

62. *The Vapour Pressures of Lead Iodide and Neodymium Tricyclopentadienide.*

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The vapour pressure of lead iodide has been precisely determined over the temperature range 290—340°. Niwa's results are critically examined. The heat of sublimation of lead iodide is found to be 37.98 ± 0.39 kcal. mole⁻¹. By use of the same apparatus, that of neodymium cyclopentadienide was found to be 23.5 ± 3.5 kcal. mole⁻¹.

In an investigation of the β -decay of ¹⁴⁴Ce-labelled cerium tricyclopentadienide in the gas phase¹ the vapour pressure of the very reactive carrier material, neodymium tricyclopentadienide, was determined by the Knudsen effusion technique² in a modification of the apparatus designed by O'Donnell.³ The apparatus was calibrated with lead iodide, a material which is easily prepared in a state of high purity; the vapour pressure of lead iodide was determined by Niwa.⁴

EXPERIMENTAL

Materials.—Lead iodide was prepared by adding a slight excess of "AnalaR" 2M-hydriodic acid to a 10% aqueous solution (200 ml.) of twice recrystallized lead nitrate. The supernatant liquid was decanted and the lead iodide digested with 0.5% hydriodic acid (200 ml.) for 1 hr., filtered hot, and washed thoroughly with hot distilled water. The product was dried under a vacuum at 150° for 24 hr.

Neodymium tricyclopentadienide was prepared by a method similar to that of Wilkinson and Birmingham,⁵ by treating anhydrous neodymium bromide with potassium cyclopentadienide in tetrahydrofuran under nitrogen. The solvent was removed by distillation and the crude neodymium cyclopentadienide, obtained by sublimation from the crude products at 250°/10⁻³ mm., was resublimed.

Vapour-pressure Apparatus.—The assembly was modified for our work from that constructed by O'Donnell.³ It consisted essentially of a steel cavity (3.2 cm. in diameter, 3.2 cm. deep) drilled into a steel block, A (7 cm. in diameter, 6.35 cm. high) into which a sample of the working

¹ Duncan and Thomas, unpublished work.

² Knudsen, "The Kinetic Theory of Gases," Methuen, London, 3rd edn., 1950; *Ann. Phys.*, 1909, **28**, 75, 999.

³ O'Donnell, *Austral. J. Chem.*, 1955, **8**, 485, 493; Ph.D. Thesis, Melbourne, 1953.

⁴ Niwa, *J. Fac. Sci. Univ., Tokyo*, 1940, Series III, **3**, 17.

⁵ Wilkinson and Birmingham, *J. Amer. Chem. Soc.*, 1954, **76**, 6210; 1956, **78**, 42.

substance was introduced in a glass cell (see Figs. 1 and 2). The cell cavity was covered by a removable steel plate, B (0.48 cm. thick) which had its upper surface polished and its lower surface dull. A hole (0.64 cm. in diameter) was drilled through the centre of this plate. The furnace block was supported in the centre of the cylindrical brass vacuum-chamber C, by the ceramic ring, D, and heated by the "Nichrome" resistance-tape windings, M, which were insulated from the block by, and covered with, glass cloth 0.0075 cm. thick. The power leads were introduced at N and N' through vacuum-seals.

The temperature of the furnace block was measured by a chromel-alumel thermocouple introduced into the vacuum-chamber at E through the wax and glass seal F. The hot junction was hammered flat and clamped to the furnace block by a steel plate at G. The cold junction was maintained at 0° and the thermal E.M.F. measured to ± 0.01 mv with a Pye potentiometer, type 7569P. The thermocouple was calibrated at the boiling points of water (100°) and sulphur (444.8°/762.1 mm. Hg.) and the melting points of "AnalaR" tin (231.9°) and cadmium (320.9°).

