

Short Communications

THE VAPOUR PRESSURES OF SEVERAL METAL-2,2,6,6-TETRAMETHYL-3,5-HEPTANEDIONE COMPLEXES MEASURED BY A KNUDSEN EFFUSION METHOD

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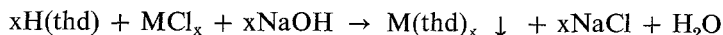
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The melting points, vapour pressures and heats of sublimation of the complexes of Ga, In, Y, La, Gd, Fe, Zn, Pb and Li with 2,2,6,6-tetramethyl-3,5-heptanedione are reported for the temperature range below the melting point of 40° to 250°C and pressures from 10 to 10⁻² torr. The measurements were made with an easily constructed Knudsen effusion cell in conjunction with a Mettler thermobalance.

In this communication, the vapour pressures and heats of sublimation are presented for a number of metal complexes of the ligand 2,2,6,6-tetramethyl-3,5-heptanedione (Hthd) in the pressure range 10 to 10⁻² torr and for temperatures up to the melting point. These compounds are of considerable interest due to their relatively high volatility particularly for rare earth and alkali metals where the occurrence of volatile compounds is rare. Sicre et al. [1] have measured the vapour pressures of the lanthanide chelates of Hthd, two of which have been measured in the present work and are included for comparison.

The Knudsen effusion technique [2, 3] was employed in which a simple design of effusion cell was used in conjunction with a Mettler thermobalance [4]. A thermobalance is very suitable for this method since the rate of weight loss through the calibrated orifice can be observed whilst the experiment is in progress. Recently, Wiedemann and Vaughan [5] described a refined apparatus for the measurement of vapour pressures in the range 1 to 10⁻⁶ torr and temperatures from -100° to +250°. The operating range of our system was from 10 to 10⁻² torr and 40° to 250°. The upper pressure limit was fixed by the minimum available orifice size which kept the weight loss within measurable limits and the upper temperature was limited by the O-ring (see below). The lower pressure limit was fixed by the vacuum of the chamber surrounding the effusion cell; in this case only a rotary pump was available which limited the pressure to 10⁻³ torr.

The compounds were prepared by reacting the ligand, sodium hydroxide and the metal chloride in a 50 per cent alcohol/water solution for about 3 hours.



After filtration, the compound was dried and purified by vacuum sublimation. Since the gallium, indium and lead compounds had not been reported in the literature, they were analysed by oxidation with nitric acid followed by ignition to

Ga_2O_3 , In_2O_3 or PbO_2 , respectively; valencies of 3, 3 and 2, respectively, were established for the metals in the compounds.

The effusion cell is shown schematically in Fig. 1. The substance under investigation is contained in an aluminium crucible the top of which is sealed with a screw cap and a diaphragm, made from 12.5 micron nickel foil. The temperature of the sample is measured with a chromel/alumel thermocouple which is sealed into the cell by a Viton O-ring and its associated screw fitting. This thermocouple takes the place of the normal thermobalance thermocouple and serves to support the cell on the balance mechanism. The furnace temperature is controlled by a separate chromel/alumel thermocouple and a temperature controller.

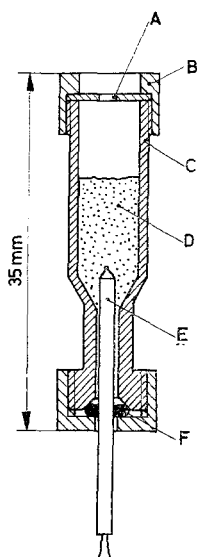


Fig. 1. Knudsen effusion cell for use with the Mettler thermobalance. *A* — Ni foil; *B* — screw cap; *C* — Al crucible; *D* — substance; *E* — thermocouple; *F* — "Viton" O-ring

To carry out a vapour pressure determination, the thermocouple was first inserted and fixed in position in the cell by means of the Viton O-ring. The sample (ca. 500 mg) was then loaded into the cell which was afterwards sealed by the screw cap and nickel foil. Next, the cell and thermocouple were placed in position on the thermobalance and heated to above the melting point of the sample. If no weight loss was observed over a 40 minute period this showed that the seal between foil and cap was gas tight. The cell and thermocouple were removed from the balance and a hole was pierced in the nickel foil with a fine needle. In this way, a hole of approximately 100 microns effective diameter could be formed. The cell was then replaced in the balance and the rate of weight loss was measured at a number of fixed temperatures over the desired temperature range.

