The Vapour Pressure of Protactinium Pentabromide

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The vapour pressure of protactinium pentabromide, measured using a silica-membrane gauge, is represented by equations (*i*) and (*ii*). Interpretation of the experimental results yields the following thermodynamic parameters:

$$\ln P(\text{atm}) = (19{\cdot}27 \pm 0{\cdot}8) - (12\,399 \pm 44)(1/T)\ (491\text{—}556\ \text{K}) \qquad (i)$$

$$\ln P(\text{atm}) = (11{\cdot}61 \pm 0{\cdot}02) - (8\,136 \pm 13)(1/T)\ (556\text{—}635\ \text{K}) \qquad (ii)$$

$\Delta H_s = 103{\cdot}1 \pm 0{\cdot}4$ kJ mol^{-1}; $\Delta S_s = 160{\cdot}2 \pm 0{\cdot}8$ J K^{-1} mol^{-1}; $\Delta H_e = 67{\cdot}6 \pm 0{\cdot}1$ kJ mol^{-1}; $\Delta S_e = 96{\cdot}6 \pm 0{\cdot}4$ J K^{-1} mol^{-1}; $\Delta H_f = 35{\cdot}40 \pm 0{\cdot}4$ kJ mol^{-1}; and $\Delta S_f = 63{\cdot}6 \pm 0{\cdot}4$ J K^{-1} mol^{-1}. The extrapolated boiling point is 701 K.

LITTLE work has been reported on vapour pressures of protactinium compounds. Thus, apart from data on protactinium pentachloride [1] and some preliminary results on protactinium metal,[2,3] the only values available are those estimated by Brewer.[4] As part of a programme involving measurement of vapour pressures of protactinium penta- and tetra-halides we have obtained data on protactinium pentabromide. These data are now reported together with calculated values for the heats and entropies of sublimation, vaporisation, and fusion.

EXPERIMENTAL

All work with protactinium was carried out either in glove-boxes, or in a fume hood converted into a glove-box because of the α activity associated with the isotope ^{231}Pa. Quantities of ^{231}Pa in the range 50—100 mg were used for each experiment. The protactinium used in this work was part of a batch isolated in 1960.[5] Samples of protactinium pentabromide prepared as described earlier [6] were sealed in silica ampoules (N) which were attached to the vapour-pressure apparatus shown in Figure 1(*a*) at a · · · a. The apparatus was constructed entirely of silica with the exception of valve (G) and joint (H), which were made of Duran glass and joined to the silica by means of a graded seal (F). Alternatively, samples of protactinium pentabromide were made *in situ* using a combination of the apparatus shown in Figure 1(*a*) and (*b*). The apparatus shown in Figure 1(*b*) was constructed of Duran glass.

Transfer of Prefabricated $PaBr_5$ *to the Vapour-pressure Gauge.*—The ampoule [(N), Figure 1(*a*)] containing $PaBr_5$ was broken at the seal (P) and the pentabromide sublimed successively into bulbs (L) and (K), with the system connected to a vacuum line and being constantly pumped (empty portions being sealed at b · · · b and c · · · c, respectively, after each sublimation). Tube (I) was then sealed in the centre using a hydrogen–oxygen flame and

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[1] F. Weigel, G. Hoffmann, and N. Ter Meer, *Proc. 3rd Protactinium Conf.*, Mittenwald, Germany, April 1969, p. 18; *Radiochim. Acta*, 1968, **11**, 210.

[2] B. B. Cunningham, *Proc. Symposium sur les Elements Transuraniens*, Liège, Belgium, April 21—22, 1969, p. 10.

[3] B. B. Cunningham, R. Dod, and T. C. Parsons, as reported by B. B. Cunningham in ref. 1, p. 14.

[4] L. Brewer, ' The Chemistry and Metallurgy of Miscellaneous Materials,' ed. L. L. Quill, McGraw-Hill, New York, 1950, p. 201.

[5] N. Jackson, F. J. G. Rogers, and J. F. Short, Report AERE 3311, 1960.

