Thermochimica Acta, 109 (1986) 55–61
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

VAPOUR PRESSURE AND THERMODYNAMIC PROPERTIES OF HEXAMETHYLDISILANE AT 305–387 K *

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(Received 18 August 1986)

ABSTRACT

The Swietoslawski's differential ebulliometer has been minimized to be usable for ca. 13 cm^3 of liquid. After a performance test with acetone, the vapour pressure of hexamethyldisilane is determined over the temperature range 304.61–386.74 K. The Antoine equation obtained is $\log_{10}(P/\text{kPa}) = 5.97097 - 1319.85/\{(T/\text{K}) - 52.96\}$ and the normal boiling point is 385.81 K. The present results agree with literature values of Suga and Seki at 287–310 K and Brockway and Davidson at 293–334 K.

INTRODUCTION

Any reliable measurement of vapour pressures needs thoroughly purified samples. To reduce the tiresome and time-consuming work of such purification and/or prevent the loss of rare samples, the minimization of sample weights needed for the proper operation of an ebulliometer was attained by constructing a relatively small differential ebulliometer based on Swietoslawski's differential ebulliometer [1,2].

After the performane test of the newly constructed ebulliometer was made with acetone, the vapour pressure of hexamethyldisilane was measured at 305–287 K.

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* Dedicated to Professor Syûzô Seki in honour of his contribution to Precise Calorimetry and Chemical Thermodynamics.

Most of this paper was presented at the 18th Annual Meeting of the Chemical Society of Japan, Tokyo, April 1965.

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0040-6031/86/$03.50

EXPERIMENTAL

Apparatus

The design of an ebulliometer which operates properly with only 12–13 cm^3 of liquid is shown in Fig. 1. It was made of borosilicate glass. The construction of its main parts is similar to our vapour–liquid equilibrium still for small samples [3]. However, the inside diameter of the Cottrell tube C is ca. 3 mm and that of a connective tube G is ca. 1 mm. Both thermometer wells E and F are 13 mm ID and 90 mm long. The two annular spaces in the equilibrium chamber A are ca. 4 mm wide for the inner one and 5–6 mm wide for the outer one. For the dew-point chamber D, annular spaces are ca. 3 mm wide and 4–5 mm wide for inner and outer, respectively. Boiler B is ca. 35 mm long and its inside diameter is ca. 15 mm. Bores of the wide connecting tubes are all 12 mm ID. The outer wall of the dew-point chamber D was wound with asbestos rope for this experiment, but it should be surrounded with a vacuum jacket in any future experiments.

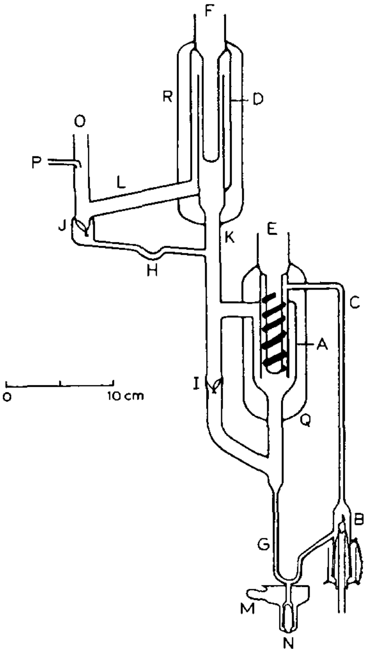

Fig. 1. Differential ebulliometer. (A) Equilibrium chamber; (B) boiler; (C) Cottrell pump; (D) dew-point chamber; (E) and (F) thermometer wells; (G) U-shaped connective tube; (H) hold-up trap; (I) and (J) drop counters; (K) path of vapour from A to D; (L) path of returning vapour and condensate; (M) cup for collecting the contents; (N) ground stopper; (O) to a total condenser; (P) vent for filling by distillation; (Q) vacuum jacket; (R) vacuum jacket (not installed in the present ebulliometer).

The arrangement of the pressure measuring apparatus was the same as that described in an earlier paper (Fig. 2 of ref. 3).

