CLXXIV.—*The Reactions of the Dioxides of Selenium and Tellurium with the Halogen Acids.*

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PREVIOUS work on the reactions of selenium and tellurium dioxides with hydrogen chloride (Parker and Robinson, J., 1928, 2853) has been amplified, and the corresponding reactions with hydrogen bromide studied. The conditions of formation of the compound $SeO_2,2HCl$ from its constituents have been reinvestigated. Further, certain physical properties of this substance and of pure selenium oxychloride have been redetermined and Sugden's values for their parachors (J., 1929, 1058) confirmed. Similar measurements on the corresponding bromine compound lead to the conclusion that it should be similarly formulated. Some observations have also been made on the colour of sublimed selenium dioxide (see Meyer and Langner, *Ber.*, 1927, **60**, 285). Finally, because of the interest attaching to Prideaux and Cox's results on the action of aqueous hydrogen fluoride on tellurium dioxide, solubilities of this oxide in hydrochloric and hydrobromic acid solutions of various concentrations have been measured.

EXPERIMENTAL.

The Compound $SeO_2,2HCl$.—We have shown that hydrogen chloride reacts with selenium dioxide in U-tubes at 100° giving material, of empirical composition $SeO_2,2{\cdot}2HCl$, believed to be a solution of hydrogen chloride in $SeO_2,2HCl$. An attempt was made to ascertain the temperature at which $SeO_2,2HCl$ could be obtained, by treating 5-g. portions of selenium dioxide with hydrogen chloride in Monax test-tubes in an oil-bath at definite temperatures. A side limb carried the exit gases into a vessel to trap any distillate, whence they passed through sulphuric acid to the air. In about ½ hour the solid was wholly converted into a liquid, but the gas stream was continued to saturation point. Table I, giving analyses of liquids prepared at the temperatures indicated, shows that 107°

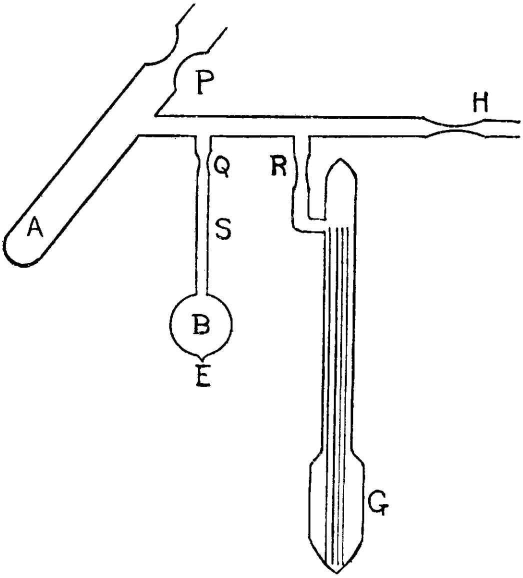
is the temperature sought, but the sample thus prepared probably contained traces of moisture.

TABLE I.

Run.	Temp.	Se, %.	Cl, %.	Mol. ratio HCl/SeO_2.	Density. $d^{16°}$.	$d^{20°}$.
1	100°	42·64	41·44	2·17	—	—
2	107	43·19	37·58	1·95	2·275	—
3	108	43·42	37·73	1·94	2·272	—
4	110	43·81	37·32	1·90	2·291	2·283
5	120	46·24	34·70	1·67	—	—

This method is unsuitable for material required for definitive physical measurements, since the density is obviously greatly affected by the selenium content. As these values are somewhat higher than those of Sugden (*loc. cit.*) on $SeO_2,2HCl$ prepared from the oxychloride, redeterminations were made on material prepared in his way, and measurements were also made on the oxychloride used.

FIG. 1.



