CCCLIX.—*The Action of Hydrogen Fluoride on Compounds of Selenium and Tellurium. Part III. Solubilities of Tellurium Dioxide and Oxyfluorides.*

By EDMUND BRYDGES RUDHALL PRIDEAUX and JOHN O'NEIL MILLOTT.

ALTHOUGH it has long been known that tellurium dioxide and its hydrate dissolve freely in hydrofluoric acid, and certain compounds have been isolated from these solutions, no quantitative determinations of the solubilities in these systems appear to have been made, nor has the solubility of the dioxide in anhydrous hydrogen fluoride been investigated. In making these determinations, we have further defined the conditions of existence of the oxyfluorides discovered by Metzner (*Ann. Chim. Phys.*, 1898, **15**, 203) and by us (J., 1926, 521), and have also put forward a theory as to the mode of interaction of the two acids. At the ordinary temperature the system TeO_2–HF–H_2O can give as solid phases the dioxide or a hydrate and one or other of the oxyfluorides which are summarised below.

EXPERIMENTAL.

Tellurous Acid.—The dioxide was used in this form in order to facilitate the attainment of equilibrium. In pure water the acid can exist for long periods at temperatures considerably below 40°, but according to Kasarnowsky (*Z. physikal. Chem.*, 1924, **109**, 287), it is metastable with respect to the oxide at all temperatures. The transformation is accelerated by acids, and we have found that hydrofluoric acid in this respect behaves similarly to hydrochloric acid (Kasarnowsky, *loc. cit.*).

The usual preparation of the dioxide from the metal was modified in order to effect a separation from copper and other impurities. A sample of tellurium, supplied by the Baltimore Copper Company, was dissolved in aqua regia, the solution boiled with an excess of alkali, acidified with nitric acid, filtered, and treated with an excess of dilute aqueous ammonia. A slight turbidity was usually noticed which was filtered off rapidly, since solutions of ammonium tellurite hydrolyse readily. The filtrate was cooled to 5° and acidified with dilute nitric acid, and the precipitated tellurous acid washed with cold water and kept slightly moist (Found : Te, 71·2. Calc. : Te, 71·7%).

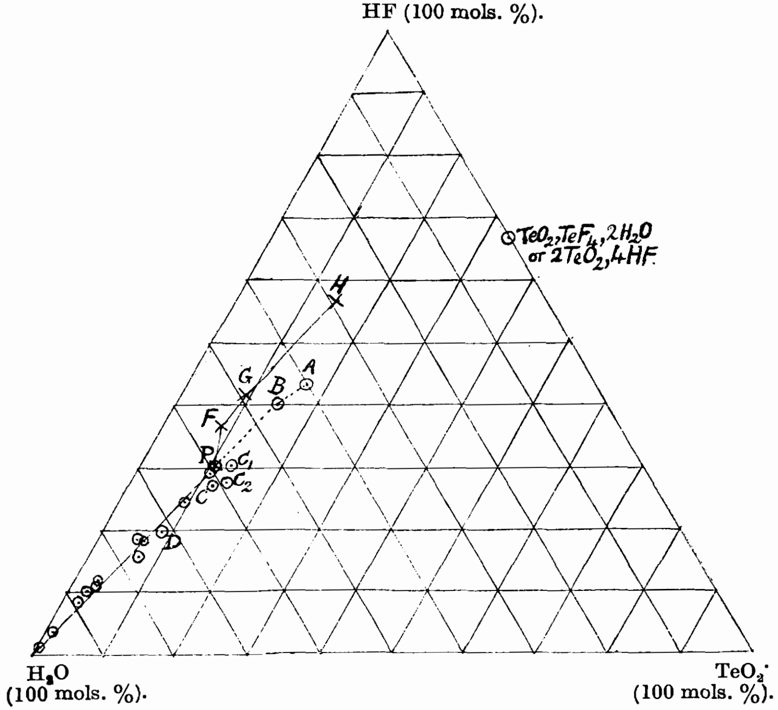
The hydrofluoric acid, of A. R. quality, was supplied in wax bottles by British Drug Houses.