Materials

Two kinds of crude products of hexamethyldisilane were synthesized. One of them (I) was obtained by the reaction of high-boiling residues (418–433 K) of the direct synthesis of methylchlorosilanes with methylmagnesium bromide in ether [4]. It was distilled repeatedly under reduced pressure, fractionated by GLC, and purified further by repeated fractional freezing. The melting point of the final product (sample I) was 287.0_5–287.1_5 K. The other product (II) was synthesized from trimethylchlorosilane with metallic sodium in an autoclave [5]. Repeated fractional distillation was carried out with a spinning-band column with reflux ratios of 100–150. Fractional freezing was repeated until sharp melting point was attained (m.p. 287.20–287.25 K). The GLC test of this product (sample II) showed only one sharp peak. However, the high-boiling residue on distillation gave a small impurity peak behind the main peak. Refractive indices $n_D^{20.0}$ of samples I and II observed on a Bausch and Lomb Precision Refractometer showed 1.4225 and 1.4224, respectively, and 1.4240 for the residue of II.

Reagent grade acetone (Wako Pure Chemical Ind.) was treated with potassium permanganate in a dark room for a long time, distilled, dried, and then fractionally distilled over reactivated 5 A Linde Molecular Sieves [6] after a long reflux time. A middle fraction of the final distillate was collected in a Pyrex ampoule with a ground taper joint and stopcock, then distilled into the ebulliometer. The acetone showed no impurity peak on GLC.

Procedures

The main procedures for the operation of the ebulliometer and for the measurement of temperature and pressure were similar to those described elsewhere [3].

RESULTS AND DISCUSSION

Performance test

The vapour pressures of acetone obtained with the newly constructed ebulliometer at 285–329 K (in the range 16–101 kPa) have been fitted by the Antoine equation:

$$\log_{10}(P/\text{kPa}) = 6.18527 - 1176.2/[(T/\text{K}) - 47.79] \qquad (1)$$

TABLE 1

Comparison of the vapour–liquid equilibrium values of acetone

Author	T_b [a] (K)	P(298.15 K) (kPa)	P(318.15 K) (kPa)
Zmaczynski [9]	329.281	30.661 [b]	68.178 [b]
Brown and Smith [7]	329.21	30.807	68.368
Jose et al. [10]			68.300
Ambrose et al. [8]	329.217	30.806	68.382
This work	329.21	30.707	68.356

[a] Normal boiling temperature.

[b] Calculated from the Antoine equation [11].

They agreed with those reported by Brown and Smith [7] from 29 to −33 Pa at 310–329 K and those by Ambrose et al. [8] from 111 to −31 Pa at 285–329 K. Comparison with the best published values is made in Table 1. Although Zmaczynski [9] used a precise method of comparative ebulliometry, his values are smaller than others. Considering the values of his densities obtained before and after ebulliometry [9], this might arise from slight absorption of moisture into acetone from the reference ebulliometer which was connected to the measuring ebulliometer only by a simple $CaCl_2$ tube.

Hexamethyldisilane

The vapour pressure determined for samples I and II are tabulated in Table 2 and shown in Fig. 2. Since sample I contained some impurities and had a larger refractive index and higher boiling point as mentioned above,

TABLE 2

Vapour pressure P of hexamethyldisilane: $\Delta P = P(\text{obs.}) - P(\text{calc.})$, where P(calc.) has been obtained from eqn. (2)

T (K)	P (kPa)	ΔP (Pa)	T (K)	P (kPa)	ΔP (Pa)	T (K)	P (kPa)	ΔP (Pa)
Sample I								
306.36	5.725	−61	346.79	30.040	−96	381.89	91.015	146
312.85	7.778	−29	362.95	51.497	−175	386.05	101.712	−271
321.66	11.406	−49	373.75	71.623	−255			
341.07	24.685	143	379.10	84.186	223			
Sample II								
304.61	5.305	−17	332.69	17.868	−25	385.65	101.042	171
309.16	6.607	10	356.35	41.771	23	386.74	103.998	73
317.01	9.409	22	384.50	97.468	−257			

