in the receiver.

The effect of the presence of free iodine upon the elimination of bromine from the bromide, as of free bromine upon the elimination of chlorine from the chloride, is clearly manifest in the results, although a part of the irregularity in the bromine determination was no doubt due to the difficulty in measuring with exactness the final volumes in so large a flask. So long as hydriodic acid remains undecomposed the formation of either iodic acid or a compound of iodine with chlorine or bromine is not possible, and so long as hydrobromic acid is present the formation of a compound in which the bromine will drag along chlorine is also an impossibility. The conditions of concentration at which the hydriodic acid and the hydrobromic acid, respectively, have been completely broken up while the free halogen remains in solution are points at which there is danger that the halogen less easily evolved will enter into combination with the volatile, free halogen. It is desirable, therefore, that the free halogen should be eliminated as it is evolved and from

* Loc. cit.

solutions safely dilute. In the experiments of Table II, the expedient was adopted of introducing steam, with the carbon dioxide, so that the volumes might be held constant above the critical concentrations until the volatile halogen had been eliminated as set free.

TABLE II.
Preliminary Distillations in Steam from Flask.
[Initial volume 100 cm³ : H₂TeO₄ 1 grm.]

KI taken grm.	KBr taken grm.	KCl taken grm.	First final volume* cm ³ .	KI found grm.	Error in terms of iodine grm.	Second final volume† cm ³ .	KBr found grm.	Error in terms of bromine grm.
A								
0.2000	0.3000	0.3	63.0	0.1992	-0.0003	19.0	0.3019	+0.0011 ¹
0.2000	0.3000	0.3	55.0	0.1996	-0.0001	18.5	0.3001	+0.0001 ²
0.3000	0.2000	0.3	66.5	0.2996	0.0000	20.0	0.1999	-0.0001
0.3000	0.2000	0.3	70.0	0.2993	-0.0002	20.0	0.1998	-0.0001
0.5000	0.5000	0.3	63.5	0.4985	-0.0006	³ 19.0	0.4973	-0.0016
0.5000	0.5000	0.3	52.0	0.4989	-0.0003	³ 17.5	0.4986	-0.0008
B								
0.0200	0.4000	0.3	52.5	0.0206	+0.0004	17.0	0.4036	+0.0021
0.0200	0.4000	0.3	64.0	0.0200	+0.0001	18.5	0.4036	+0.0021
0.0200	0.3000	0.3	64.0	0.0201	+0.0001	17.0	0.3031	+0.0018
0.0200	0.3000	0.3	63.0	0.0200	+0.0001	19.5	0.3026	+0.0015
0.0200	0.0200	0.5	62.5	0.0200	+0.0001	17.5	0.0240	+0.0028
0.0200	0.0200	0.5	66.0	0.0200	+0.0001	19.5	0.0235	+0.0021

* H₂SO₄ of lower concentration.

† H₂SO₄ of higher concentration.

¹ slow boiling } below 30 cm³
² rapid boiling }

³[H₂TeO₄ = 0.2 grm. added.]