Values of the equilibrium vapour pressure were calculated from the ideal Knudsen equation assuming that the molecular weight of the compounds is the same in the vapour as in the solid

$$P = \frac{\Delta m}{\Delta t} \cdot \frac{1}{A} \frac{(2\pi RT)^{\frac{1}{2}}}{M}$$

where P = vapour pressure in dyne cm^{-2}

$\frac{\Delta m}{\Delta t}$ = rate of weight loss in $\text{g} \cdot \text{sec}^{-1}$

A = orifice area

R = gas constant (8.314×10^7 erg $^{\circ}\text{C}^{-1}$ mole $^{-1}$)

T = temperature in Kelvin

M = molecular weight

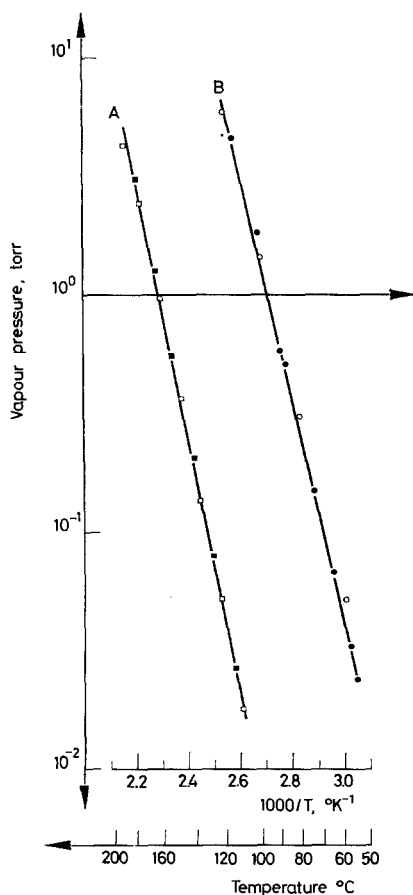


Fig. 2. Clausius-Clapeyron plots. Curve *A*: $\text{Ga}(\text{thd})_3$, \blacksquare Run 1, \square Run 2; Curve *B*: Benzoic acid, \bullet measured, \circ literature [6]. Solid line: Least squares fit to the measured points

The area of the effusion orifice was determined photographically from its area on a photomicrograph. Constants A and B were determined by a least squares fit of the measured data (typically twelve points) to the equation:

$$\log_{10} P = A - \frac{B}{T}$$

which was found to be sufficiently accurate by Wiedemann and Vaughan [5] over small ranges of temperature.

The results obtained for one known substance (benzoic acid) and one unknown substance (gallium 2,2,6,6-tetramethyl-3,5-heptanedionide) are shown in Fig. 2. The reproducibility of the technique is illustrated by curve A for $\text{Ga}(\text{thd})_3$. From the value of B , an estimate of the heat of sublimation ΔH_s was obtained from the equation

$$\log_{10} P = \frac{-\Delta H_s}{2.303 RT} + \text{constant}$$

$$\text{ie } \Delta H_s = -4.576 B \text{ calories per mole.}$$

The results are summarized in the Table 1 which gives values for A and B , the heat of sublimation and the melting point.

Table 1

Values for the constants of the equation $\log_{10} P = A - B/T$, the melting point and heat of sublimation for the metal-thd complexes

Compound	Melting point, °C	A	B	H_s , kcal/mole
Ga (thd) ₃	228–231	12.2	5334	24.4
In (thd) ₃	172–173	15.6	6740	30.9
Y (thd) ₃	174–176	154	6831	31.3
La (thd) ₃ *	290–216	17.5 (15.1)	8578 (7498)	39.3 (34.31)
Gd (thd) ₃ *	183–185	18.8 (18.6)	8549 (8427)	39.1 (38.6)
Fe (thd) ₃	166–167	12.8	5581	25.5
Zn (thd) ₂	133–145	17.5	7093	32.5
Pb (thd) ₂	131–133	8.4	3875	17.7
Li (thd)	283–285	18.2	9112	41.7

* Values reported in reference [1] are shown in parentheses. The maximum error in the measured values of vapour pressure is estimated to be about 5% in the 10^{-2} torr range and 0.5% in the 1 torr range.

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References

1. J. E. SICRE, J. T. DUBOIS, K. J. EISENTRAUT and R. E. SIEVERS, *J. Am. Chem. Soc.*, 91 (1969) 3476.
2. M. KNUDSEN, *Ann. Phys.*, 28 (1909) 999.
3. M. KNUDSEN, *Ann. Phys.*, 29 (1909) 179.
4. H. G. WIEDEMANN, *Chem. Ing. Techn.*, 11 (1964) 1105.
5. H. G. WIEDEMANN and H. P. VAUGHAN, *Proc. 3rd Toronto Symp. on Thermal Analysis*, 1969 p. 233.
6. S. KLOSKEY, L. WOO and R. J. FLANNIGAN, *J. Am. Chem. Soc.*, 49 (1927) 1280.