[6] D. Brown and P. J. Jones, *J. Chem. Soc.* (*A*), 1966, 262.

the two ends sealed at e · · · e and f · · · f, respectively. Protactinium pentabromide was then sublimed successively from bulb (K) into (J) and then into the membrane bulb (A), d · · · d and h · · · h being sealed after the appropriate sublimation.

Preparation of Protactinium Pentabromide in situ.—The apparatus shown in Figure 1(*b*) was attached to that illustrated in 1(*a*) at (H). For this experiment, no break-seal was present in bulb (N) [Figure 1(*a*)] in which a mixture of protactinium penta-oxide and carbon (contained in a silica tube stoppered with silica wool) had been placed before it was sealed at the right-hand end. Prior to the preparation, trap (Z) was cooled with liquid nitrogen and the whole apparatus thoroughly flamed using a hand torch. Trap (Z) was then exchanged for a fresh trap; vessel (V) was filled with carbon tetrachloride, saturated with chlorine, through tube (X) which was then sealed at j · · · j. Boron tribromide, contained in a 30 cm³ syringe, was next injected into bulb (U) through (W) and (W) sealed at i · · · i.

Vessel (V) was cooled with liquid nitrogen, the system thoroughly evacuated, and valve (Y) then closed while (G) remained open. A tube furnace was placed around bulb (N) and heated to 500—550 °C. The liquid-nitrogen coolant was removed from around vessel (V) and the CCl_4–Cl_2 mixture allowed to warm up so that its vapour filled the system. Lemon-yellow crystals of protactinium pentachloride soon began to form in (M). When formation of $PaCl_5$ crystals had subsided, vessel (V) was recooled, the system evacuated, and (V) then rewarmed. Repeating this operation several times served to remove gaseous reaction products from the reaction zone and replace them by fresh carbon tetrachloride–chlorine. When all the protactinium penta-oxide originally contained in bulb (N) had been converted to the pentachloride and all the $PaCl_5$ had been collected in (M), (N) was sealed off at a · · · a. The $PaCl_5$ was then purified by subliming it to bulb (L), following which b · · · b was sealed.

At this point, vessel (V) was again cooled to the temperature of liquid nitrogen, the system evacuated, and (V) sealed at k · · · k. The break-seal (T) was opened by means of a magnet hammer contained in (S), while BBr_3 in bulb (U) was kept at the temperature of liquid nitrogen. The coolant was then removed, the BBr_3 allowed to warm up and its vapour admitted to the system. When the $PaCl_5$ contained in bulb (L) was sublimed to (K) in an atmosphere of BBr_3 it was quantitatively converted into $PaBr_5$, which formed as orange-red crystals in (K). After the $PaBr_5$ had been collected in (K), bulb (L) was sealed off at c · · · c. All succeeding operations were then the same as those described above for transfer of prefabricated $PaBr_5$, except that prior to the next sublimation all BBr_3 and other boron halides were condensed into bulb (U), which was sealed at l · · · l.

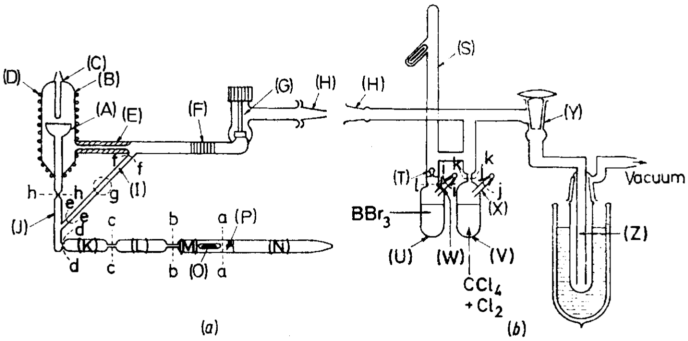

FIGURE 1 Side views of the apparatus used for: (*a*), transfer of $PaBr_5$ from bulb (N) to vapour-pressure gauge (A); and (*a*) and (*b*), preparation of $PaCl_5$ and $PaBr_5$ *in situ*

