441. *The Liquid–Vapour Equilibrium as a Function of Temperature for the System Arsenic Trichloride–Germanium Tetrachloride.*

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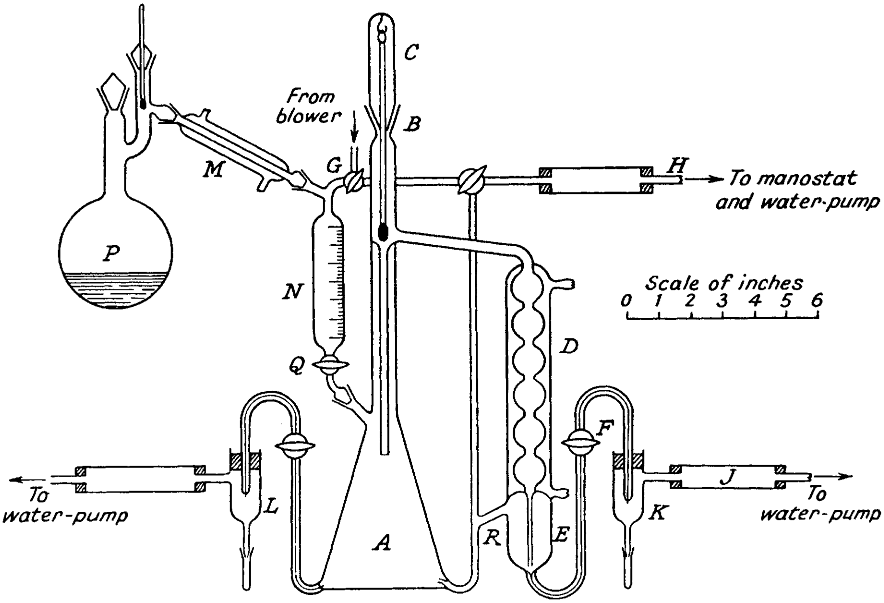
The liquid–vapour equilibrium for the system arsenic trichloride–germanium tetrachloride has been investigated. The curve shows no azeotropes, and therefore the two components can be separated by fractional distillation.

Arsenic is an almost invariable contaminant of naturally occurring germanium, and its removal by purely chemical means is a laborious process. However, at some stage in its extraction it is usual to distil germanium as the volatile tetrachloride from a fairly concentrated hydrochloric acid solution. Under these conditions much of the arsenic remains in the residue, but it has been a matter of experience that, although the boiling point of germanium tetrachloride is 83·1° and that of arsenious chloride is 130·0°, some arsenic trichloride invariably distils with the germanium tetrachloride. The vapour–liquid equilibrium for the binary mixture arsenic trichloride–germanium tetrachloride has now been investigated.

Fig. 1.

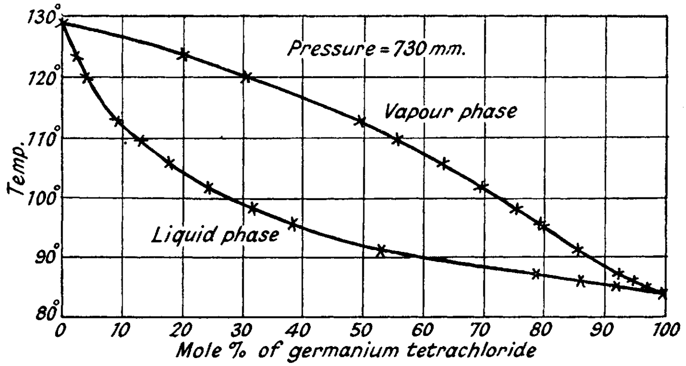


The method used was basically that of the Othmer still (Othmer, *Ind. Eng. Chem.*, 1943, **35**, 614). Some modification was necessary for the following reasons: (*a*) because of the comparative rarity and high cost of germanium care had to be taken that no germanium tetrachloride was lost; (*b*) as germanium tetrachloride is readily hydrolysed by atmospheric moisture, all access to the outside atmosphere had to be controlled; (*c*) in view of the dangerously poisonous nature of arsenic trichloride, this precaution reduced hazards from that source; and (*d*) a further difficulty arose because of the solvent effect of both these covalent compounds on tap-greases. Even silicone greases, though better than hydrocarbon tap-greases, failed to prevent leakage completely, and mercury seals were unsuitable as arsenic trichloride readily attacks mercury. The final form of the apparatus which overcame most of these difficulties is shown in Fig. 1.

A was basically the Othmer still, made from a 750-ml. Erlenmeyer flask; the neck *B* was longer than would normally be necessary, because a sensitive thermometer with a ground-glass fitting was not available. As arsenic trichloride attacks rubber, a rubber stopper could not be used; the thermometer, therefore, was suspended completely inside the apparatus from a glass hook inside stopper *C*, platinum wire being used. *D* was a condenser, enabling the distillate representative of the vapour phase to be collected in *E*, with overflow running back into *A* through the tube *R*, which was inserted into the boiler *A* by means of a narrow inner-sealed tube. In the original Othmer design, the distillate was sampled through a tap directly below *E*, but because of the solvent effect of the liquids on the tap-grease, this arrangement was modified by having a capillary tube of swan-neck design with a tap *F* above the level of the liquid in *E*. In this way, direct contact of the liquid with the tap, except when sampling, and thus loss of liquid due to gravity leakage, was avoided. When required for sampling, a small positive pressure in the apparatus was produced with dried (phosphoric oxide) air from a blower circuit, introduced through tap *G*, and the liquid pushed over. After sampling, the liquid was returned to *E*, by slight suction through the circuit *H*. This connected the apparatus to a water-pump through a phosphoric oxide trap.

