74. *The Vapour Pressure of ββ′-Dichlorodiethyl Sulphide.*

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In a paper on the volatility of certain organic compounds (*Kolloidchem. Beih.*, 1926, **23**, 313), Herbst reports the measurement, by an air-saturation method, of the vapour pressure of an impure specimen of ββ′-dichlorodiethyl sulphide (m. p. 12·85°) at 22° and 39°. Apart from this, there appears to be no record of the determination of the vapour pressure of this substance at ordinary temperatures, though a number of values are quoted in the literature. These, however, are very discordant, ranging from 0·01 mm. to 0·051 mm. at 10°, and from 0·06 mm. to 0·11 mm. at 20° (see Table I).

For the b. p. of the sulphide under reduced pressures, Clarke (J., 1912, **101**, 1583) gives 98°/10 mm., Steinkopf, Herold, and Stöhr (*Ber.*, 1920, **53**, 1007) 108°/15 mm., Herbst (*loc. cit.*) 97°/10 mm. and 105°/15 mm., Lewin (*J. pr. Chem.*, 1928, **118**, 282) 104—105°/13 mm., and Mumford and Phillips (J., 1928, 155) 107°/15 mm. From these points the curve $\log_{10} p = -2612{\cdot}8/T + 8{\cdot}0425$ is obtained, extrapolation of which gives 0·13 mm. at 20°, thus affording support of the correctness of the higher values in Table I. This has now been confirmed by the determination, by an air-saturation method, of the vapour pressure of the pure material from 0° to 60°, the value found for 20° being 0·115 ± 0·007 mm.

EXPERIMENTAL.

The method used consisted essentially in the saturation of a slow " auxiliary " air stream with vapour of ββ′-dichlorodiethyl sulphide at the required temperature, subsequent admixture of this saturated air stream with a larger " main " flow of air, and final estimation of the sulphide in the combined flow by its adsorption in, and reaction with, very dilute acidified permanganate solution.

The auxiliary air flow (*ca.* 2 c.c./min.) was maintained by displacement with water from a graduated vessel, immersed in a suitably heated water-bath. This air was subsequently dried with calcium chloride, brought to the exact temperature of the experiment in a pre-heating coil, and saturated with vapour of the sulphide by passing it through a 45-cm. long, flat U-tube filled with dry pumice soaked in pure ββ′-dichlorodiethyl sulphide, and provided with plugs of glass wool to prevent formation of spray, the U-tube, and the pre-heating coils for the auxiliary and main air flows, being contained in an electrically regulated air thermostat. The main air flow (100 c.c./min.), maintained by suction from a water pump, was purified (by passing through absorbent cotton wool, activated charcoal, and acidified permanganate solution) and dried; then, after being pre-heated to the required temperature, it was admixed with the auxiliary flow, and the whole of the combined flow passed through an absorption bubbler containing a known volume of standard dilute acid permanganate solution.

In making a determination, the apparatus was allowed to remain at the requisite temperature for at least an hour before the air flows were started, and after a further 5—10 mins. to clear the tubes of accumulated vapour and to attain equilibrium, the combined flow was passed into the absorption bubbler. The volume registered on the displacement vessel was simultaneously noted, and again read at the end of the run, as indicated by complete decolorisation of the permanganate solution.

The permanganate solution, prepared by dilution from an approximately 0·1*N*-solution, contained 0·006372 g. per litre (except at temperatures above 40°, where a solution of double this concentration was used) acidified with 20% of 6*N*-sulphuric acid, preliminary experiments having indicated that with such solutions, at the rate of flow employed, ββ'-dichlorodiethyl sulphide is quantitatively removed from the air stream and oxidised to the corresponding sulphone. The complete decolorisation of 10 c.c. of this permanganate solution is thus equivalent to 0·08016 mg. of the sulphide, or to $8{\cdot}016/10^5 d_t$ c.c. of its vapour at $t°$, where d_t, the density at $t°$ is given by

$$d_t = \frac{273}{273+t} \times \frac{159{\cdot}04}{2{\cdot}016} \times 8{\cdot}988 \times 10^{-5} = \frac{273}{273+t} \times 7{\cdot}091 \times 10^{-3}\ \text{g./c.c.},$$