Vapour-pressure Measurements.—For the actual vapour-pressure measurement, a membrane bulb charged by one of the above procedures was assembled into the set-up shown in Figure 2(*a*). The lower part of (A) was placed inside the wall of a copper block (AA), and joint (H) was connected to mercury manometer (GG) and a vacuum manifold by means of flexible stainless-steel tubing (DD). A silica bell (C) was then placed over bulb (B) and a thermocouple inserted into the thermocouple tube attached to joint (C). Another thermocouple (II) was placed through a horizontal port in (AA) in such a manner that its hot joint was in contact with the lower end of (A). A quartz thermometer (CC) was used for calibration purposes. The sample could be observed through two ports (BB) which were closed by means of two quartz rods having optically polished ends. A laser beam (JJ) [Figure 2(*b*)] was directed onto the surface of membrane (A), its reflection being observed on a screen. Movement of the image (JJ′) served as a very sensitive indication of any deformation of the membrane (A) as shown. The laser beam thus provided an additional, optical, indicator of the ' clicking ' of the membrane described below.

The main heating coil wound on (AA) was slowly heated; at the same time, the auxiliary heating coil (D) around (B) was maintained at a temperature *ca*. 50 °C higher than that of (AA), thus preventing condensation of halide on the inner surface of membrane (A). When the system was heated the halide in (A) vaporised and pressure developed. This was counterbalanced by applying outside pressure in bulb (B). As soon as the pressure in (B) was higher by 41—43 Torr than that in (A), the membrane warped with a sharp ' click.' At the same time, the image (JJ′) of the laser beam jumped into a different position on the screen. The outside pressure in (B) was then slowly decreased until, when it was *ca*. 26—28 Torr higher than the pressure inside, the membrane again warped with an audible ' click,' and again the laser-beam image jumped to a different position. Pressure differences at which the ' clicks ' occurred were related to the true pressure inside (A) by the calibration procedure described below. Thus,

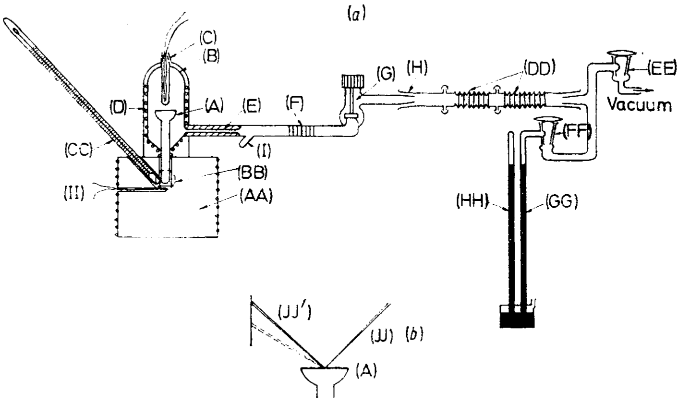

FIGURE 2 (*a*), Apparatus for vapour-pressure measurements; (*b*), illustration of laser-beam deflection each pressure value was determined by two independent measurements, using simultaneous acoustic and optic signals, respectively. Using the membrane in this manner as a zero instrument, quite accurate measurements of vapour pressures inside (A) are therefore possible by reading the counter pressure on manometer (GG), by means of a cathetometer, to the nearest 0·1 Torr.

Each experiment with $PaBr_5$ took *ca.* 1 day and 1 night; five independent samples were investigated.

Calibration of the Gauge.—Since the calibration of the membrane gauge was a somewhat complicated operation, the detailed procedure is given. The calibration, which consisted of two steps, was required prior to each vapour-pressure determination, since a new gauge was used each time. In the first step, pressure differences across the membrane, which caused the membrane to warp, were determined. In the second step the gauge was calibrated using mercury as the standard.

Pressure differences across the membrane were determined using the apparatus illustrated in Figure 3. These were measured at room temperature, *ca.* 200 and *ca.* 400 °C membrane temperature, at oil-pump vacuum and atmospheric pressure, because the pressure differences Δp and $\Delta p'$ causing the two different warps of the membrane were found to be dependent on membrane temperature and the absolute pressure.