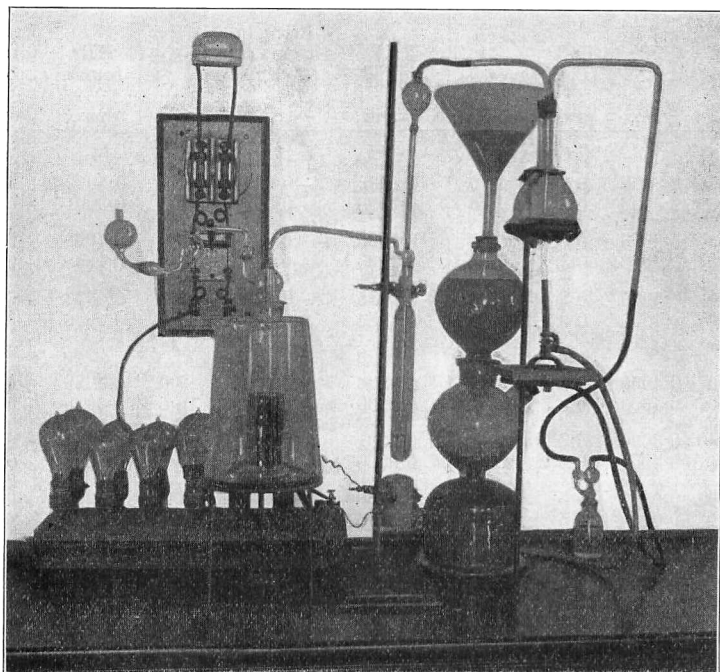
In Table II the results indicate that with the use of steam the iodine may be removed from potassium iodide at volumes ranging between 70 cm³ and 52 cm³, but there seems to be a tendency toward a very slight deficiency in the iodine (A) except when small amounts (B) of the iodide are used; while the bromine determinations are high if the boiling is continued after the complete removal of that element, as is the case when the concentration is carried to 17 cm³ after the prolonged boiling. Rapid concentration after a volume of 30 cm³ has been reached tends to lessen the error.

With the apparatus used in these experiments much difficulty was encountered in regulating the final volumes, which cannot be read with an accuracy of more than 5 cm³. The exact and final readings of volumes recorded in the table were determined after the experiment by removing the solution to a

graduate and reading the volume while still warm. For the final experiments, therefore, an apparatus (shown in fig. 2) was devised which permits more exact reading of the volumes.

A tubular flask 25.6cm^3 high and 3.2cm in diameter with a capacity of 150cm^3 , and provided with a ground-glass stopper and delivery tube extending to the bottom of the flask, was substituted for the distillation flask. Etched lines at 1cm^3 in-

FIG. 2.



tervals in the locality of final volumes furnished a very accurate and simple means for determining the concentrations. An asbestos collar wound with nichrome wire (offering a resistance of 16 ohms) was used on a 110 volt current (with a 12 bulb lamp-board) as a means for heating, and was lowered on the flask as the solution evaporated. Steam was passed in at such a rate that the solution never became highly colored with the liberated halogen. A series of tests, Table III (A), shows that all the bromine eliminated from 0.5 gm. of potassium bromide can be removed by concentrating from a volume of 70cm^3 to a volume of 28cm^3 – 25cm^3 with the aid of steam.

TABLE III.
Distillation in Steam from Tubular Flask.
[Initial volume 100 cm³ : H₂TeO₄ 1.0 grm.]

KI taken grm.	KBr taken grm.	KCl taken grm.	First final volume* cm ³ .	KI found grm.	Error in terms of iodine grm.	Second final volumet cm ³ .	KBr found grm.	Error in terms of bromine grm.
A								
-----	0.3000	--	---	-----	-----	25	0.3001	+0.0001
-----	0.3000	--	---	-----	-----	28	0.3002	+0.0001
-----	0.3000	--	---	-----	-----	26	0.3000	0.0000
B								
0.2000	0.3000	0.3	66	0.2000	+0.0001	24	0.3003	+0.0001
0.2000	0.3000	0.3	66	0.2000	+0.0001	24	0.3001	+0.0001
0.3000	0.2000	0.3	65	0.2995	-0.0001	25	0.2004	+0.0002
0.3000	0.2000	0.3	60	0.2996	0.0000	24	0.2004	+0.0002
0.5000	0.5000	0.3	64	0.4989	-0.0003	¹ 23	0.4995	-0.0003
0.5000	0.5000	0.3	60	0.4989	-0.0003	¹ 24	0.4995	-0.0003
[0.5000	0.5000	0.3	64	0.4989	-0.0003	¹ 23	0.5018	+0.0010]
0.5000	0.5000	0.5	62	0.4993	-0.0001	¹ 23	0.4999	-0.0001
0.5000	0.5000	0.5	64	0.4994	-0.0000	¹ 23	0.4998	-0.0001
0.0200	0.4000	0.3	64	0.0201	+0.0001	25	0.4009	+0.0005
0.0200	0.4000	0.3	64	0.0200	+0.0001	24	0.4009	+0.0005
0.0200	0.3000	0.3	64	0.0205	+0.0004	24	0.2997	-0.0001
0.0200	0.3000	0.3	64	0.0205	+0.0004	24	0.2998	-0.0001
0.0200	0.0200	0.5	65	0.0200	+0.0001	24	0.0213	+0.0007
0.0200	0.0200	0.5	64	0.0200	+0.0001	24	0.0201	+0.0001