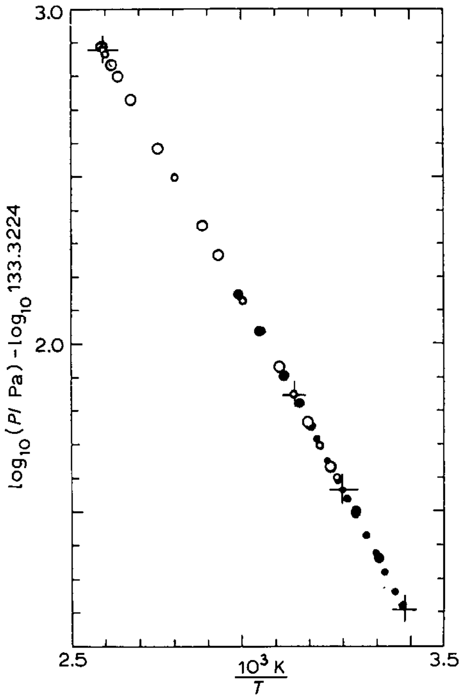

Fig. 2. Vapour pressure of hexamethyldisilane: (O) sample I; (o) sample II; (●) Brockway and Davidson [14]; (•) Suga and Seki [15]; (+) calculated from eqn. 2.

the values determined for sample II were fittted by the method proposed by Willingham et al. [12] to the Antoine equation:

$$\log_{10}(P/\text{kPa}) = 5.97097 - 1319.85/\{(T/\text{K}) - 52.96\} \tag{2}$$

with the calculated standard deviation of the fit:

$$S_f = \left\{\sum(\Delta P)^2/(n-k)\right\}^{1/2} = 143 \text{ Pa} \tag{3}$$

where $k = 3$. The normal boiling point is 385.81 K* and $(\mathrm{d}P/\mathrm{d}T)_{101.3250\text{kPa}}$ is 2780.0 Pa K^{-1}. The values obtained for sample I are on average ca. 42 Pa smaller than those for sample II. The agreement of the present values with two series of published values at low temperatures [13,14] is good, as shown in Fig. 2.

Combining the Clapeyron–Clausius equation and the Antoine equation, the molar enthalpy of evaporation is calculated from the equation:

$$\Delta_v H_m = 2.3026BPT \cdot \Delta V_m/(T-C)^2 \tag{4}$$

where

$$\Delta V_m = V_m(\text{g}) - V_m(\text{l}) \tag{5}$$

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* A deviation of 143 Pa corresponds to a deviation of 0.05 K at normal boiling point.

TABLE 3

Molar enthalpies of evaporation determined from eqn. (6), molar entropies of evaporation calculated by $\Delta_v H_m/T$, and literature values

T (K)	$\Delta_v H_m$ (kJ mol^{-1})	$\Delta_v S_m$ (J K^{-1} mol^{-1})
385.81 [a]	33.9	88.0
313.90 [b]	36.6	116
299.00 [b]	37.3	125
293.45–334.35	36.8 [c]	
287.65–310.35	37.2 [d]	

[a] Normal boiling point.

[b] Middle temperature of the literature data.

[c] Brockway and Davidson [14].

[d] Suga and Seki [13].

When $\Delta V_m = RT/P$ is approximately valid, eqn. (4) becomes

$$\Delta_v H_m = 2.3026BRT^2/(T-C)^2 \quad (6)$$

The molar enthalpies of evaporation determined by eqn. (6) are compared with the published values in Table 3. The enthalpies determined here agree with the published ones at each temperature. The calculated values of the molar entropy of evaporation show that this compound is a typical, normal liquid.

By a survey of the literature 2,3,3-trimethylpentane [12] was found to have a very similar set of Antoine parameters to the present compound, i.e.

$$\log_{10}(P/\text{kPa}) = 5.96843 - 1328.046/\{(T/\text{K}) - 52.775\}$$

and (7)

$$T_b = 387.91 \text{ K}$$

The molar enthalpy and entropy of evaporation are calculated to be 34.06 kJ mol^{-1} and 87.8 J K^{-1} mol^{-1}, respectively, at the normal boiling point. The similarity of the Antoine equations and the derived thermodynamic properties may arise from the resemblance between molecular surfaces of both compounds. The Si–Si core of hexamethyldisilane is surrounded by six methyl groups. The C(2)–C(3) core of 2,3,3-trimethylpentane is surrounded by five methyl groups, a CH_2 group and an H atom. Both molecules may vibrate in a very similar fashion in the liquid phase.

ACKNOWLEDGEMENT

This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan.

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