Selenium Oxychloride.—Several methods of preparation were suggested by Lenher (*Jour. Amer. Chem. Soc.*, 1920, **42**, 2498), but the dehydration of $SeO_2,2HCl$ proved most convenient. Crude material, from the action at 110—120° of hydrogen chloride on selenium dioxide, was thrice distilled from phosphoric oxide and then thrice fractionated at about 8 mm., Brühl's apparatus being used. Distillation in a vacuum was impracticable because of bumping, but passage of a fine stream of dry air through the liquid obviated this difficulty. 100 C.c. of the crude liquid yielded about 15 c.c. of colourless or light straw-coloured liquid [Found: Se, 47·3; Cl, 42·7. Calc. for $SeOCl_2$: Se, 47·6; Cl, 42·8%]. For density and surface-tension determinations, an apparatus (Fig. 1) designed to minimise contact with air was used, consisting of a test-tube *A* constricted at the neck, with a side limb attached (i) to the bulb *B*, of about 3 c.c. capacity and having a capillary stem of 1—2 mm. internal diameter, and (ii) to the vessel *G*, similar to that of Mills and Robinson (J., 1927, 1823), carrying three capillary tubes. The usual constrictions for removal under vacuum were provided at *P*, *Q*, and *R*. This Monax-glass apparatus was cleaned with nitric–chromic acid mixture, washed with distilled water, alcohol, and ether, and finally dried by six-fold evacuation at 150° and refilling with phosphoric oxide-dried air. Selenium oxychloride was quickly transferred through a thistle-funnel into *A* whilst dried air passed from *H* to *A*, and, after the air stream had been stopped, *A* was sealed. The oxychloride was then frozen, and the apparatus evacuated, but before sealing was effected at *H* the solid was remelted and refrozen twice to release dissolved gas, traces of which, however, still remained. Vacuum distillation being impracticable, liquid was poured in up to the point *S* on the stem of the density bulb *B*, which was drawn off at *Q*; the remainder of the oxychloride was similarly transferred to the surface-tension vessel *G*, which was also sealed. The density bulb was maintained successively at 12°, 16°, and 20° in a thermostat, and the height of the meniscus from the point at the base of the bulb *E* was measured by a cathetometer at each temperature. The stem was then carefully scratched conveniently near the top, and the bulb and stem were cleaned and weighed. The stem was cleanly broken at the scratch under conditions which enabled any fragments to be collected, and the bulb was cleaned, dried, and weighed; the weights of both glass and liquid were thus obtained. The volume was measured by filling the vessel with water to points near to those registered for the oxychloride, measuring the heights exactly at a known temperature, and weighing the water.

In the determination of surface tension, the apparatus was kept at a definite temperature in the bath for 2 hours, then tilted to wet the capillaries, and finally kept for 45—60 mins. to allow the liquid columns to come to rest. The capillaries were those previously calibrated and designated F, D, and C by Mills and Robinson (*loc. cit.*). Two separate preparations of oxychloride gave the following results :

(1) $d^{12^\circ} = 2{\cdot}456 \pm 0{\cdot}001$; $d^{16^\circ} = 2{\cdot}448$; $d^{20} = 2{\cdot}438$; $\gamma^{12^\circ} = 49{\cdot}60 \pm 0{\cdot}20$; $\gamma^{16^\circ} = 48{\cdot}83$; $\gamma^{20^\circ} = 48{\cdot}80$ dynes per cm.

(2) $d^{12^\circ} = 2{\cdot}453 \pm 0{\cdot}001$; $d^{16^\circ} = 2{\cdot}444$; $d^{20^\circ} = 2{\cdot}431$; $\gamma^{16^\circ} = 48{\cdot}30 \pm 0{\cdot}20$; $\gamma^{20^\circ} = 48{\cdot}15$ dynes per cm.

Sugden (*loc. cit.*) records $d^{16^\circ} = 2{\cdot}445$; $d^{15^\circ} = 2{\cdot}443$; and $\gamma^{17^\circ} = 48{\cdot}1$ and $\gamma^{15^\circ} = 48{\cdot}8$ respectively on two separate specimens.

