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ANTOINE VAPOUR-PRESSURE EQUATIONS AND HEATS OF VAPORIZATION FOR THE DIMETHYLS OF ZINC, CADMIUM AND MERCURY

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Abstract—Accurate vapour-pressure data over the range below atmospheric pressure have been determined for highly purified specimens of zinc dimethyl and mercury dimethyl, and the corrected values obtained used to derive the corresponding Antoine equations, corrected boiling points, heats of vaporization and Trouton constants. The corresponding values for cadmium dimethyl are computed from published data. The rather anomalous values for cadmium dimethyl are not to be attributed to association.

ALTHOUGH precision vapour-pressure data for cadmium dimethyl have been reported,[1,2] published values [3] for zinc dimethyl and mercury dimethyl are of a lower order of accuracy (and in the case of zinc dimethyl were obtained with a specimen which, according to its mode of preparation from methyl iodide, was in all probability seriously contaminated). The plot of $\log p$ vs. reciprocal temperature is in fact close to linear for none of these compounds. For these reasons, a more accurate re-investigation of the zinc and mercury compounds using the highly purified materials which had been prepared for another purpose[4] seemed well worth while.

MATERIALS AND PROCEDURE

The mercury dimethyl was prepared from methyl magnesium iodide and mercuric chloride according to the method[5] of GILMAN and BROWN. After thorough drying with anhydrous calcium chloride it was purified by four successive fractionations through a 1 m column packed with glass helices, appreciable head and tail fractions being rejected with each operation. The final product has a corrected boiling point of 92·5°C.

Some of the mercury dimethyl was converted to zinc dimethyl by prolonged heating with excess zinc amalgam at 100°C in a sealed tube.[6] (This method is greatly to be preferred to the usual method from methyl iodide and zinc–copper couple[7] which gives a product from which the last traces of methyl iodide, on account of its similar volatility, cannot[8] be separated by fractionation.) The zinc dimethyl obtained was rigorously purified by repeated fractional condensation *in vacuo* until the head, middle and tail fractions exhibited identical vapour pressures.

For both compounds the vapour pressures were studied over the range 10–760 mm. For the temperature region below room temperature, this was accomplished in the usual way in high-vacuum apparatus using a manometer with an antiparallax mirror scale which could be read to within 0·1 mm with the aid of a lens. The temperature was recorded with a thermometer calibrated in tenths of a degree. As a check, the measurements were repeated on a second sample. Above room temperature the measurements were carried out according to a method described elsewhere.[9] All temperature

[1] R. D. ANDERSON and H. A. TAYLOR, *J. Phys. Chem.* **56**, 161 (1952).
[2] J. C. M. LI, *J. Amer. Chem. Soc.* **78**, 1081 (1956).
[3] H. W. THOMPSON and J. W. LINNETT, *Trans. Faraday Soc.* **32**, 681 (1936).
[4] J. CATTANACH and L. H. LONG, *Trans. Faraday Soc.* **56**, 1286 (1960).
[5] H. GILMAN and R. E. BROWN, *J. Amer. Chem. Soc.* **52**, 3314 (1930).
[6] E. FRANKLAND and B. F. DUPPA, *J. Chem. Soc.* **17**, 28 (1864); *Liebigs Ann.* **130**, 117 (1864).
[7] R. R. RENSHAW and C. E. GREENLAW, *J. Amer. Chem. Soc.* **42**, 1472 (1920).
[8] C. H. BAMFORD, D. L. LEVI and D. M. NEWITT, *J. Chem. Soc.* 468 (1946).
[9] R. T. SANDERSON, *Vacuum Manipulation of Volatile Compounds*, p. 83. J. Wiley, New York (1948).

measurements were corrected for exposed thermometer stem and all pressure measurements reduced to values for mercury at 0°C and standard gravity.