After adjusting the temperature of jacket (C) (Figure 3) the whole system was evacuated. Then valve (LL) was closed and air was admitted to bulb (B) until an audible ' click ' and a jump of the laser-beam image were observed. The pressure required to bring this about was read at manometer (MM) with an accuracy of better than 0·1 Torr. By slowly turning valve (NN), bulb (B) was then slowly evacuated until another warp of the membrane was indicated. The pressure at (MM) was again read.

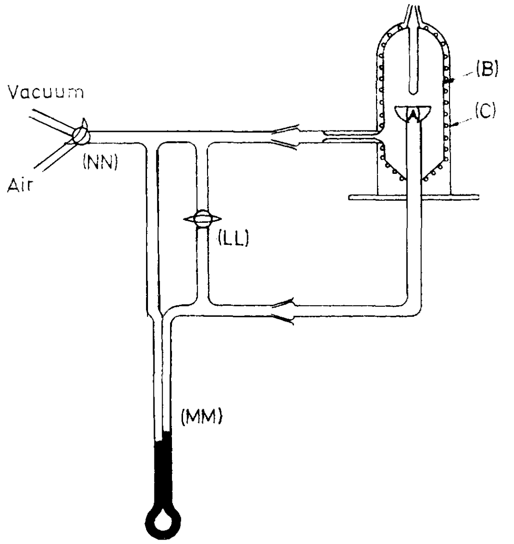

FIGURE 3 Apparatus for calibration of membrane gauge

[It should be noted that, when the second ' click ' was observed, there was still a slight overpressure of air in bulb (B) and the interior of (A) was still evacuated.]

The system was then filled to atmospheric pressure with air, while valve (LL) remained open. The pressure was slowly reduced to *ca.* 50 Torr below atmospheric pressure. Valve (LL) was then closed and air slowly admitted through (NN) until membrane (A) warped with a ' click.' Again, air was slowly evacuated through (NN) until the second warp of the membrane was observed. In each case, the necessary pressure differences were read at (MM). The whole procedure was then repeated at temperatures in the vicinity of 200 and 400 °C, then again in reverse order of temperature to ensure that no thermal deformation of the membrane had occurred. This was necessary because thermal flow of the membrane was observed above 550 °C.

The results of the calibration were then plotted in the manner shown in Figure 4, *i.e.* Δp and $\Delta p'$ were plotted against membrane temperature and absolute pressure. These curves were used to reduce measured pressures from vapour-pressure experiments to their true values. Pressures given in Tables 1 and 2 of Supplementary Publication No. SUP 21004 (3 pp.) * are averages from measurements at the two warp positions of the membrane. In the ideal case, the two measurements should yield identical values for the true pressure at a given temperature.

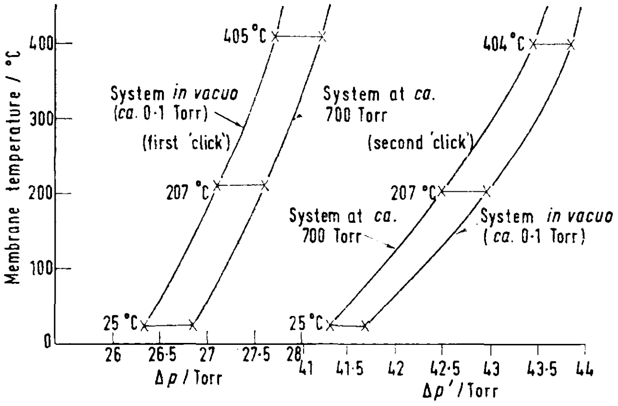

FIGURE 4 Calibration curves for membrane gauges

RESULTS AND DISCUSSION

Preliminary measurements on protactinium pentabromide showed that glass-sickle gauges of the type used for measurements on protactinium pentachloride[1] were unsuitable. Such gauges invariably shattered in the concave part of the gauge which was under constant mechanical strain during the experiment, probably due to attack by the pentabromide vapour. Similar sickle gauges constructed of silica also proved to be unsuitable, being either too fragile or insensitive. It was therefore necessary to develop the all-silica gauge described in the Experimental section, which is similar to the glass gauge used by Smith and Taylor.[7] The all-silica gauge proved to be suitable for the experiments with protactinium pentabromide, being extremely sturdy, very sensitive, and reliable.

