386. *The Vapour Pressure of Plutonium Tetrafluoride.*

By C. J. Mandleberg and D. Davies.

The vapour pressure of plutonium tetrafluoride has been measured by Knudsen's effusion method, as modified by Phipps *et al.* Between 700° and 1200° c, the vapour pressure can be represented by $\log_{10} p$ (mm. Hg) $= 5\cdot58 - 10{,}040/T$; above 1200° a more volatile species occurs, whose vapour pressure can be represented by $\log_{10} p$ (mm. Hg) $= 36\cdot1 - 54{,}180/T$. Above 1200° the residue remaining in the effusion pot is plutonium trifluoride and it is tentatively suggested that the species effusing above 1200° is the pentafluoride.

Phipps *et al.*[1] describe an elegant method of determining the vapour pressure of radioactive substances in which they use a modification of the classical Knudsen effusion method. In the latter, vapour effuses for a definite time from an oven maintained at a constant temperature, and the mass of the material which has effused is determined by weighing the oven before and after the experiment. The vapour pressure at the temperature is calculated from Knudsen's formula.

The modification enables a known fraction of the effusing material to be collected on a counting tray. The total amount effused is determined by normal counting of the activity collected during the time of the experiment. The vapour pressures of plutonium trifluoride, trichloride, tribromide, and dioxide, and metallic americium were measured by Phipps, and other workers have measured the vapour pressures of other compounds, for instance, beryllium oxide,[2] by similar techniques.

The method is fully described in the literature and only those points which directly concerned the design of our apparatus will be discussed here.

The spatial distribution of molecules which flow into an evacuated space through a small hole in an infinitely thin boundary was discussed by Knudsen,[3] and Clausing [4] has extended the treatment to a finite boundary where the hole resembles a short tube. The spatial distribution of the molecules does not affect the total number effusing from such a hole in unit time, or the validity of the classical Knudsen effusion method. Clausing shows that, where the length of the hole L is twice the radius r, then, at an angular displacement of 5°, the number of molecules entering into an element of unit volume is 0·9444 of that predicted by the cosine law. Although there is disagreement (cf. Mayer [5]) about the magnitude of this departure from the cosine law, such departure will be a minimum when

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[1] Phipps, Sears, Seifert, and Simpson, NNES XIVb paper 6.1a; Phipps, Sears, and Simpson, *ibid.*, 6.1b; Erway and Simpson, A.E.C.D. 2733 (1948).

[2] Erway and Seifert, M.D.D.C. 9030 (1946).

[3] Knudsen, *Ann. Phys.*, 1909, **28**, 75; 1909, **29**, 179.

[4] Clausing, *Z. Phys.*, 1930, **66**, 471.

[5] Mayer, *Z. Phys.*, 1928, **52**, 235; 1929, **58**, 373.

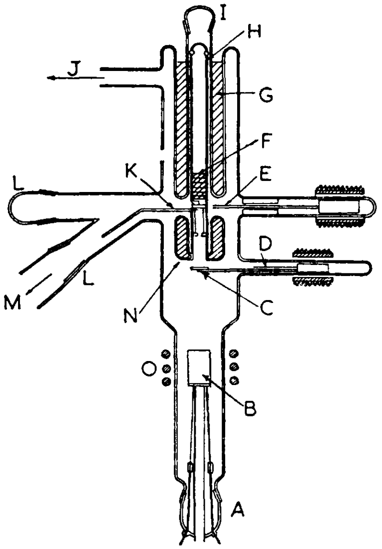
(*a*) the thickness of the boundary is not large compared with the diameter of the orifice and (*b*) the diameter of the collimator subtends a small angle at the orifice.

Since the validity of the cosine law is assumed in this work, conditions (*a*) and (*b*) were of prime importance in designing the apparatus. In every case $L < r/4$ and the angle subtended by the collimator was about 2°. Thus departure from the cosine law could be safely assumed to be negligible.