The second preparation above was converted into SeO_2,2HCl by adding the requisite water, with cooling to avoid loss of hydrogen chloride. This material behaved similarly to that from the direct addition of hydrogen chloride to selenium dioxide in that it decomposed on boiling and set to a glass on freezing [Found: Se, 42·9; Cl, 37·9. Calc. for $SeO_2,2HCl$: Se, 43·0; Cl, 38·5%]. As density and surface-tension measurements of this substance could not be made in a vacuum owing to loss of hydrogen chloride, the former was determined in the 5-c.c. specific gravity bottle used for the data in Table I, and the latter in an atmosphere of dry air in the same type of apparatus and the same capillaries as already described. The results obtained were:

$d^{16°} = 2{\cdot}258 \pm 0{\cdot}001$; $d^{20°} = 2{\cdot}252$; $\gamma^{16°} = 51{\cdot}9 \pm 0{\cdot}2$, $\gamma^{20°} = 51{\cdot}6$; $[P] = 218{\cdot}8, 218{\cdot}9$ respectively. Sugden gives $d^{16{\cdot}2°} = 2{\cdot}251$; $\gamma^{16{\cdot}2°} = 52{\cdot}48$; $[P] = 220{\cdot}1$.

The System Selenium Dioxide–Hydrogen Bromide.

Ditte (*Ann. Chim. Phys.*, 1877, **10**, 82) found that selenium dioxide vigorously absorbed hydrogen bromide with liberation of heat, giving steel-grey plates which continued the absorption; when these were warmed to 40—50°, a little hydrogen bromide was evolved, leaving $SeO_2,4HBr$, stable below 55°, but decomposing above that temperature. He was unable to obtain the compound $SeO_2,2HBr$, but by treating his $SeO_2,4HBr$ with hydrogen bromide at − 15° he claimed to have produced $SeO_2,5HBr$. Lenher and Muehlberger (*J. Amer. Chem. Soc.*, 1925, **47**, 1842) state that at the ordinary temperature there is formed $SeO_2,2HBr$, a liquid of $d^{22°} = 3{\cdot}077$, which decomposed on boiling and reacted with selenium dioxide to give selenious acid and the oxybromide. They confirmed the existence of Ditte's first compound but not of his second. In view of this disagreement, a systematic reinvestigation of the reaction between − 7° and 60° was undertaken.

Materials.—Divers and Haga (J., 1899, **75**, 537) prepared the dioxide by dissolving selenium in nitric acid, evaporating the solution several times after successive additions of water, and finally subliming the oxide. Meyer (*Ber.*, 1922, **55**, 2082) burned selenium in oxygen and collected the sublimate; he noted that a trace of the oxides of nitrogen favoured the formation of a pure white product, but that alkalis or glass caused coloration. By substituting careful drying below the decomposition temperature in an electric oven for Divers and Haga's sublimation, we obtained material giving identical results with theirs but having the advantage that it could readily be finely powdered. Such oxide was used in most of the following work, but when further sublimation was required, the dioxide in a porcelain boat was placed in a Pyrex tube (30″ × $\frac{3}{4}$″) and heated to about 400° in a combustion furnace in a stream of oxygen dried by passage through 1 m. of concentrated sulphuric acid and 2 m. of phosphoric oxide. Above 300°, volatilisation was reasonably rapid, and the yellow vapour, having passed through a platinised asbestos plug, was condensed in a tube, 12″ long, forming a sleeve inside the combustion tube. The sublimate first formed was reddish owing to traces of selenium, but the later material was white. In the absence of the plug of platinised asbestos all the sublimate was tinted pink, whether the starting material was imperfectly dried (and presumably contained traces of nitric acid) or whether a glass or silica sleeve tube was used. The evidence pointed to some dissociation of the vapour in the hot zone, followed by a cooling rapid enough to forestall recombination—an inference confirmed by preheating the sleeve tube, which afforded a white product throughout the entire process whether the plug was used or not. The platinised asbestos apparently functions, not as a catalyst, but rather as a reservoir of heat preventing a rapid fall in the temperature of the vapour. Meyer and Langner (*loc. cit.*) state that the yellow colour of the dioxide is intrinsic and not due to dissociation, and in view of the present findings an examination of its absorption spectrum was undertaken in collaboration with Mr. S. F. Evans of the Physics Department of this College. Two observations were made at about 400°; the first, upon pure crystalline selenium dioxide, showed the anticipated absorption of light, whilst the second, upon pure selenium under identical conditions, gave no absorption. Further investigation by Evans (*Nature*, 1930, **125**, 528) showed dissociation to take place to such an extent in a well-evacuated tube that finally the spectrum of selenium dioxide disappeared; it could, however, be rendered permanent by starting with some oxygen in the tube. The dissociation here may have been photochemical as well as thermal.