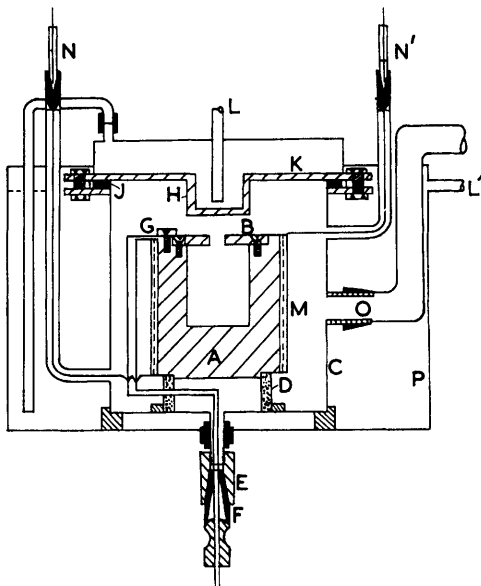


FIG. 1. The apparatus. For key see text.

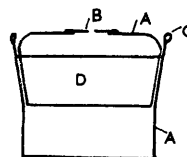


FIG. 2. The effusion cell. A, glass; B, platinum; C, glass eyelets for attaching copper wire carrier; D, ground glass joint.

The vacuum chamber, C, was surrounded by a cooling bath, P, and fitted with a removable bronze cover-plate, H, to which the cooling head, K, was soldered. Cold water entered at L, passed through the cooling head, K, and cooling tank, P, and flowed out at L'. The gasket, J, cut from 0.48 cm. thick "Hycar O.R. 15" rubber, was lightly coated with "Apiezon T" grease to give an airtight seal when compressed between the cover-plate and the flange attached to the vacuum-chamber. The vacuum-chamber was connected to the vacuum-system at O by means of a standard B29 brass cone waxed into a glass socket.

The effusion cell used for the vapour-pressure measurements of lead iodide (Fig. 2) consisted of a glass base, 2.0 cm. in diameter, with ground, tapered sides into which fitted a glass lid with a hole, 1.0 cm. in diameter, in the top. The lid and base were ground to ensure a tight fit. A piece of platinum foil (0.055 mm. thick) was fused to the glass over the opening in the lid and an orifice was drilled in the centre of the platinum. The orifice was studied by optical enlargement (109-fold magnification) and found to be practically circular, with an area of 8.68×10^{-2} cm.², and a mean radius of 5.26×10^{-2} cm. The effusion cell was transferred to and from the furnace with the aid of a copper wire carrier which hooked through the eyelets attached to the upper edge of the base of the cell.

Calibration of Apparatus.—The vapour pressure of lead iodide was determined by a gravimetric technique which eliminated the use of the shield, shutter, and target employed by O'Donnell. The effusion cell containing about 3 g. of lead iodide was weighed on a microbalance (sensitivity 5 μ g) and placed in the furnace. The plate B, the thermocouple hot junction and

the cover-plate H were screwed into place and the system evacuated. To eliminate the slight darkening of lead iodide which occurred in air, nitrogen was admitted to the system through an inlet on the main vacuum-manifold to a pressure of 6.0 cm. Hg. Water was passed through the cooling system and the furnace heated to the required temperature. The furnace was kept at this temperature for 15 min. and the residual nitrogen was pumped out. The pressure was maintained at 10^{-5} mm.² with the temperature constant to $\pm 0.2^\circ$ throughout the experiment, the duration of which was noted. Effusion of lead iodide was stopped by introducing nitrogen to the system to a pressure of 10 cm. (A trial run, in which the above procedure was performed throughout with a nitrogen pressure of 6 cm. Hg. and a temperature of 350° maintained for 2 hr. showed that the weight of the cell and contents decreased by only 8 μ g.) The furnace was allowed to cool and the cell removed and weighed. From the loss in weight, the time of the run, and the temperature and the characteristics of the cell, the vapour pressure of lead iodide was calculated. Nine determinations of the vapour pressure of lead iodide were made in the temperature range 290 — 340° with this sample, the temperature decreasing in successive experiments throughout the series. A fresh charge of lead iodide was then placed in the cell and four more determinations of the vapour pressure were made at 290° , 310° , 320° , and 340° , in that order.

Vapour Pressure of Neodymium Tricyclopentadienide.—This was determined in the temperature range 170 — 200° by a similar method. The microbalance was assembled in a nitrogen-filled glove-box. The effusion cell was transferred from the glove-box to the furnace in a 600-ml. nitrogen-filled, stoppered beaker, during which process, a steady stream of nitrogen was passed through the vapour pressure apparatus from the vacuum line *via* O. The constancy of the blue colour of the neodymium tricyclopentadienide during these operations was used as a sign that decomposition was insignificant.

