The Purification of Germanium : The Germanium Tetrachloride– Arsenic Trichloride System.
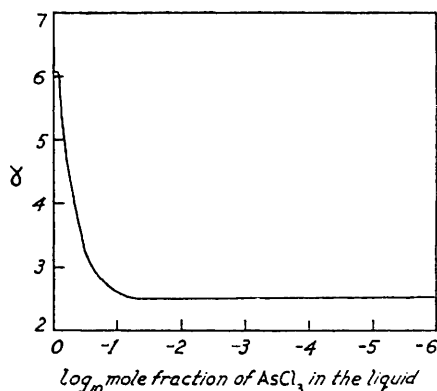
By Mino Green and James A. Kafalas.

The vapour–liquid equilibrium has been determined over a wide concentration range in the anhydrous system : germanium tetrachloride–arsenic trichloride. A relative volatility of 2·52 ± 0·035 was found for mixtures containing less than 0·05 mole fraction of arsenic trichloride in the liquid. Distillation in a Pyrex glass assembly or a quartz assembly gave theoretically predicted values of fractionation if the arsenic concentration was followed with radioactive ^{74}As. However, if the arsenic fractionation was determined by absolute arsenic analysis the Pyrex assembly gave very low fractionation whereas the quartz assembly gave nearly ideal values. This discrepancy for a Pyrex distillation unit is attributed to the leaching of arsenic from the glassware. Germanium tetrachloride containing less than $6·30 \times 10^{-10}$ mole fraction of arsenic trichloride was obtained by distillation in a quartz apparatus.

THE purification of germanium tetrachloride has attracted attention because of its importance in the preparation of pure germanium (Thompson and Musgrave, *J. Metals*, 1952, **4**, 3). The anhydrous system germanium tetrachloride–arsenic trichloride has been investigated by Sebba (*J.*, 1951, 1975), who found that the vapour–liquid equilibrium curve showed no azeotropes and so concluded that the two compounds could be separated by fractional distillation. The system was also studied in a packed fractionating column by Cluley and Chirnside (*J.*, 1952, 2275). They reported high overall separation when the mole fraction of arsenic trichloride was 10^{-5} or greater, but comment 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." The present investigation was undertaken to test the practicability of fractional distillation as a method for obtaining pure germanium tetrachloride (*i.e.*, $[AsCl_3]/[GeCl_4] < 10^{-8}$), and, if possible, to explain the results obtained by Cluley and Chirnside. In particular it seemed difficult to understand the rapid decrease in fractionation at low concentrations of arsenic trichloride.

Variation of relative volatility with composition.

The re-examination of the $GeCl_4$–$AsCl_3$ vapour–liquid system has given results in substantial agreement with Sebba's data. In addition, a more detailed study of the system in the region poor in arsenic trichloride shows that the relative volatility is constant from 5×10^{-2} mole fraction of arsenic trichloride in the liquid down to 6×10^{-10}. This is not surprising since every arsenic trichloride molecule must be entirely surrounded by germanium tetrachloride molecules and so mutual interactions between arsenic trichloride molecules are negligible. In the part of the system which is poor in germanium tetrachloride the same reasoning applies and the relative volatility becomes constant at about 5×10^{-2} mole fraction of the latter. This is not obvious from the Figure because of the use of a logarithmic scale for mole fractions. There was no evidence of azeotrope formation.