Hydrogen bromide was prepared by passing hydrogen successively through water, concentrated sulphuric acid, pure bromine, and concentrated sulphuric acid and then over heated platinised asbestos, residual bromine being converted in turn into hydrogen bromide by moistened phosphorus spread on glass beads. The resulting gas was dried by passage through a long tube packed with fused calcium bromide. Thus prepared, the gas gave results identical with those obtained with hydrogen bromide from the action of bromine on benzene, but for convenience the former method was generally used.

Reaction of Hydrogen Bromide with Selenium Dioxide.—(a) *From* − 7° *to* 30°. 0·2—0·5-G. portions of selenium dioxide were introduced into **U**-tubes and dispersed with sand in nitrogen at 0°.

Hydrogen bromide was passed over the materials for periods of 30 mins., replaced by nitrogen, and the increase in weight found, passage of the gas being continued until constant weight was obtained. As dissociation was relatively slow, this use of nitrogen did not involve the loss of appreciable quantities of hydrogen bromide. The products are solid, and complete conversion is difficult to attain: it appears that the original grain size may affect the results, for, as shown in Table II, Runs 1—8 (excluding 6), which relate to finely powdered material, corresponded to the formation of $SeO_2,4\cdot6 \pm 0\cdot2HBr$ (compare also Run 11), whereas Runs 9 and 10, on crystalline material, corresponded to $SeO_2,4HBr$. Weight increased linearly with time until it reached a well-defined limit. The solid was orange-brown, appeared to be homogeneous, and developed little pressure at the ordinary temperature (contrast analogous compound of hydrogen chloride).

In certain cases, the substance obtained by the reaction at 0° was further treated at other temperatures (see Table II) with hydrogen bromide to constant weight. In this way material which had already gained 4·6 mols. of hydrogen bromide at 0° only rose to 4·8 mols. at — 7°, whilst crystalline dioxide took up only 4·2 mols. at — 7°; in each case the colour became lighter but deepened again at 0°. Similarly, at 18° slight loss of hydrogen bromide occurred (to 4·4 mols.) and the colour deepened. In Run 6, the dioxide itself was treated with hydrogen bromide first at 18°, and the increase was again 4·4 mols. At 50° and 100° there was evident decomposition, and red crystals sublimed on the sides of the reaction tube.

TABLE II.

Run.	SeO_2, g.	Mols. HBr per mol. SeO_2 at				
		— 7°.	0°.	18°.	50°.	100°.
1	0·2036	—	4·5	4·4	2·7	2·4
2	0·1822	—	4·8	—	—	—
3	0·3106	—	4·7	—	—	—
4	0·2208	—	4·6	—	—	—
5	0·5184	—	4·6	—	—	—
6	0·4422	—	—	4·4	—	—
7	0·3246	4·8	4·6	—	—	—
8	0·1486	—	—	—	3·2	2·0
9*	0·2058	—	4·2	—	—	—
10†	0·3418	4·2	3·8	—	—	—
11‡	0·2645	—	4·5	—	—	—

* Crystalline material. Addition ceased after 32 hours.

† Crystalline material. Addition ceased after 6 hours.