In order to sample the liquid from *E*, without its exposure to moist atmosphere, the arrangement at *K* was used. *K* was connected to the water-pump by way of tube *J*, which contained solid sodium hydroxide to collect any germanium tetrachloride vapours, and a tube which contained phosphoric oxide. At the bottom of *K* was a small ground-glass joint to which a tared weighing-bulb, fitted with a ground-glass joint, could be attached. A sample could be pushed into the weighing bulb by operating the blower and opening *F*. The bulb with its sample was then quickly stoppered. *K* was closed by attaching a second small bulb at the bottom and any excess of liquid pumped off through the sodium hydroxide trap, the water-pump being used.

FIG. 2.



For sampling the liquid phase in *A*, there was an identical arrangement at *L*. To introduce a sample of either of the pure components into the apparatus in the absence of moisture, it was distilled from concentrated sulphuric acid in flask *P*, through condenser *M* into a metering cylinder *N*, which was graduated so that known quantities could be introduced through tap *Q*. The distillation proceeded more smoothly if carried out below atmospheric pressure, and therefore this circuit was connected by way of tap *G* through sodium hydroxide and phosphoric oxide traps to the water-pump.

To maintain constant pressure during the period of equilibrium between the liquid and the vapour phase, the Othmer still was connected through *P* to a manostat and manometer to circuit *H*. The most convenient working pressure was about 2 cm. below normal atmospheric. It was found advantageous to cover the neck of the still with loosely fitting aluminium foil to prevent too much heat loss.

The arsenic trichloride was prepared by the action of dry chlorine on arsenic metal in a combustion tube. The arsenic trichloride which distilled was freed from chlorine by shaking it with finely divided arsenic metal and redistilled.

The germanium tetrachloride was prepared from reasonably pure germanium dioxide by the addition of concentrated hydrochloric acid, and distillation. The distillate was collected under concentrated sulphuric acid, and freed from hydrogen chloride by bubbling dry air through it for half an hour. The only contaminant was a trace of arsenic trichloride, and because of the nature of this investigation, it was not necessary to remove it.

The flask containing the germanium tetrachloride, under concentrated sulphuric acid was placed in position *P*, and 100 ml. of the chloride distilled into the metering cylinder *N*, at a pressure of about 500 mm. The germanium chloride was then run into the boiler *A*. Flask *P* was interchanged with the flask containing the arsenic trichloride, and small quantities, as required, usually in 10-ml. portions, were distilled into *N*, again under reduced pressure, and run into the boiler *A*. The mixture in *A* was then boiled gently, and the distillate collected in *E*, the overflow returning to boiler *A*. The distillation was carried out at a fixed pressure of 730 mm., adjustment being made on the manostat, before an experiment, to allow for changes in the barometric pressure. At frequent intervals a few bubbles of dry air were allowed to leak into *E* and *A* through the swan-neck tubes, to ensure mixing of the small amount of liquid trapped in the bends.

When the temperature had remained steady for some 20 minutes, it was recorded, the distillation was stopped, and after cooling and a preliminary flushing of the swan-neck tubes with the liquid in *A* and *E*, samples were collected at *L* and *K* as previously described. After being weighed, the stoppered weighing-tubes were opened under dilute sodium hydroxide solution. The solution obtained was neutralised with sodium hydrogen carbonate, and the arsenic titrated with standard iodine solution. The germanium chloride content was obtained by difference.

After the determination with the 50–50 mixture, the boiler *A* was cleaned, and the procedure repeated starting with pure arsenic trichloride in the boiler and adding small quantities of germanium tetrachloride.

Fig. 2 shows the results obtained, plotted as molar percentage composition of the vapour and the liquid phase against temperature. The curve showed that these two components give no azeotropes, and it should, therefore, be comparatively simple to separate the two components by use of an efficient fractionating column. This was confirmed by fractionally distilling a mixture of arsenious trichloride and germanium tetrachloride through an 18-in. column filled with Fenske glass helices. In these circumstances the germanium tetrachloride distillate showed no sign of arsenic contamination by macroanalytical tests.

This conclusion offers no evidence that the same conditions will apply when the distillation is carried out in the presence of the extra components, hydrogen chloride and water. On the contrary, experience indicates that the distillates from such a mixture are complex, the germanium tetrachloride distilling in two stages, some at about 80° and the rest at about 105°. The reasons for this are unknown and therefore this system merits fuller investigation.

It is suggested, however, that in order to obtain germanium tetrachloride free from arsenic trichloride by a distillation process, it should first be distilled from hydrochloric acid and collected under sulphuric acid, whereby it is dried. After being freed from hydrogen chloride by bubbling air through it, the germanium chloride should be distilled through an efficient fractionating column; this should give a product sufficiently free from arsenic contamination for most chemical purposes, though for use in rectifying valves further refinement may be necessary.

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