A temperature of 10° was maintained by water freshly drawn from an underground supply. At 0°, some of the solutions would have been so viscous that equilibrium would have been attained only very slowly, whereas at 15—20° the solubilities would have been inconveniently high at the higher concentrations of hydrogen fluoride, and such solutions would also have lost considerable amounts of the acid during manipulation.

The solubilities were determined in a platinum crucible of about 25 c.c. capacity and with a tightly fitting lid. 2—3 C.c. of hydrofluoric acid of various concentrations were stirred with a slight excess of tellurous acid for several hours, successive analyses having proved that equilibrium was attained in this time. The filtrates were weighed in a small platinum crucible with a tightly fitting lid, and analysed as previously described. They were all colourless and without turbidity, and fumed slightly at the higher concentrations; the loss of hydrogen fluoride during manipulation was, however, not serious—in one experiment the initial titration showed 39·5%, and the final 39·10% of hydrogen fluoride. The solutions were not noticeably decomposed by ether, which can be used for freeing precipitates from mother-liquor. Alcohol gave a dense white precipitate, which, after being washed with more of the reagent, was found to contain very small amounts of fluoride; alcohol therefore decomposes the solution, with precipitation of tellurium dioxide.

Crystalline Hydrated Oxyfluorides.—These substances have been obtained by three principal methods: (1) By cooling solutions in acid of about 40% concentration to below −30°: the method is of doubtful efficacy on account of possible admixture with ice or with hydrates of hydrofluoric acid; (2) by slow evaporation of solutions in nearly 100% acid; (3) by evaporation in a vacuum over concentrated sulphuric acid. The last method, which appears to have been mentioned first by Högborn (*Bull. Soc. chim.*, 1881, **35**, 60), is very convenient and has been principally employed in the present work. The crystals may appear as small transparent needles which form first on the surface of the liquid, or they may be aggregated as rosettes. The other, and commoner, form, which grows on the bottom of the vessel or when the liquid solidifies *en masse*, is that of

The system TeO_2–HF–H_2O *at* 10°.



hard milk-white nodules of radiating crystals. The dihydrate was obtained in both forms, and the monohydrate as rosettes of clear crystals in the present work, but previously as nodules. The dihydrate occurred far more often than the monohydrate. Occasionally, substances were obtained of rather divergent composition which we are inclined to class as mixtures containing tellurium dioxide, being formed near the transition point (see fig. and below).

TABLE I.

The hydrated oxyfluorides of tellurium.

Mode of preparation, appearance, and formula. (Data denoted by M are due to Metzner.)	Analysis,	
	Te, %.	F, %.
First product of solution of TeO_2 in HF is redissolved in aqueous 43% HF. Transparent crystals, sometimes spheres. (M.)	63·56 64·6	15·94 15·16
Calc. for $2TeF_4,3TeO_2,6H_2O$.	64·25	15·26
Mother-liquors from foregoing strongly cooled. Small milky crystals. (M.)	63·4 63·4	18·4 18·7
Calc. for $TeF_4,TeO_2,2H_2O$.	64·0	19·0
Solution of H_2TeO_3 in 40% HF evaporated in a vacuum over conc. H_2SO_4—several preparations; also solution of H_2TeO_3 in 90% HF treated in same way. Small transparent needles, sometimes rosettes, or hard, milk-white nodules containing radial crystals.	64·3 64·2 63·0 64·3 64·3	19·1 19·0 19·3 19·1 19·1
Calc. for $TeF_4,TeO_2,2H_2O$.	64·0	19·0
TeO_2 dissolved in anhydrous HF, and allowed to evaporate over conc. H_2SO_4. Crystalline nodules.	66·1 66·6	20·4 20·0
Calc. for TeF_4,TeO_2,H_2O.	66·8	20·0
Solution of H_2TeO_3 in 40—50% HF evaporated in a vacuum over conc. H_2SO_4. Rosettes of transparent needles.	65·0	20·0
Calc. for TeF_4,TeO_2,H_2O.	66·8	20·0
Solution of H_2TeO_3 in 40% HF evaporated over conc. H_2SO_4. Occasionally whitish crystals.	74·5	18·5
Calc. for $2TeF_4,3TeO_2$.	72·0	18·5

Solubilities of the Dioxide.—Analyses of the solid phase wetted with various amounts of mother-liquors, as well as those of the dried solid, show that this is the dioxide :

(Calc. for TeO_2 : Te, 79·7%.)