EXPERIMENTAL

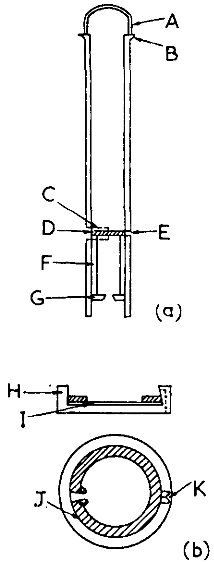
The apparatus (Fig. 1) was used for runs II—V; run I was made in one differing slightly from this design. Also in run I, the effusion oven was of nickel; tantalum ovens were used for the others. In the final form the apparatus consisted of a glass container in which the pressure could be reduced to *ca.* 10^{-6} mm. Hg. The tube was as narrow as possible in the region of the effusion pot to achieve the best linkage between it and the radiofrequency induction coil. Above this, the cassette magazine (Fig. 2a) was accommodated in a jacket holding liquid air. A shield could be moved across by means of an energised coil to control the times during which

FIG. 1. *Vapour-pressure apparatus.*



A, B50 *Cone and socket.* B, *Crucible surrounded by radiation shield.* C, *Vapour cut-off.* D, *Glass guides for ejector and vapour solenoids cut-off.* E, *Cassette ejector.* F, *Cassettes.* G, *Liquid oxygen for cooling cassettes.* H, *Cassette holder.* I, B40 *Cone and socket.* J, *To vacuum line.* K, *Aluminium cassette guide.* L, B34 *Cone and socket.* M, *To cassette collector.* N, *End of oxygen trap extended inwards to form a ledge to support cassette holder.* O, RF *Coil.*

FIG. 2. (a) *Cross-section of cassette holder.*
(b) *Detail of cassette.*



A, *Handle for lowering holder into position.* B, *Ridge to prevent side-play.* C, *Slot to allow discharge of cassettes.* D, *Cassette in position.* E, *Hole to admit ejector rod.* F, *Glass sleeve to hold cassette in position.* G, *Collimator.* (N.B. *Cassettes are inserted when loaded in the holder*).
H, *Aluminium holder.* I, *Platinum collecting tray.* J, *Metal circlip to hold platinum tray.* K, *V-Shaped cut-away to accelerate pumping-out.*

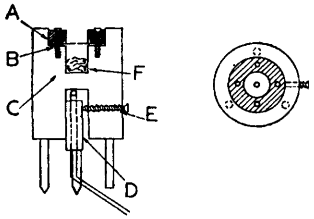


FIG. 3. *Cross-section of tantalum crucible (enlarged plan).*

A, *Collar clamping foil in position.* B, 2/1000″ *Foil with orifice pierced in centre.* C, *Tantalum crucible* (7/8″ *diam.*). D, *Thermocouple secured in twin-bore silica tubing.* E, *Tantalum grub screw.* F, PuF_4 *charge.*

the targets were exposed to the effusing vapour. A second coil enabled the lowest cassette holding an exposed target to be pushed out so that it fell down a sloping platform into a removable tube. When the pusher was retracted, the column of cassettes fell under gravity so that the lowest took the place of that one which had been ejected. The collimator was a circular knife-edged hole accurately ground in a glass disc, and fused on to the bottom of the magazine. The magazine was removable through the top of the apparatus.

The targets were discs of platinum, 2 cm. in diameter and 5/1000″ thick, held in aluminium cassettes, 0·5 cm. thick, by means of circlips (Fig. 2*b*). The maximum number which could safely be held in the magazine was 25, but for various reasons as many as this were never employed at one time. Before use, the targets were checked for alpha-contamination in a low-background scintillation-counter, and then refluxed for some hours in carbon tetrachloride to remove grease, this being necessary in order to provide a surface with a high accommodation coefficient and thus to ensure that the maximum incident molecules adhered to the target. For the same reason the targets were surrounded by an outer vessel containing liquid air, since the accommodation coefficient is considerably increased by cooling (cf. refs. 6 and 7).

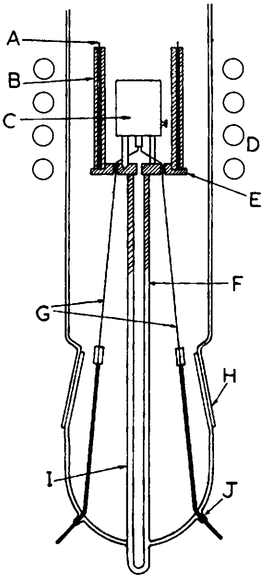


FIG. 4. *Cross-section of crucible arrangement.*
□ *Glass.* ▨ *Silica.*

A, *Platinum foil radiation-shield.* B, *Silica sleeve to support shield.* C, *Tantalum crucible.* D, RF *coils.* E, *Silica platform.* F, *Graded silica seal.* G, *Thermocouple leads.* H, B50 *Pyrex cone and socket.* I, *Glass supporting pillar.* J, *Metal–glass seal.*

The apparatus was evacuated by a standard rotary and diffusion pump system.