* H₂SO₄ of lower concentration.† H₂SO₄ of higher concentration.¹[H₂TeO₄ = 0.3 grm. added.]

In the final tests recorded in Table III (B) the solution (consisting of the three halogen salts ranging as high as 0.5 grm. each with 15^{cm³} of sulphuric acid [sp. gr. 1.015] and 1 grm. of telluric acid) was concentrated to a volume of 64^{cm³}–66^{cm³} for the removal of the iodine; and after the addition of 10^{cm³} of sulphuric acid [1 : 1] was evaporated to a volume of 24^{cm³} for the removal of the bromine. On large charges the amount of telluric acid consumed by the oxidation of the iodide is calculated from the iodine found in the receiver and replaced before determining the bromine in order to insure an excess of 0.5 grm. of telluric acid at the final concentration.

The results of these experiments show that the method may be relied upon to determine with accuracy amounts of iodine up to 0.35 grm. (0.5 grm. of potassium iodide) and of bromine up to 0.3 grm. (0.5 grm. of potassium bromide) associated with

0.25 grm. of chlorine combined in the form of chloride (0.5 grm. of potassium chloride).

According to the procedure found to be effective, the three haloid salts are introduced into the tubular flask with 50^{cm}³ of water. The flask and the inlet tube of the receiver, the latter charged with 200^{cm}³ of a 1.5 per cent solution of potassium iodide, are connected after moistening the surface of the ground-glass joint. Telluric acid, 1 grm., dissolved in 15^{cm}³ of sulphuric acid, sp. gr. 1.015, measured from a burette is introduced through the separating funnel with sufficient water to make the volume 100^{cm}³. Carbon dioxide and steam are passed very slowly through the solution and the boiling mixture is not allowed to concentrate below 100^{cm}³ until all traces of color due to liberated iodine has left the solution. The mixture is then evaporated, with only enough steam to prevent the return of any color, to a volume of 64^{cm}³ to 67^{cm}³. The amount of heat is regulated by the lamps in the resistance board and the furnace is always kept just below the surface of the solution in the tubular flask. At the final volume the source of heat is withdrawn and as soon as the apparatus is cool enough to be conveniently handled the receiver is disconnected and the free iodine in the receiver and trap is titrated with standard sodium thiosulphate. The receiver is then again charged with 200^{cm}³ of 1.5 per cent potassium iodide solution and connected after moistening the surface of the ground-glass joint with sulphuric acid to serve as a lubricant and lute. Sulphuric acid, 10^{cm}³ of the [1 : 1] mixture, is introduced through the separating funnel and carbon dioxide is passed very slowly through the apparatus. As soon as the boiling mixture shows any discoloration steam is passed in at a rate just sufficient to compensate for the vapor carried over until all color is removed, when the concentration is slowly continued with the help of steam to a volume of 30^{cm}³, from which point the remaining solution is rapidly boiled to a volume of 24^{cm}³. The furnace is removed and, as soon as the apparatus is sufficiently cool to disconnect, the free iodine in the receiver and trap is titrated with standard sodium thiosulphate and taken as the measure of the bromine liberated.

By the procedure described it is possible to determine with a good degree of accuracy any amount of iodine or bromine up to 0.3 grm. when associated in the haloid salts with amounts of chlorine up to 0.25 grm. The entire operation need not occupy more than two hours and a half.

In conclusion the author gratefully acknowledges her indebtedness to Professor Gooch for his valuable advice and assistance given during the progress of this work.