RESULTS AND DISCUSSION

Vapour Pressure of Lead Iodide.—The results of these measurements are given in Table 1 and are plotted in Fig. 3. The vapour pressure was calculated by using the Knudsen relationship,² modified by Clausing⁶ for orifices of finite thickness:

$$p = \frac{G}{wat} \left[\frac{2RT}{M} \right]^{\frac{1}{2}}, \quad (1)$$

where p is the vapour pressure in dyne cm.⁻², G is the weight in g. of the vapour of molecular weight, M , in equilibrium with its condensed phase at an absolute temperature, T , which passes through an orifice of area a cm.² into an evacuated space in a time t sec.; R is the gas constant; and

$$w = 1/[1 + 0.5(l/r)] \quad (2)$$

is the Clausing probability factor, *i.e.*, the probability that a molecule impinging on an orifice of radius r cm. and length l cm. will pass right through without striking the orifice walls. For the effusion cell used in this work, $w = 0.950$. Insertion of physical data, etc., into equation (2) gives

$$p = 2.080 \times 10^3 (G/t)(T/M)^{\frac{1}{2}}, \quad (3)$$

where p is now in mm. Hg.

The relationship between $\log_{10} p$ and $1/T$, determined from the results by the method of least squares, was found to be

$$\log_{10} p \text{ (mm. Hg.)} = -8304/T + 11.4860; \quad (4)$$

from which the heat of sublimation of lead iodide in the temperature range 290 — 340° is $H_s = 37.98$ kcal. mole⁻¹ with a standard error of 0.39 kcal. mole⁻¹.

The only other values reported for the vapour pressure of lead iodide in this temperature range are those of Niwa,⁴ also plotted in Fig. 3, for which

$$\log_{10} p \text{ (mm. Hg.)} = -8288/T + 11.002, \quad (5)$$

⁶ Clausing, *Ann. Phys.*, 1932, **12**, 961.

and $H_s = 37.9 \pm 0.5$ kcal. mole⁻¹ are quoted. While the slope of the plot of $\log_{10} p$ against $1/T$ obtained from this work agrees very well with that obtained by Niwa, the vapour pressures are greater than Niwa's by a factor of about 2.8. There are two features which could explain the discrepancy.

(a) *Finite thickness of the orifice.* In calculating the vapour pressure of lead iodide Niwa did not use the Clausing probability correction for the finite thickness of the orifice, which was ground through the quartz lid of the effusion cell.^{4,7} We were unable to grind such an orifice with a wall thickness less than 0.2 mm. without the orifice becoming irregular in shape owing to crumbling of its edges. If the thickness of the orifice (radius 0.426 mm.)

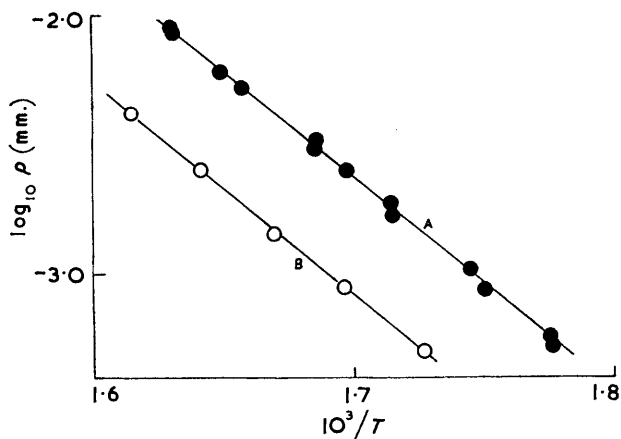


FIG. 3. $\log_{10} p$ as a function of $1/T$ for lead iodide. A, this work; B, Niwa's results.

TABLE I.
Vapour pressure of lead iodide.