Distillation showed that the $GeCl_4$–$AsCl_3$ mixtures behaved perfectly normally if concentration changes were followed by a radiotracer method, but the results of absolute arsenic analyses indicate that there is a source of arsenic in the closed distillation assembly. Since an increase in arsenic concentration was detected in a Pyrex distillation assembly but not in a quartz assembly it was concluded that the additional arsenic was obtained by

the leaching action of germanium tetrachloride on the glass. To confirm this hypothesis, germanium tetrachloride of high purity was refluxed in a Soxhlet extractor and the material re-analysed, whereupon an increase in the concentration of arsenic trichloride was detected. The level of contamination with the latter as a result of exposure to Pyrex glass was not always the same as would be expected since the amount of leachable arsenic might well be related to the history of the glassware—*e.g.*, how much previous leaching had occurred or how the glass had been treated, such as the extent of fire polishing or whether it had been cleaned with detergents or dilute hydrofluoric acid. The temperature at which exposure of germanium tetrachloride to Pyrex glass occurred also appears to be important. The species of arsenic leached from the glass is not known. These studies would help to explain Cluley and Chirnside's results.

Finally, it may be said that germanium tetrachloride can be obtained extremely pure if a quartz distillation column is used. The relative volatility is sufficiently large for a column of a small number of plates at total reflux to be used at large take-off rates to give a product sufficiently pure for the making of germanium semiconductors (see Table 2).

EXPERIMENTAL

The experimental work involved the measurement of ratios of concentrations of arsenic trichloride and germanium tetrachloride in the boiler liquid and the vapour condensate of an equilibrium still, and in the still-pot and still-head of a fractionating column.

Materials.—Germanium tetrachloride was obtained commercially (Eagle–Picher Co., Joplin, Mo.); it contained about 0·5 μg. of arsenic per ml. C.P. arsenic trichloride was used.

Arsenic-74 (17·5 days) was used as a tracer in some of the experiments : it was prepared by bombarding germanium with 16-Mev deutrons in the M.I.T. cyclotron. Other radio-nuclides were formed, but these were short-lived compared with ^{74}As. The only long-lived species was ^{73}As but its radiations were not detectable with the counting arrangement used. The germanium target was processed four weeks after irradiation when essentially all the activity was due to ^{74}As. The target was burned in chlorine in a closed system from which the germanium tetrachloride formed was distilled and carried away about 30% of the arsenic activity available; this amounted to about 1 mc. A superior method for isolating ^{74}As from arsenic-containing germanium samples (90% arsenic recovery) has been developed since this work was completed (Green and Kafalas, *J. Chem. Phys.*, 1954, **22**, 760). Only tervalent arsenic is volatile and so we have the radioactive arsenic as the trichloride.

Estimation of Arsenic Concentrations.—Tracer ^{74}As was used for measuring ratios of arsenic concentrations : only in cases where the specific activity of the starting material was known could the absolute arsenic concentration be determined. The term " specific activity " is used here to mean the ratio of the inactive arsenic concentration to the counting rate, for 1 ml. of solution under certain fixed, arbitrary, conditions. A measure of the arsenic activity was obtained by using a scintillation counter arrangement. A thallium-activated, cylindrical sodium iodide crystal with a coaxial cylindrical hole extending two-thirds of the way into the crystal was used to detect the radiation from ^{74}As.

Absolute arsenic concentrations, in the very low concentration range, were determined by the method of neutron-activation analysis (Smales and Pate, *Analyt. Chem.*, 1952, **24**, 717). The lower limit of arsenic detection was 6·3 × 10^{-10} mole fraction of AsCl$_3$ (Leddicotte, personal communication). Higher arsenic concentrations were determined by the following standard procedure. 1 ml. of the mixture was transferred from a pipette into a weighing bottle and the sample weighed. The mixture was then placed in a dilute solution of sodium hydroxide and finally neutralized with sodium hydrogen carbonate. The weight of arsenic present was determined by titration against a standard iodine solution.

Vapour–Liquid Equilibrium.—The vapour–liquid equilibrium still used was a version of Gillespie's (*Ind. Eng. Chem. Anal.*, 1946, **18**, 575) slightly modified by replacing the usual straight-bore stopcocks with oblique-bore stopcocks having a liquid seal cup, which was filled with mercury. Both germanium and arsenic chlorides react with mercury, the latter reacting more rapidly, but the area of mercury exposed to the binary mixture was very small and so no significant amount of chemical reaction occurred. This was necessary since no stopcock grease was available which was inert to both chlorides. The apparatus was dried thoroughly before charging it with the mixture to avoid hydrolysis.