RESULTS AND DISCUSSION

About fifty separate measurements were recorded for zinc dimethyl and about thirty for mercury dimethyl. From these the well spaced values listed in Tables 1 and 2

TABLE 1.—EXPERIMENTAL AND CALCULATED VAPOUR-PRESSURE VALUES FOR $Zn(CH_3)_2$

Temperature (°C)	Vapour-pressure (mm) observed	Vapour-pressure (mm) calculated from Antoine constants
−34·6	16·1	15·8
−19·4	42·7	42·6
−5·5	92·5	92·9
11·1	207·7	207·7
19·2	296·4	296·1
31·2	477·3	478·6
39·8	656·6	656·9

TABLE 2.—EXPERIMENTAL AND CALCULATED VAPOUR-PRESSURE VALUES FOR $Hg(CH_3)_2$

Temperature (°C)	Vapour-pressure (mm) observed	Vapour-pressure (mm) calculated from Antoine constants
−11·2	8·7	8·7
0·8	17·7	17·8
8·0	26·4	26·6
23·7	58·8	58·6
35·8	102·0	101·2
51·7	192·9	193·1
64·0	305·5	303·7
85·1	608·3	608·3

were selected and used as described[10] elsewhere to derive the constants for the Antoine equation

$$\log_{10} p_{\text{mm}} = A - \frac{B}{C + t}$$

(where t is the temperature in degrees Centigrade). The constants are presented in Table 3, and very accurately reproduce the experimental vapour-pressures over the

TABLE 3.—ANTOINE CONSTANTS, BOILING POINTS AND HEATS OF VAPORIZATION OF $Zn(CH_3)_2$, $Cd(CH_3)_2$ AND $Hg(CH_3)_2$

Alkyl	Range (mm)	Antoine constants			Mean deviation (%)	b.p. (corr.) (°C)	Heat of vaporization at 25°C (corr.) (kcal/mole)	Trouton's constant
		A	B	C				
$Zn(CH_3)_2$	10–760	6·76271	1009·3	216	0·3	44·0	7·058	21·6
$Cd(CH_3)_2$*	2–760	6·71742	1165·0	198	0·5	105·7	9·528	21·8
$Hg(CH_3)_2$	10–760	7·01688	1342·2	232	0·6	92·5	8·264	21·3

* Calculated from the data of ANDERSON and TAYLOR[1]

[10] G. W. THOMPSON, *Chem. Rev.* **38**, 1 (1946).

whole range, as can be verified by comparing the second and third columns in both Tables 1 and 2.

For the sake of completeness, the vapour-pressure relation for cadmium dimethyl has been recalculated in the form of the Antoine equation and included in Table 3. Of the two published sets of vapour-pressure data, the measurements[1] of ANDERSON and TAYLOR were utilized in preference to those[2] of LI, not only because the latter do not extend above 23°C, but because his product was almost certainly contaminated with mercury dimethyl arising from a room-temperature reaction[11] with the mercury of his manometer. This conclusion is confirmed by the fact that LI's specimen melted about 0·3°C lower than the value of −2·4°C observed[1,11] by other workers, and also exhibited a vapour-pressure at the melting point some 20 per cent higher than the sample of ANDERSON and TAYLOR. In addition, it yielded a value for the heat of vaporization by direct measurement approximately 10 per cent lower than that derived here from the vapour-pressure relation, a value, moreover, that corresponds to an unreasonable value for Trouton's constant for a non-associated compound such as cadmium dimethyl. In accepting the data of ANDERSON and TAYLOR, it has been assumed (in the absence of any statement) that these investigators have already corrected the temperature and pressure measurements they report.

From the Antoine equations, the heats of vaporization at 25°C have been calculated in the usual way. The values recorded in the penultimate column of Table 3 have been corrected for the volume taken up by the liquid in each case. There are no direct measurements of the heats of vaporization for comparison except the unreliable one for cadmium dimethyl already referred to. The heats of vaporization at the respective boiling points were also calculated and used to deduce the corresponding Trouton's constants. In all cases these are normal for non-associated liquids, so that the anomalously high boiling point, high heat of vaporization and low C constant in the Antoine equation for cadmium dimethyl would appear not to arise from association, but rather from enhanced van der Waals forces arising from the anomalously long[12] metal–carbon bond.

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[11] L. H. LONG and R. G. W. NORRISH, *Phil. Trans. Roy. Soc.* **241**, 587 (1949).
[12] K. S. RAO, B. P. STOICHEFF and R. TURNER, *Canad. J. Phys.* **38**, 1516 (1960).