‡ Crystalline material, finely powdered. Addition ceased after $2\frac{3}{4}$ hours.

$SeO_2,2HBr$. By using the method outlined, material of this composition is obtained at 30° (*vide infra*) and decomposes below its boiling point. Confirmatory evidence of its existence has been obtained from its parachor: $d^{16^\circ} = 3{\cdot}077$; $d^{20^\circ} = 3{\cdot}067$; $\gamma^{16^\circ} = 61{\cdot}15$; $\gamma^{20^\circ} = 60{\cdot}77$; $[P] = 248{\cdot}1$, $248{\cdot}8$ respectively (mean 248·5); the calculated value is 247·5 if the value for bromine (68·0) is substituted for that of chlorine (54·3) in Sugden's determination upon the analogous $SeO_2,2HCl$.

(b) *From* 30° *to* 60°. Selenium dioxide was treated with hydrogen bromide in a test-tube, the side limb of which led to a similar vessel and thence to a drying tube. As liquid formed, it was poured into the second tube until no solid remained, after which the gas was bubbled through the liquid to saturation. The black liquids transmitted ruby-red light. At 30° the liquid had Se, 28·45; Br, 58·25 (Calc. for $SeO_2,2HBr$: Se, 28·9; Br, 58·6%), and at 45°, Se, 30·8; Br, 52·4%, but there was a small loss of hydrogen bromide due to fuming. Between 50° and 60° the liquids deposited crystals on cooling which redissolved on warming. After being separated by decantation and centrifuging, these crystals were light brown through adhesion of mother-liquor, and gave Se, 54·5; Br, 7·0; *i.e.*, SeO_2, 76·6; HBr, 7·1%; if the remaining 16·3% is due to water, one has $SeO_2 : H_2O = 1{\cdot}07 : 1$, pointing to contamination of selenious acid with mother-liquor containing bromine. (The mother-liquor in two experiments gave Se, 30·8; Br, 55·3%.) Lenher suggests that selenium dioxide may dehydrate $SeO_2,2HBr$ to give selenious acid and the oxybromide. Probably at the above temperatures the compound dissolves the dioxide, by which it is slowly dehydrated so that, on cooling, crystalline selenious acid separates; for the acid is not formed by direct action of the hydrogen bromide, which has been shown to react vigorously with selenious acid, forming at 20° a liquid and a solid, the latter containing 4 mols. of bromine per mol. of selenium.

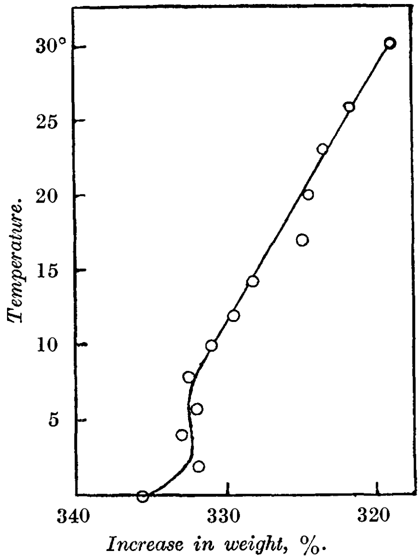
Composition–Temperature Curve, SeO_2–HBr, *between* 0° *and* 30°.—In a preliminary experiment, material which had been treated with hydrogen bromide at 0° in a U-tube (the tube from Run 2, Table II) was raised to successively higher temperatures for definite times, during which nitrogen was passed over the material, and after which the weight of the tube was ascertained. When these results were plotted, there appeared indications of a stable complex at 9°. In investigating this further, material from Run 4 (Table II) was allowed to come to equilibrium at a series of successively higher temperatures with the taps of the U-tube closed. The hydrogen bromide thus liberated was swept out with nitrogen for 5 mins. and the tube was then filled with this gas at 0° and weighed. Typical results are given in Table III and plotted in Fig. 2. The curve has a marked break about 9° and 4·5 mols. of hydrogen bromide, and as this has been found in two further experiments it is interpreted as indicating a stable complex in this region, and the material at 30° has approximately the composition $SeO_2,4HBr$ (*vide infra*).