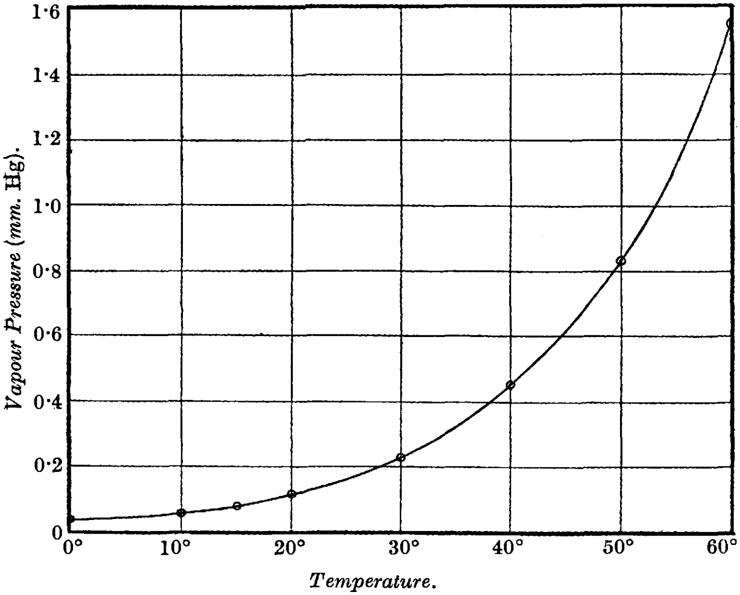
the vapour being assumed unimolecular. [No measurements of the vapour density have been recorded, but the molecular weight of the liquid, determined cryoscopically in benzene (Mumford and Phillips, *loc. cit.*), is normal.]

In view of the small magnitudes involved and of the errors inherent in the method—in particular, the difficulty of ascertaining the precise decolorisation point of the permanganate solution, and the impracticability of measuring the volume of the auxiliary air to within 1 c.c.—the slight lowering of vapour pressure due to the presence of air has been neglected, and the vapour pressure (p) calculated from the simple formula $p = 8{\cdot}016 \times 10^{-5}(B - b)/d_t V_t$ mm., where B mm. is the barometric pressure, b mm. the negative pressure in the displacement vessel and saturation tube (*ca.* 2·4 mm.) caused by maintaining the main flow, and V_t c.c. the volume of auxiliary air passing during a determination, corrected for temperature, *i.e.*, $V_t = V_\theta(273 + t)/(273 + \theta)$, V_θ being the actual volume of water at θ° (a temperature near *t*°) run into the displacement vessel.

The ββ'-dichlorodiethyl sulphide used was purified by fractional distillation and freezing, and had f. p. 14·4°, b. p. 107°/15 mm. Its physical constants, which agree well with those given for the pure compound in the literature, are summarised in the following equations: $D_{4^\circ}^{t^\circ} = 1{\cdot}2960 - 0{\cdot}001068t$; $n_{\mathrm{D}}^{t^\circ} = 1{\cdot}5292 - 0{\cdot}00044(t - 15)$, whence $[R_L]_{\mathrm{D}} = 38{\cdot}36$ (calc. 38·38); $\gamma_{t^\circ} = 43{\cdot}3 - 0{\cdot}12(t - 15)$ dynes/cm.; $\eta_{t^\circ} = 0{\cdot}001117/(1/D_{t^\circ} - 0{\cdot}7589)$ dynes/cm.². The temperature range of the equations is from the f. p. to 25°, except that for the density, which incorporates determinations made on the supercooled liquid down to 0°.

FIG. 1.

Vapour pressure of ββ'-dichlorodiethyl sulphide.



