239. *Some Physicochemical Properties of* cis-2-*Chlorovinyldichloroarsine.*

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The physicochemical constants—freezing point, vapour pressure, density, refractive index, and viscosity—for *cis*-2-chlorovinyldichloroarsine have been determined and compared with the data for the *trans*-isomer.

The substance of which the isolation and configuration are described in the two preceding papers is characterised by the following measured and derived physicochemical constants, which can be compared (col. 3) with those of the more abundant *trans*-isomer.

Table I.

Physicochemical constants of cis- *and* trans-2-*chlorovinyldichloroarsine.*

Property.	*cis*-Isomer.	*trans*-Isomer.
Freezing point	−44·7°	−1·2°
Vapour pressure (mm. Hg) at 25°	1·562	0·40
log p (mm. Hg)	8·4131—2450·2/T	48·660—13·297 log T −4815·3/T
B. p./760 mm.	169·8°	196·6°
Latent heat of vaporisation at 25°, $L_V^{25°}$ (cal./g.-mol.)	11,220	15,150
L_V at the b. p.	11,220	9,620
Molar b. p. depression	34·7°	45·6°
$d_4^{25°}$	1·8598	1·8793
$d_4^{t°}$	1·9018—0·00168t	1·9210—0·00167t
$n_D^{25°}$	1·5859	1·6076
$n_D^{t°}$	1·6003—0·000575t	1·6201—0·0050t
$[R_L]_D$	37·388	38·089
η at 25° (g./cm.-sec.)	0·0169	0·0205
log η	590/T − 3·751	699/T − 4·033

Experimental.

Purity.—The purest material tested (Preparation III, supplied by Dr. Hewett) consisted of 17 ml. of a liquid which froze continuously and completely during 20 minutes at − 44·7°, constant to ± 0·05°. The 3-ml. sample first prepared (Dr. Hewett's Preparation I) froze at 2·0° lower; whilst Preparations IV, V, etc. (after extraction with benzene and distillation), also froze at a lower temperature, besides showing some deviation in density and refractive index. In view of the prevailing possibility of disproportionation to arsenic trichloride and dichlorovinylchloroarsine (see Hewett, this vol., p. 1203), the above-mentioned freezing behaviour may be taken as a satisfactory test of the purity of Preparation III. The consistent and reproducible vapour-pressure relations of Preparation III support that assumption.

Freezing Point.—In order to obtain a uniform and slow rate of cooling of small specimens, the apparatus shown in Fig. 1 was used. The substance under investigation was contained in a small jacketed tube *A* just large enough to hold a 1-mm. layer of liquid around the bulb of a calibrated thermometer, reading to 0·1° and rigidly held by a clamp. The envelope of tube *A* was surrounded by a cooling bath *B* of alcohol and solid carbon dioxide, held several degrees below the temperature of the thermometer; and any desired rate of cooling was obtained by appropriate evacuation of the jacket through the side arm and tap *C*. Agitation was effected by moving *A* against the tension of a piece of elastic *D*, and seeding was done (in dry nitrogen) by introducing nuclei from a subsidiary frozen sample in the same bath, on the end of thin glass needles. The time–temperature graphs obtained by reading the temperature every 10—30 seconds gave unmistakable indications, both of the freezing point and of the degree of impurity, for every sample tested.

Vapour Pressure.—The vapour pressure was determined by distillation of the liquid from a heated "Pyrex" bulb of 50 ml. capacity into another bulb of the same capacity in a freezing mixture against several arbitrary pressures established in the system after thorough evacuation. The distillation temperatures were measured by a calibrated thermometer, in a mercury pocket projecting into the distillation stream, whilst the pressures were measured on a mercury manometer, and reduced to mm. of mercury at 0°. The mid-fractions of five distillations yielded 16 points on a smooth curve, and the corrected readings, given in Table II, were used for calculating the equation in Table I by the method of least squares. The points agreed with the formula to an average deviation of 2% on the pressure readings.

Table II.