TABLE III.

Temp.	0°	2°	4°	6°	8°	10°	12°	14°	17°	20°	23°	26°	30°
Increase, %	336	332	333	332	332·5	331	329·5	328·5	325	324·5	323·5	321·5	319
HBr/SeO_2 (mols.)	4·61	4·55	4·57	4·55	4·56	4·54	4·52	4·51	4·46	4·45	4·44	4·41	4·38

Thus it appeared that the product from the treatment of the dioxide first at 0° and subsequently at intermediate temperatures up to 30° might contain as much as 4 mols. of hydrogen bromide per mol. of selenium dioxide, whereas if the dioxide was treated with hydrogen bromide at 30° material corresponding exactly to the composition $SeO_2,2HBr$ was formed. In support of this conclusion, it was found that if material of the composition $SeO_2,2HBr$ was treated at 0° with hydrogen bromide to constant weight, the product corresponded to $SeO_2,4{\cdot}5HBr$, and this on being heated to 30° in the presence of hydrogen bromide did not revert to $SeO_2,2HBr$ but yielded a red crystalline sublimate, a black residue, and a trace of distillate which was $SeO_2,2HBr$. A large-scale preparation of the red substance showed it to be a basic compound possessing approximately the composition Se : Br : H_2O = 1 : 4 : 5—6.

FIG. 2.



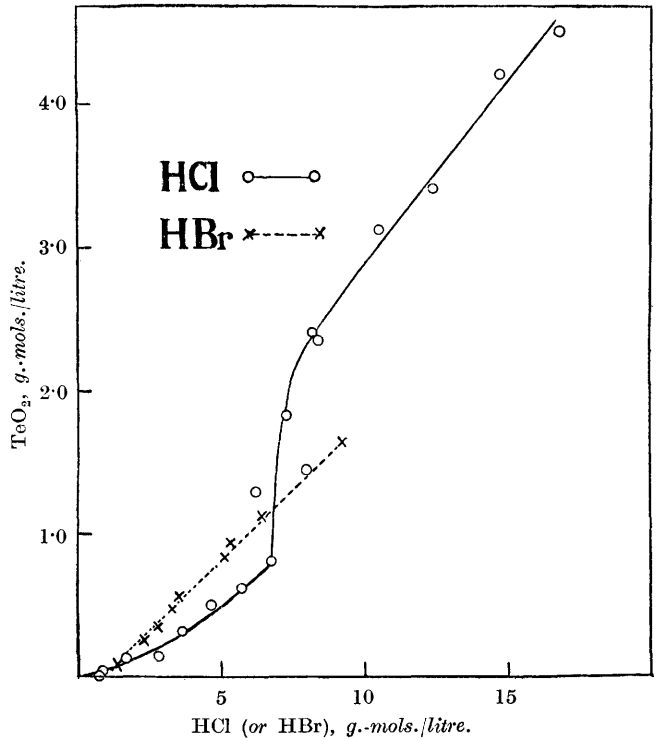
The System Tellurium Dioxide–Hydrogen Bromide.

Ditte (*loc. cit.*) states that tellurium dioxide and hydrogen bromide at — 15° give $TeO_2,3HBr$, which decomposes at 50° to $TeO_2,2HBr$, at or below 70° to the oxybromide, and above 70° to the tetrabromide.

We treated small quantities in U-tubes with hydrogen bromide as above, but absorption was extremely slow; for instance, at 0°

after 180 hours the increase in weight corresponded to an addition of 6·0 mols. of hydrogen bromide, and (in a second experiment) after 67 hours to 5·1 mols. The latter material was further treated at 5°, attaining 6·9 mols. after 114 hours, and then at 10°, reaching 7·4 mols. after 110 hours. We are of opinion that these additions are due rather to moisture accumulated during these long periods dissolving hydrogen bromide than to any chemical reaction, and in any case these results do not confirm previous work.