Temp. (T) (K)	$10^3/T$	G (10^{-3} g.)	t (sec.)	p (10^{-3} mm.)	$\log_{10} p$
Series 1.					
613.2°	1.631	13.72	3760	8.752	-2.0579
606.2	1.650	12.14	4995	5.919	-2.2278
603.2	1.658	12.86	5860	5.220	-2.2823
593.2	1.686	9.77 ₂	7330	3.14 ₅	-2.5024
589.2	1.697	7.78 ₆	7325	2.49 ₉	-2.6022
583.2	1.715	4.67 ₄	5820	1.87 ₉	-2.7260
573.2	1.745	4.09 ₃	9305	1.02 ₁	-2.9909
571.2	1.751	3.32 ₂	9015	0.853	-3.0691
563.2	1.776	2.06 ₈	8760	0.542	-3.2659
Series 2.					
563.2	1.776	2.52 ₂	10,450	0.556	-3.2552
583.2	1.715	4.78 ₉	6680	1.67 ₇	-2.7755
593.2	1.686	7.10 ₈	5195	3.22 ₈	-2.4911
613.2	1.631	25.30	7020	8.644	-2.0633

used by Niwa in his determination of the vapour pressure of lead iodide were 0.25 mm., then the Clausing probability factor would be about 0.77; *i.e.*, the vapour pressures calculated by Niwa without this correction could well be about 30% low.

(b) *Temperature measurement.* Probably the greatest source of the difference in the two sets of vapour-pressure measurements arises from the difficulties of measuring accurately the temperature of the cell and, particularly, of the orifice. In work with the original apparatus O'Donnell found³ that (i) the vapour pressure of zinc at a given block temperature was only 40% of the accepted value when the cover-plate through which the orifice was

⁷ Niwa, *J. Fac. Sci. Univ., Tokyo*, 1938, Series III, 2, 183.

drilled was 0.16 cm. thick steel plate, and (ii) the orifice temperature was 20–30° less than the block temperature. When the thickness of the cover-plate was 0.48 cm. these discrepancies were eliminated. Thus, if the orifice temperature were lower than the cell temperature, condensation of the vapour of the working substance about the orifice would occur and result in a low apparent vapour pressure.

In Niwa's apparatus the hot junction of the thermocouple was not in contact with the cell; and the cell and the thermocouple were heated independently by radiation from the furnace windings outside the evacuated tube in which the cell was suspended. They would be expected to absorb heat with different efficiencies, and because of the poor thermal conductivity of quartz a temperature differential of 10–15° might well have resulted. This would cause Niwa's results to be low by 40–55%.

In the current work, the effusion cell was completely surrounded by the furnace block and occupied most of the volume of the cavity, so that it was heated by both conduction and radiation. The temperatures of the orifice and of the glass cell (base) were compared with that of the block (at various temperatures) with the aid of a second calibrated thermocouple, both when the apparatus was evacuated and when it was filled with nitrogen at a pressure of 10 cm. Hg. It was found in all cases that, when the block temperature was steady, it was the same as the cell temperature ($\pm 0.25^\circ$) and the orifice temperature ranged from that of the block to a maximum of 1° below that of the block.

From these considerations we conclude that the values of the vapour pressure of lead iodide obtained in this work are more accurate than those previously reported by Niwa, and that the apparatus was reliable enough for determination of the vapour pressure of neodymium tricyclopentadienide.

Vapour Pressure of Neodymium Tricyclopentadienide.—By use of the same cell as for lead iodide, the values obtained for the vapour pressure of neodymium tricyclopentadienide

TABLE 2.

Vapour pressure of neodymium tricyclopentadienide.

Temp. (T) (K)	$10^8/T$	G (10^{-3} g.)	t (sec.)	p (10^{-3} mm.)	$\log_{10} p$
473.2°	2.114	13.89	7240	4.48	–2.349
473.2	2.114	11.03	7400	3.50	–2.456
473.2	2.114	10.15	6230	3.81	–2.419
463.2	2.159	7.93	6660	2.75	–2.561
443.2	2.257	3.64	11,210	0.733	–3.135

were as given in Table 2. The relatively poor reproducibility of the results at 200° ($\pm 12\%$), compared with that for lead iodide, is probably due to a small amount of decomposition of the blue neodymium tricyclopentadienide although this was not visually apparent. The mean value of the vapour pressure at 200° is $(3.93 \pm 0.60) \times 10^{-3}$ mm. Hg. Using the values of the vapour pressure at 170° and 190° in conjunction with those at 200° gives the heat of sublimation of neodymium tricyclopentadienide as 23.5 ± 3.5 kcal. mole⁻¹.

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