LXVIII.—*The Vapour Density of Zirconium Tetrachloride.*

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The only published data on the vapour density of zirconium tetrachloride appear to be those of Deville and Troost (*Compt. rend.*, 1857, **45**, 821), who, using Dumas's method at the boiling point of sulphur, obtained the values 8·10 and 8·21 (Calc.: 8·09; air = 1). These results were of particular interest at the time, since they indicated that zirconium was quadrivalent, in opposition to the general belief in its tervalency. The second value for the density is somewhat greater than the theoretical. Apart from error of observation, this might be accounted for by the presence of hafnium, although the possibility of association of the tetrachloride deserves consideration.

During experiments on the volatilisation of pure zirconium tetrachloride in a current of chlorine, it had frequently been observed by one of us that brown fumes were formed characteristic of zirconium trichloride (Ruff and Wallstein, *Z. anorg. Chem.*, 1923, **128**, 96). It seemed of interest, therefore, (i) to determine if association could be detected in the vapour at temperatures only slightly above that at which volatilisation begins, and (ii) to follow up the observed dissociation into trichloride at higher temperatures with vapour-density measurements.

EXPERIMENTAL.

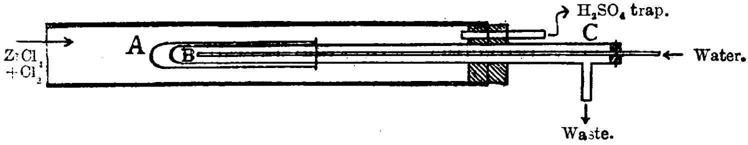
Purification of Materials.—Elimination of hafnium was effected by a method based on the observation that zirconium is more readily precipitated from solution by citric acid than is hafnium (Drophy and Davey, *Physical Rev.*, 1925, **25**, 882). A sample of "pure" zirconia was converted into sulphate by heating with concentrated sulphuric acid, and the solution diluted and filtered. The hydrated oxide was precipitated with ammonia from the boiling solution, washed, and dissolved in pure nitric acid; the clear solution was evaporated to dryness, the residue dissolved in water and filtered, and citric acid added in sufficient amount to precipitate about half the zirconium as citrate, any hafnium together with the remainder of the zirconium being retained in solution. The precipitate was filtered off, washed, ignited to oxide, and the process repeated. A very pure sample of zirconia was thus obtained.

Test for cerium. The following test for traces of ceria in zirconia was found useful. Cerium colours a borax bead yellowish-green when heated in the oxidising flame. A borax bead weighing 0·056 g. was perceptibly coloured (in daylight) by 0·0015 g. of zirconia containing 4% of ceria.

Purity of the zirconia. Several attempts were made to follow the elimination of hafnia from zirconia by density measurements (Hevesy, J., 1924, **125**, 2372). The results, however, were not sufficiently concordant to be of service, possibly owing to the mechanical loss of oxide during ignition, which it is extraordinarily difficult to avoid (see Venable and Bell, *J. Amer. Chem. Soc.*, 1917, **39**, 1599). The equivalent of the zirconium was therefore determined chemically from the ratio $Zr(SO_4)_2 : ZrO_2$. A weighed quantity of the purified zirconia was heated with concentrated sulphuric acid for at least an hour. The rate of solution of the oxide was found to depend upon its previous history, frequent ignition rendering it very refractory. In none of our experiments were we able to effect complete solution of the sample taken. After cooling, the mixture was poured into excess water, and heated to boiling, any undissolved zirconia being filtered off, ignited, and weighed.

The solution of zirconium sulphate was evaporated to dryness in a platinum dish, the heating being carefully controlled towards the close of the experiment in order to drive off the excess of acid without decomposing the sulphate. When a constant weight had been obtained, the temperature was raised and the sulphate ignited to oxide. In every case the weight of oxide thus obtained was slightly less than that originally dissolved, presumably owing to mechanical loss. For instance, in two experiments, the initial weights of zirconia were 0·4051 and 0·2707 g. and the final weights 0·3926 and 0·2687 g. respectively. As calculated from the initial weights, the values obtained for the equivalent weight of zirconium were 22·04, 22·00, mean 22·02; the accepted value for 1929 being 91·2/4 = 22·8. Our value is somewhat low in common with early atomic-weight determinations by this method [compare Weibull (*Lund. Årsskrift*, 1881—1882, vol. xviii), who obtained the mean value of 89·54/4 = 22·39], probably owing to the difficulty of completely expelling the acid without simultaneously decomposing the sulphate. The results, however, indicate the absence of appreciable quantities of hafnium.