The results of the vapour-pressure determinations are given in Table II. They are represented by the equation $\log_{10} p = 8{\cdot}3937 - 2734{\cdot}5/T$ (see Table II, last column), which gives, for the b. p. under 10, 13, and 15 mm. pressure, 97°, 103°, and 106° respectively, in good agreement with the observed values quoted above.

TABLE I.

Recorded values for the vapour pressure of ββ′-dichlorodiethyl sulphide.

t.	(1).	(2).	(3).	(4).	(5).	(6).	(7).	(8).	(9).
0°	—	0·025	0·01	—	0·01295	0·012(*b*)	0·031	0·021	—
5	—	—	0·016	—	0·0186	—	—	—	—
10	0·01	0·040	0·026	—	0·0272	0·031(*b*)	—	0·051	0·05
13·9	—	—	—	—	—	—	0·07	—	—
15	—	0·047	0·042	0·0417	0·0417	—	—	—	—
20	0·06	0·062	0·065	0·065	0·065	0·080(*b*)	0·11	0·11	—
22	—	—	—	0·0773	—	0·090(*b*) 0·087(*a*)	—	—	—
25	—	0·074	0·10	0·0996	0·0996	—	—	—	—
30	0·09	0·090	0·15	0·150	0·150	0·174(*b*)	—	—	—
35	—	—	—	0·222	0·222	—	—	—	—
39	—	—	—	—	—	0·344(*b*) 0·358(*a*)	—	—	—
40	—	—	—	—	—	—	0·45	—	0·45
59	—	—	—	—	—	1·39(*b*)	—	—	—
60	—	—	—	—	—	—	1·51	—	—

References.—(1) *Official History of the Great War*, Medical Services, 1923, Vol. II, p. 425. (2) Lamb, Carleton, Hughes, and Nichols, *J. Amer. Chem. Soc.*, 1920, **42**, 78. (3) Leitner, *Militarwis. u. Techn. Mitteilungen*, 1926, **47**, 662 (see also, Hanslian, " Der Chemische Krieg," Berlin, 1927, p. 383). Vapour pressures calculated from the quoted persistencies : $S = p'\sqrt{M'T}/p\sqrt{MT'}$, where p' = vapour pressure of water (mol. wt. = M') at 15° (= T'° Abs.), and p = vapour pressure of the sulphide (mol. wt. = M) at T° Abs. (4) Vedder, " Medical Aspects of Chemical Warfare," Baltimore, 1925, p. 127. (5) *Voina i Technicka*, 1928, **7**, 60. (6) Herbst, *loc. cit.* Vapour pressures calculated from the quoted volatilities : $F_t = Mp_t \times 10^6/760V_t$ mg./cu. m., where p_t is the vapour pressure of the sulphide (mol. wt. = M) at t°, and V_t its molecular volume (in litres) at the same temperature, *i.e.*, $V_t = 22{\cdot}412 \times (273 + t)/273$. Those marked (*a*) are from actual determinations by an air-saturation method; those marked (*b*) have been extrapolated from boiling points at higher pressures. (7) Vedder, *op. cit.*, p. 14; also quoted by Hanslian, *op. cit.*, p. 50. (8) Kostevitch, *Z. ges. Schiess. u. Sprengstoffwesen*, 1928, **23**, 365. Vapour pressures calculated from the quoted volatilities as under (6). (9) " Manual of Treatment of Gas Casualties " (H.M.S.O., 1930), p. 13.

TABLE II.

Experimental vapour pressures of ββ′-dichlorodiethyl sulphide.

	Vapour pressure (obs.).			
Temp.	Mean *p*, mm.	Max. deviation from mean, ±.	No. of determinations.	Vapour pressure (calc.).
0°	0·035	0·007	20	0·024
10	0·055	0·005	17	0·054
15	0·075	0·008	15	0·079
20	0·115	0·007	18	0·115
30	0·225	0·025	19	0·23
40	0·45	0·05	24	0·45
50	0·83	0·1	32	0·85
60	1·55	0·15	19	1·52

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