FIG. 3.



The Solubility of Tellurium Dioxide in Solutions of Hydrogen Bromide and Chloride.—Prideaux and Cox (J., 1929, 2708) have shown that oxyfluorides can be isolated from solutions of tellurium dioxide in hydrofluoric acid, and indications of such compounds are given by the form of their solubility curve.

Tellurous acid was prepared according to Prideaux and Cox, and pure solutions of hydrogen bromide and chloride by saturating distilled water with the purified gases, these liquids being used as stock solutions for the preparation of the more dilute solutions.

In the determination of the solubilities, 5—6 c.c. of acid and an excess of tellurous acid were shaken in a thermostatic bath maintained at 12° ± 0·1° for 4 hours and then kept in the bath until the supernatant liquid was clear. For analysis, the liquids were decanted rapidly through a filter into another test-tube, filtration being assisted by slight suction.

The results are given in Table IV (concentrations being in mols./litre and the ratios molar) and plotted in Fig. 3. Analyses of the solids in the case of hydrobromic acid showed a progressive increase in bromine content with rise in hydrogen bromide concentration, but in no case did it reach that required for tellurium tetrabromide.

TABLE IV.

Concs.		Ratio,	Concs.		Ratio,	Concs.		Ratio,
TeO_2.	HCl.	HCl/TeO_2.	TeO_2.	HCl.	HCl/TeO_2.	TeO_2.	HCl.	HCl/TeO_2.
0·019	0·83	43·7	0·65	5·73	8·8	2·42	8·22	3·4
0·052	0·93	17·9	0·82	6·80	8·3	3·15	10·49	3·3
0·14	1·70	12·1	1·30	6·30	4·9	3·42	12·38	2·9
0·16	2·90	18·1	1·47	8·00	5·4	4·22	14·79	3·5
0·35	3·56	10·2	1·86	7·34	4·0	4·53	16·65	3·7
0·52	4·69	9·0	2·39	8·34	3·5	3·13	15·07	4·8

Concs.		Ratio,	Concs.		Ratio,	Concs.		Ratio,
TeO_2.	HBr.	HBr/TeO_2.	TeO_2.	HBr.	HBr/TeO_2.	TeO_2.	HBr.	HBr/TeO_2.
0·0199	0·735	36·9	0·144	1·719	11·9	0·569	3·496	6·1
0·0204	0·763	37·4	0·181	1·616	8·9	0·852	5·082	6·0
0·070	1·115	15·9	0·265	2·298	8·7	0·952	5·279	5·6
0·085	1·172	13·8	0·367	2·776	7·6	1·137	6·329	5·6
0·103	1·396	13·6	0·471	3·140	6·7	1·667	9·170	5·5

From the curves it is clear that the course of the reaction with hydrobromic acid is different from that with hydrochloric acid. It is probable that the straight-line graph for the former indicates continuous formation of tetrabromide, whilst the break in the curve for the latter may define regions above and below which tetrachloride and oxychlorides respectively are in solution.

Summary.

The reactions of hydrogen chloride with the dioxides of selenium and tellurium have been further investigated. Only SeO_2,2HCl is formed at 107°. The properties of this compound and of selenium oxychloride have been reinvestigated.

SeO_2,2HBr is formed at 30°. Its density and surface tension have been measured. Below 30° solids are produced, and at higher temperatures liquids are formed which deposit selenious acid on cooling. Temperature–composition curves show a region of stability between 2° and 8° corresponding to SeO_2,4·5HBr.

Conclusive results have not been obtained in the reaction of tellurium dioxide with hydrogen bromide.

The solubilities of tellurium dioxide in solutions of hydrogen chloride and hydrogen bromide have been measured.

It would appear that when selenium dioxide is sublimed dissociation takes place in the vapour state, but that the colour evinced is that of the dioxide and is not due to free selenium.

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