425. *The Separation of Germanium Tetrachloride from Arsenic Trichloride by Fractional Distillation.*

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The separation of germanium tetrachloride from arsenic trichloride by fractional distillation of mixtures of the two liquids has been studied. Efficient fractionation has been found to yield in a single treatment germanium tetrachloride containing only a few parts of arsenic per million.

There is little information in the literature on the separation by distillation of germanium tetrachloride–arsenic trichloride mixtures under anhydrous conditions. This two-component system has recently been studied by Sebba (*J.*, 1951, 1975) who found that no azeotrope was formed and concluded that good separation should be possible by efficient fractional distillation; he stated that he had confirmed this conclusion by fractional distillation of germanium tetrachloride–arsenic trichloride mixtures, using an 18-in. column, to yield a germanium tetrachloride distillate in which arsenic could not be detected, but he gave no details of the distillation method and no indication of the sensitivity of the tests for arsenic.

During work carried out before publication of Sebba's paper, on the preparation of high-purity germanium for crystal valves, it became necessary to devise a method for the purification of crude germanium tetrachloride which contained substantial proportions of arsenic trichloride as the main impurity. It was found that efficient fractional distillation could yield germanium tetrachloride containing only a few parts of arsenic per million; in view of the absence from Sebba's paper of quantitative data for this separation it is thought useful to record briefly some of the experimental results obtained.

Experimental

The distillation apparatus, capable of handling 2-l. batches of germanium tetrachloride, consisted wholly of Pyrex-glass components fitted with ground joints. The fractionating column was 1 in. in diameter and 4 ft. long, packed with Pyrex-glass single-turn 4-mm. helices. The still-head was of a conventional type which permitted control of the reflux ratio. The flask and column were electrically heated.

In the distillation experiments a prolonged refluxing period, usually 3 hours, was given. This was frequently necessary to evolve from the germanium tetrachloride dissolved hydrogen chloride, the presence of substantial proportions of which were always manifested by low and fluctuating b. p.s. After the refluxing, distillation was commenced at a selected reflux ratio which was kept constant throughout the distillation. The boil-up rate employed was approximately 1 l. per hour, so a reflux ratio of 9 : 1 corresponded to a rate of distillation of about 100 ml. per hour.

The arsenic contents of the initial germanium tetrachloride–arsenic trichloride mixtures were determined by forming a complex of the germanium with oxalic acid and separating the arsenic by precipitation as sulphide. The arsenic contents of the fractionated products were determined by a Gutzeit method applied without separation of the germanium. It was found that the presence of germanium in the latter tests resulted in a partial inhibition of the evolution of arsine, and it was therefore necessary to add germanium of negligible arsenic content in the preparation of the standard Gutzeit stains used for comparison. The lower limit of determination of this method was 1 p.p.m. of arsenic.

Some of the results obtained are shown in the table. Expts. 1—5 record results obtained on the distillation of crude germanium tetrachloride which on occasion contained more than 25% of arsenic trichloride. It will be seen that, by using reflux ratios of 9 : 1 or greater, the arsenic content of such material could be reduced to less than 10 p.p.m. in a single step.

With very slow rates of distillation some striking results could be obtained, as shown by the re-treatment of distillation residues (Expts. 6 and 7). In Expt. 7, where the reflux ratio used was 100 : 1, the arsenic trichloride content was reduced from 89% to 8 p.p.m., *i.e.*, reduction by a factor of more than 100,000.

Expts. 8—11 exemplify attempts to effect still further purification by redistillation of the products of earlier fractionation experiments. It will be seen that when the starting material contained only a few parts per million of arsenic the purification factor achieved was very small and this work showed that redistillation was of little value in completing the purification of the once-distilled product. To obtain germanium tetrachloride of the very high purity required for preparation of germanium for crystal valves it was in fact necessary to employ a chemical purification treatment of the fractionated product, involving reaction with metallic copper, to remove the last traces of arsenic.

Results of fractional distillation of germanium tetrachloride–arsenic trichloride mixtures.

Expt. no.	Starting material	Estimated reflux ratio	$AsCl_3$ content of starting material, %	$AsCl_3$ content of distillate, %
1	Crude $GeCl_4$	3 : 1	3·5	0·07
2	,,	7 : 1	26·3	0·006
3	,,	9 : 1	19·0	0·007
4	,,	9 : 1	6·1	0·0007
5	,,	33 : 1	17·0	0·0004
6	Distillation residues	33 : 1	50	0·0005
7	Distillation residues	100 : 1	89	0·0008
8	Distilled $GeCl_4$	3 : 1	0·0015	0·0004
9	,,	7 : 1	0·005	0·0004
10	,,	7 : 1	0·0004	0·0002
11	,,	25 : 1	0·0003	0·0001

A crystalline germanium tetrachloride derivative was formed during some of the distillation experiments. In one experiment, where germanium tetrachloride of low arsenic content was being distilled, colourless crystals appeared on the walls of the flask towards the end of the distillation, and a further yield of crystals was obtained when the distillation residue cooled. The same phenomena occurred in greater degree when the distillate from this experiment was re-distilled. Spectrographic examination of the crystalline material showed germanium to be the only metallic element present. The material resembled germanium tetrachloride in its reaction with water to form germanium dioxide and in its solubility in certain organic solvents. In both distillations where this crystalline product appeared, copious quantities of dissolved hydrogen chloride were present in the germanium tetrachloride and it seems possible that the material formed was a chloro-acid of germanium, but its constitution has not been elucidated.

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