Vapour pressure of cis-2-*chlorovinyldichloroarsine.*

	p (mm. Hg).			p (mm. Hg).			p (mm. Hg).			p (mm. Hg).	
Temp.	Obs.	Calc.	Temp.	Obs.	Calc.	Temp.	Obs.	Calc.	Temp.	Obs.	Calc.
67·6°	16·9	16·3	76·8°	26·1	25·7	85·9°	39·1	38·7	100·1°	70·7	71·0
72·2	19·9	20·8	78·0	27·7	27·2	87·1	39·8	40·8	102·6	76·2	77·9
72·4	20·7	21·0	80·9	31·3	31·0	91·2	49·1	48·7	107·1	92·6	89·5
76·8	26·2	25·7	85·3	37·5	37·7	94·7	56·6	56·4	109·3	100·0	101·3

Density.—This was determined in duplicate in a type of pycnometer shown in Fig. 2. It consisted of a hemispherical "Pyrex" bulb of 10-ml. capacity, fitted with two capillary necks (of 0·2 mm. internal diameter, and graduated in mm.), the lower of which (*A*) was provided with a grooved stopper as shown. Filling was effected through the capillary *A* from a burette at atmospheric pressure. The true volume of the pycnometer, at any temperature, and measured to any graduations, was obtained by previous calibration with distilled water, all the usual precautions being used. The figures obtained agree with the formula in Table I to ± 0·0001 :

Density of cis-2-*chlorovinyldichloroarsine.*

Temp.	$d_{4°}^{t°}$.	Temp.	$d_{4°}^{t°}$.	Temp.	$d_{4°}^{t°}$.
20·00°	1·86831, 1·86821	25·00°	1·85980	30·00°	1·85149

Refractive Index.—The refractive index was determined in an Abbé refractometer, adjusted to a standard prism, and checked with distilled water. Readings were taken when the temperature of water circulating from a thermostat had been constant to 0·1° for ten minutes. The readings obtained on rising and falling temperature sequences agree with the formula in Table I to ± 0·0002.

FIG. 1.

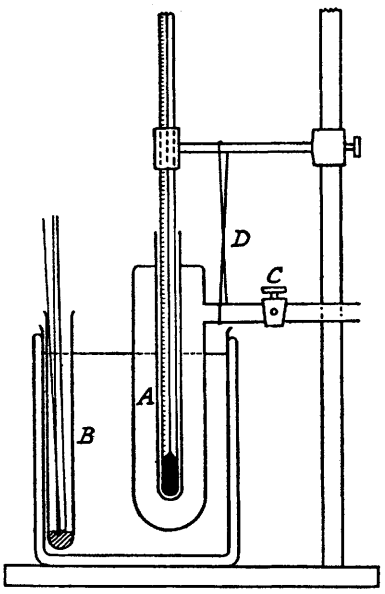
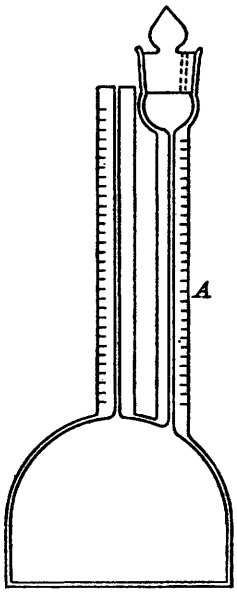


FIG. 2.



Refractive index of cis-2-*chlorovinyldichloroarsine.*

Temp.	21·0°	25·0°	30·0°	35·0°	37·0°	27·0°	23·0°	20·0°
$n_D^{t°}$	1·5882	1·5860	1·5832	1·5802	1·5791	1·5848	1·5869	1·5888

Viscosity.—The viscosity of the liquid was determined in a BSS Ostwald-type viscometer in a thermostat steady to 0·1° at temperatures from 20° to 35°, and in dried air. The results obtained agree with the formula in Table I to 0·001 in log η in all cases but one.

Viscosity of cis-2-*chlorovinyldichloroarsine.*

Temp.	20·0°	25·0°	30·0°	35·0°
η (g./cm.-sec.)	0·01831	0·01690	0·01561	0·01461

Data for the trans-*Isomer.*—The comparable data for *trans*-2-chlorovinyldichloroarsine, given in Table I, form part of a comprehensive review of standard data for the physicochemical properties of toxic materials, which was conducted at the Chemical Defence Research Establishment during the last war, and which it is hoped to publish in due course.

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