Initial concentration of acid before saturation with H_2TeO_3, HF%	4·0	13·5	19·1
Te% in the dried solid	79·3	79·6	79·2

The solutions in equilibrium with this solid extend to 29% of hydrogen fluoride (Table II). The molecular ratio HF/TeO_2 in the solution decreases rapidly at first, showing an increased solvent action per mol. of hydrogen fluoride at the higher concentrations, a fact which is comprehensible on our theory that the TeO_2–HF complex is formed by the polymeride H_2F_2.

At higher concentrations of hydrogen fluoride, the compositions of the solutions become more variable. This is due to the formation of oxyfluorides, or alternatively, of solutions supersaturated with respect to dioxide. The points *A* to *D* were obtained in endeavours to locate the transition point of these two solid phases. Solutions *A* and *B* were made by decomposing the oxyfluorides with water. They appear to be on the metastable solubility curve of tellurium dioxide. Solutions C_1 and *D* (the latter is obviously on the normal solubility curve of tellurium dioxide) were made by treating an acid containing more than 40% of hydrogen fluoride with various quantities of tellurous acid. C_2 was made by allowing a saturated aqueous solution of the oxyfluoride (dihydrate) to stand over calcium carbonate with stirring. In all these cases the white solid was obviously tellurium dioxide (Metzner had noticed the decomposition of the oxyfluoride by water). *C* was made by stirring tellurous acid into an acid containing more than 50% of hydrogen fluoride; the solid in this case contained a small amount of undecomposed oxyfluoride. It was considered that solution C_1 was probably nearest to that formed at the transition point. An acid containing hydrogen fluoride and water in the ratio 16·5 : 44·3 was saturated with tellurium dioxide. The solution and solid were then treated with an excess of oxyfluoride, and the whole was stirred until equilibrium was obtained. The solid was then found to contain about 10·5% of the oxyfluoride and 89·5% of the dioxide. The composition of the solution in equilibrium with both solids is given by point *P*.

The points *F*, *G*, *H* are on the solubility curves of the oxyfluorides, the analyses of which are given in Table I. *F* is in equilibrium with $TeF_4,TeO_2,2H_2O$, *H* with TeF_4,TeO_2,H_2O, and *G* with the two hydrates; the last is therefore a transition point. It would be difficult to work in open vessels with a solution containing a higher proportion of hydrogen fluoride than *H*.

TABLE II.

The solubilities of tellurium dioxide and of tellurium oxyfluorides in aqueous hydrofluoric acid at 10°.

In 100 g. solution.		In 100 mols. solution.			In 100 g. solution.		In 100 mols. solution.		
HF.	TeO_2.	HF.	TeO_2.		HF.	TeO_2.	HF.	TeO_2.	
0·221	0·12	—	—		15·8	46·2	24·6	9·1	
0·29	0·26	—	—		17·5	50·2	29·1	10·5	
1·22	1·26	1·14	0·145		22·6	63·0	43·0	17·0	*A*
3·89	8·3	3·8	1·00		20·5	59·0	40·0	14·5	*B*
7·83	16·8	8·4	2·28		15·2	54·0	27·0	12·0	*C*
9·10	19·1	10·2	2·66		16·5	55·7	30·2	12·9	C_1
10·0	24·0	11·0	3·50		14·8	57·0	27·8	13·4	C_2
10·3	24·4	12·0	3·55		18·2	50·5	30·9	10·7	*P*
13·5	36·0	18·2	6·1		24·0	42·6	36·9	8·15	*F*
13·9	34·5	18·4	5·8		26·4	45·7	41·7	9·0	*G*
13·0	44·5	19·75	8·5	*D*	28·5	58·0	56·2	14·3	*H*