Preparation of Zirconium Tetrachloride.—This was effected by Demarçay's method (*Compt. rend.*, 1887, **104**, 1136), *viz.*, by passing chlorine, laden with carbon tetrachloride vapour and dried by phosphoric oxide, over heated zirconia as described by Venable and Bell (*loc. cit.*). The chloride was collected in a long tube and transferred by shaking into a bottle. It invariably contained traces of zirconia carried over mechanically. To obtain the pure chloride, the first batch was returned to the apparatus and re-sublimed in a very slow current of chlorine—about 2 bubbles per second, as recommended by Lely and Hamburger (*Z. anorg. Chem.*, 1914, **87**, 223). Since the tetrachloride is very susceptible to moisture, it was condensed on tube A (see fig.), which easily slid over the water-cooled tube BC. When sufficient had collected, BC was withdrawn and A rapidly slid into a slightly wider tube, which thus enclosed the tetrachloride. After being weighed, this double tube was used as the dropping bottle in the Victor Meyer apparatus. It was ascertained that no condensation of carbon tetrachloride took place along with the zirconium salt under our experimental conditions.



Venable and Bell state that formation of chloride in their experiments began a little above 300° and was rapid at 450—500°, though Lely and Hamburger found it necessary to employ a temperature of 800° to obtain the chloride in bulk. We attempted to determine the lowest temperature by passing chlorine and carbon tetrachloride vapour over zirconia in a tube supported vertically in a metal-bath, the temperature of which was slowly raised, and noting the first appearance of sublimate. This occurred at 355°, but the whole of the oxide was not converted into chloride even at 500°. The temperature necessary evidently varies with the physical condition of the oxide.

Determination of Vapour Density.—A modification of Victor Meyer's apparatus was used, the heated portion consisting of a silica vaporising tube of 350 c.c. capacity, supported vertically in an electric furnace. The upper part of the apparatus was of glass and fitted into the silica tube with a ground joint lubricated with phosphoric acid. The whole was thoroughly dried, and the vertical portion filled with dried chlorine. Traces of moisture were rigidly excluded, as they reduced the vapour density enormously. In all the experiments at 700° the sublimate in the tube at the close of the tests was tinged with brown.

The results are given below, the vapour density being referred to that of air as unity.

	At 400°.			At 445°.	
$ZrCl_4$, g.	0·0875	0·0842	0·0396	0·0890	0·0880
V.D.	7·32	7·83	6·96	5·94	6·30

At 500°.

$ZrCl_4$, g.	0·1271	0·1215	0·1105	0·1100	0·1051	0·1042	0·0974	0·0894	0·0425
V.D.	8·81	6·18	7·50	6·42	9·18	9·25	8·52	7·94	6·20

At 700°.

$ZrCl_4$, g.	0·1362	0·0790	0·0762	0·0626	0·0613	0·0584	0·0444	0·0430	0·0253
V.D.	9·00	4·51	5·68	5·26	4·78	7·64	3·81	4·68	4·13

Conclusions.—Consideration of the results shows that (1) there is no evidence of association at 400° or above. The four high results at 500° and the one at 700° are believed to be due to decomposition as indicated below. (2) The vapour density of zirconium tetrachloride in chlorine falls with rise of temperature, and appears to fall slightly with dilution. Presumably the vapour first dissociates into the trichloride and free chlorine, $2ZrCl_4 \rightleftharpoons 2ZrCl_3 + Cl_2$. The decomposition can hardly end there, however, since according to Ruff and Wallstein (*loc. cit.*) the trichloride also dissociates above 330°, thus: $2ZrCl_3 \rightleftharpoons ZrCl_4 + ZrCl_2$; moreover, above 600° the dichloride deposits zirconium, $2ZrCl_2 = ZrCl_4 + Zr$. The reactions in the vaporising tube may thus be very complex and it is not regarded as possible that a complete equilibrium could be obtained in the brief course of an experiment.

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