Mixtures containing a known amount of ^{74}AsCl$_3$ were distilled into the apparatus. After equilibrium was reached (in about 1½ hr.), 1-ml. samples of the boiler liquid and the vapour

condensate were drawn off. In the range from 0·09 mole fraction of arsenic trichloride in the starting material to the maximum arsenic trichloride concentration used, the mole fraction was determined by iodine titration. The values obtained were checked by comparing the [74]As activity for a 1-ml. sample of solution against the [74]As activity of 1 ml. of the starting material, whose specific activity was known. For lower arsenic concentrations the solutions were assayed by comparing ratios of arsenic activities.

The vapour–liquid equilibrium still was not kept at a fixed pressure since it was unnecessary to obtain extremely precise equilibrium values. We required to know the value of the relative volatility, α, for low concentrations of arsenic trichloride in order to study the behaviour of germanium tetrachloride–arsenic trichloride mixtures in a fractionating column, but it was not possible to calculate reliable values of α from Sebba's work (*J.*, 1951, 1975). The average pressure was 762 mm. (max. 772; min. 749 mm.). Since pressure variations were small, the values for boiling temperatures of the mixtures were corrected by use of the approximate Clapeyron equation. The results obtained are summarized in Table 1.

TABLE 1. *Results of vapour–liquid equilibrium measurements.*

Temp.	$10^3 \times$ Mole Fraction of AsCl$_3$		α *	Temp.	$10^3 \times$ Mole Fraction of AsCl$_3$		α *
	Liquid	Vapour			Liquid	Vapour	
125·8°	973	856	6·08	85·3°	82·5	33·4	2·60
117·4	914	635	6·11	84·8	60·5	25·1	2·50
111·5	858	514	5·71	84·8	58·1	23·4	2·58
99·9	669	282	5·15	84·1	13·3	5·24	2·56
96·8	575	227	4·61	84·1	11·6	4·76	2·45
93·7	428	161	3·90	83·6	6·05	2·55	2·38
91·8	339	135	3·29	83·6	1·36	0·51	2·67
90·2	280	107	3·24	83·6	0·136	0·054	2·52
87·2	151	56·1	2·99	83·6	0·0096	0·0040	2·40
85·6	98·4	39·3	2·67	83·6	0·0084	0·0032	2·63

* Relative volatility, $\alpha = [GeCl_4]_{vap.} \times [AsCl_3]_{liq.}/\{[AsCl_3]_{vap.} \times [GeCl_4]_{liq.}\}$.

The variation of α with composition is shown in the Figure, from which it can be seen that α is approximately constant for concentrations below 0·05 mole fraction of arsenic trichloride in the liquid; the average value in this range is 2·52 ± 0·035.

Distillation Studies.—The distillation studies were made with very dilute solutions of arsenic trichloride, in which α is essentially invariant with composition. It was possible to use the Fenske equation and similar relations in interpreting the experimental results obtained.

A fractionating assembly was made from Pyrex glass; the column, which was vacuum jacketed, was 60 cm. long and 2·0 cm. in internal diameter, and was packed with ⅛-inch diameter Pyrex glass single-turn Fenske helices. A 500-ml. vacuum-jacketed still-pot was used and heating was provided by an internal Pt–10% Rh resistance heater. A still-head as described by Payne and Perrins (*J. Appl. Chem.*, 1952, **2**, 208) was used : it was possible with this vapour-dividing still-head to vary the take-off rate continuously from 1 part in 10 to 1 part in 500.