The System TeO_2–HF.—The solubility of the dioxide in hydrogen fluoride is very high, and the freezing points of the solutions are low. Some hydrogen fluoride was condensed at 0° in a platinum crucible contained in a copper receiver. By means of a current of dry air the vapour was passed over tellurium dioxide contained in a platinum crucible and enclosed in a metal case. The solution was stirred and twice decanted, and was therefore a nearly saturated solution in hydrogen fluoride. It was solidified by immersion in liquid air, and partly melted in solid carbon dioxide and alcohol. The melting point was about $-78°$. Portions of the solid were quickly separated, melted, and analysed, the hydrogen fluoride being determined as sodium salt as well as by titration. The weights of hydrogen fluoride and tellurium dioxide found agreed within about 2% with the weight taken. On an average, the solid contained 71% of hydrogen fluoride, and the liquid in equilibrium with it 91% of this acid. Since the total weights of solid and liquid were nearly equal, the original saturated solution contained about 81% of hydrogen fluoride. We believe that this solid was tellurium dioxide containing hydrogen fluoride of crystallisation, analogous to a crystalline hydrate. The combination to form oxyfluorides only took place in the presence of some water, as when the saturated solution was allowed to evaporate for some hours.

Nature of the Action of Solutions of Aqueous Hydrofluoric Acid on Tellurous Acid.—The high solubilities and the preparation of crystalline oxyfluorides show that the hydrolysis of fluorides in solution is much less than that of the corresponding chlorides, or that the basigenic character of tellurium is more markedly displayed towards hydrofluoric acid (Kasarnowsky, *loc. cit.*). There must be some complex formation in solution. The determination of the hydrogen-ion activities of hydrofluoric acid alone and also when saturated with tellurous acid was undertaken with results which are detailed elsewhere (*Trans. Faraday Soc.*, 1929, **25**, 579). The hydrogen-ion activity as measured by the quinhydrone electrode was found to be practically unaffected by the presence of the tellurous acid. The activity of the hydrogen ion in a $33{\cdot}5M$-solution, which dissolves tellurous acid very freely, is hardly greater than that in $3{\cdot}0M$-hydrochloric acid, which has a much slighter solvent action on tellurium dioxide. The solubility of the dioxide is therefore certainly not a function of hydrogen-ion activity alone, nor does tellurous acid use up this ion in forming the dissolved complex. The solubility is mainly dependent on hydrogen fluoride *molecules*. We would suggest the following explanation. The first dissociation constant of tellurous acid, as measured by hydrolysis, is $2{\cdot}7 \times 10^{-3}$ (Blanc, *J. Chim. physique*, 1920, **18**, 39) and is probably of the same order as the second dissociation constant of H_2F_2, which will come into play in more concentrated solutions. Even at dilutions below 0·02*N*, the dissociation constant of hydrofluoric acid as determined by conductivity is only $7{\cdot}4 \times 10^{-4}$ (Wynne-Jones and Hudleston, J., 1924, **125**, 1031). The addition of the tellurous acid, which is mainly ionised as $H^{\cdot}$ and $HTeO_3'$, represses the ionisation of an equivalent amount of HF_2', and removes it as the complex anion of hydrogen dioxodifluorotellurium according to the equation

$$2H^{\cdot} + HTeO_3' + HF_2' \rightleftharpoons 2H^{\cdot} + TeF_2O_2'' + H_2O.$$

This acid then crystallises from concentrated solutions as the dihydrate according to the equation

$$2H_2[TeO_2F_2] \longrightarrow 2(TeOF_2,H_2O) = TeF_4,TeO_2,2H_2O.$$

UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, October 15th,* 1929.]