Experimental results for solid and liquid protactinium pentabromide are listed in SUP 21004 and are plotted

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, **1973**, Index issue (items less than **10** pp. are supplied as full-size copies).

[7] D. F. Smith and N. W. Taylor, *J. Amer. Chem. Soc.*, **1924**, **46**, 1393.

in Figure 5 where they are compared with data available[8] for tantalum pentabromide. Comparison with actinoid-(V) bromides is not possible since the only other one known, UBr_5,[9,10] is unstable above 80 °C. The results for solid and liquid protactinium pentabromide are represented, respectively, by equations (1) and (2).

$$\ln P(\text{atm}) = (19{\cdot}27 \pm 0{\cdot}08) - (12\,399 \pm 44)(1/T) \quad (491\text{—}556\ \text{K}) \quad (1)$$

$$\ln P(\text{atm}) = (11{\cdot}61 \pm 0{\cdot}02) - (8\,136 \pm 13)(1/T) \quad (556\text{—}635\ \text{K}) \quad (2)$$

The position of intersection of the plots for liquid and solid pentabromide indicates a melting point for $PaBr_5$ of 556 ± 3 K (283 ± 3 °C), which is somewhat lower than the value predicted by Brewer[4] (600 K). The extrapolated boiling point is 701 ± 3 K. Thermodynamic parameters calculated from the vapour-pressure results are compared with those predicted by Brewer[4] in the Table.

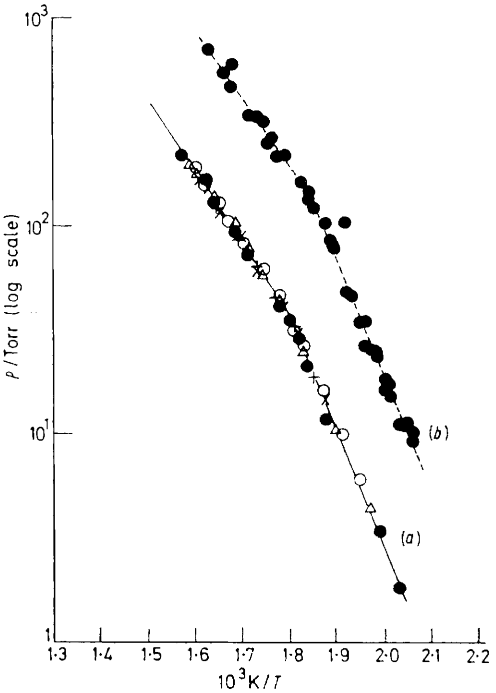

FIGURE 5 Vapour-pressure curves for (*a*) $PaBr_5$ (5 runs) and (*b*) $TaBr_5$ (from ref. 8)

Thermodynamic parameters for $PaBr_5$

ΔH_s/kJ mol^{-1}	103·1 ± 0·4 (113)
ΔS_s/J K^{-1} mol^{-1}	160·2 ± 0·8 (159)
ΔH_e/kJ mol^{-1}	67·6 ± 0·1 (75)
ΔS_e/J K^{-1} mol^{-1}	96·6 ± 0·4 (96)
ΔH_f/kJ mol^{-1}	35·4 ± 0·4 (38)
ΔS_f/J K^{-1} mol^{-1}	63·6 ± 0·4 (63)

s = Sublimation, e = vaporisation, and f = fusion. Predicted values of the parameters (from ref. 4) are given in parentheses.

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[8] E. L. Wiseman and N. W. Gregory, *J. Amer. Chem. Soc.*, 1949, **71**, 2344.

[9] F. Lux, G. Wirth, and K. W. Bagnall, *Chem. Ber.*, 1970, **103**, 2807.

[10] A. Blair and H. Ihle, *J. Inorg. Nuclear Chem.*, 1973, **35**, 3795.