The germanium tetrachloride–arsenic trichloride system, at very low concentrations of arsenic trichloride ($<10^{-6}$ mole fraction), was studied in this assembly. Germanium chloride containing [74]AsCl$_3$ was distilled into the still-pot and the column was operated at a boil-up rate of 3·42 moles per hr. at atmospheric pressure. 1-ml. samples were taken from the still-head and still-pot and the arsenic activities measured; it was then possible to calculate the fractionation obtained. The effect of take-off rate on the fractionation is shown in Table 2. It can be seen that the fractionation is not a very sensitive function of the take-off rate, and this is to be expected for systems where α is large. At total reflux the column had a plate equivalence of 10·6 ± 0·42, which corresponded closely to the values obtained by using a methyl*cyclo*hexane–*n*-heptane test mixture. The platage error was calculated by use of the equation $dn/n = - d\alpha/(\alpha \log_e \alpha)$, where n is the number of theoretical plates, and it was assumed that the errors due to assaying were negligible.

TABLE 2.

Take-off rate *	0·0	0·014	0·032	0·087	0·092	0·176	0·214
$10^{-2} \times$ Fractionation †	266	266	246	61	46	20·8	6·87

* Ratio of amount withdrawn to the boil-up rate. † Ratio of [[74]As] in still-pot to that in still-head.

Measurements of the absolute arsenic concentration were also made, by neutron-activation analysis, and the results are shown in Table 3. In all cases samples were stored in pure quartz

TABLE 3. *Fractionation calculated from absolute and radioactive assay for Pyrex and quartz stills at total reflux.*

Still	Absolute mole fractions of $AsCl_3$		Fractionation (Absolute)	Fractionation (^{74}As)
	Still-pot	Still-head		
Pyrex	$2·98 \times 10^{-7}$	$3·08 \times 10^{-8}$	9·7	2×10^4
	$3·27 \times 10^{-7}$	$2·90 \times 10^{-8}$	11·3	2×10^4
Quartz	$1·64 \times 10^{-7}$	$<6·30 \times 10^{-10}$	>260	300
	$1·64 \times 10^{-7}$	$<6·30 \times 10^{-10}$	>260	600

vessels. Owing to the large discrepancy between the values of fractionation obtained in a Pyrex system by the radioactivation method and the radiotracer method, the germanium tetrachloride–arsenic trichloride system was examined in a quartz fractionating assembly.

A vacuum-jacketed pure quartz-glass column (60 cm. long and 2·0 cm. in internal diameter) was packed with Raschig rings (3 mm. long; 3 mm. diameter) made from quartz tubing. The quartz still-head contained a solenoid-operated liquid divider of the tilting-funnel type. The same Pyrex still-pot was used with the same procedure. The boil-up rate was 3·42 moles per hour and the column efficiency, as measured with tracer arsenic, was $7·0 \pm 0·42$ theoretical plates at total reflux. The average fractionation obtained from this system, as measured with tracer arsenic, was 400. Two pairs of samples were analysed by neutron-activation analysis and the results of the average of each pair are given in Table 3. The arsenic concentration of the still-head samples was lower than the limit of detection possible by neutron-activation analysis; therefore the values in Table 3 of mole fraction of arsenic trichloride in the still-head and absolute fractionation are given as upper and lower limits, respectively.

To confirm the possible existence of leaching of arsenic from Pyrex, the following experiment was carried out. Germanium tetrachloride, previously purified in a quartz column, was refluxed for 24 hr. in a Soxhlet extractor packed with Fenske helices. The germanium tetrachloride was analysed for arsenic and the results showed a marked increase in arsenic concentration (before refluxing $<6·3 \times 10^{-10}$ mole fraction; after refluxing $2·52 \times 10^{-9}$ mole fraction of $AsCl_3$). This increased arsenic concentration, while being significant, is somewhat lower than the values obtained in the distillation assembly. However, the two systems are not entirely comparable, in particular because the temperature of the liquid in contact with the Fenske helices in the distillation column was 83° while the temperature of the contacting liquid in the extractor was about 40°. Further, we expect the leaching to be somewhat erratic.

LINCOLN LABORATORY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
LEXINGTON, MASS., U.S.A.