Each furnace pot (Fig. 3) holding tetrafluoride was $\frac{7}{8}''$ in diameter. The tantalum foil in which the effusion orifice was pierced rested on the " step " and was secured by a tantalum collar held by four tantalum grub screws. During the initial stages of the heating the tantalum appeared to sinter slightly (perhaps owing to traces of absorbed oxygen); the collar and foil became firmly attached to the pot so that it is not thought that an appreciable quantity of vapour could effuse except through the orifice. The pot had three tantalum legs, two ground to a point, the other flat so that the vessel could be accurately located by a V-section hole and groove on the flat silica supporting platform (cf. Erway and Simpson [1]). A hole drilled in the base of the pot held the platinum–platinum-10% iridium thermocouple, which was insulated by a short length of twin-bore silica tubing and secured by a long tantalum screw. The junction was separated from the charge in the pot by about $\frac{1}{8}''$ of tantalum, and was assumed to be at the same temperature. The thermocouple had previously been calibrated at the melting points of sodium nitrate (306·8°), lithium bromide (535°), sodium bromide (740°), and sodium chloride (803°). At higher temperatures, the temperature equivalent of the E.M.F., which was measured on a " Pye " millivolt potentiometer, was estimated by extrapolation and from the standard tables.

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[6] Fraser, " Molecular Rays," Cambridge Univ. Press, 1931.

[7] Cockcroft, *Proc. Roy. Soc.*, 1928, **119**, 293.

The effusion pot was surrounded by a radiation shield of two concentric silica tubes, 2½″ high with strips of 1/1000″ platinum foil between them. In the earlier experiments with the nickel pots, the inside of the inner tube became somewhat plated with a skin of nickel, and the whole formed a very efficient shield. Various types of resistance heating were first used, but, for all the runs in which measurements are reported, eddy-current heating was employed. The power input was from a 4½ turn copper coil connected to a 7 kw RF generator.

The furnace pot and radiation shield stood upon a silica platform (Fig. 4) which was supported on a hollow silica pillar sealed through a silica-to-Pyrex graded seal to a B40 cone. Into the base of the cone were sealed metal rods to which the thermocouple leads were attached. The B40 cone with the Pyrex-and-silica pillar and platform fitted into a socket at the base of the vapour pressure apparatus itself.

The orifices were pierced in 2/1000″ tantalum foil by Mr. C. F. Wright to whom our thanks are offered. The initial hole was pierced with a sharpened needle on a micro-lathe of special construction, and this was ground out by hand with a specially prepared reamer. The final hole appeared to be a knife-edged channel through the tantalum sheet which remained perfectly plane. The diameters of the holes were measured both by a Zeiss measuring microscope and a projection microscope. Four measurements were made in every case and none deviated by as much as 1% from the mean.

The method of operation was as follows. The grease-free targets, each stamped with a reference number near its edge, were loaded into their cassettes, great care being taken to avoid contaminating the surfaces. They were then placed in the magazine which was lowered into the apparatus, and one disc was pushed out to test the alignment of the pusher. This was all done with plutonium absent, to avoid any alpha-contamination of the clean targets. The pot was then loaded with about 50 mg. of plutonium tetrafluoride. The foil with the orifice hole was attached to the pot and its alignment checked visually. With the furnace pot and the radiation shield on the pillar, and the thermocouple in position, the B40 cone was secured in its socket with Apiezon W vacuum-wax.

The plutonium tetrafluoride had been made by the hydrofluorination of plutonium dioxide by hydrogen fluoride and oxygen at 350°. It contained 23·95% of fluorine (calc. for PuF_4: F, 24·1%) and no phase other than the tetrafluoride could be detected in *X*-ray diffraction photographs.

The apparatus was evacuated for 2—3 days. The insert around the cassette magazine was then filled with liquid air, the target screened by the shutter, and the temperature slowly raised to 550°. Degassing of the heated surfaces occurred but after about an hour the pressure was once more less than 10^{-5} mm. Hg, and the first target was then exposed for a measured time to the effusing vapour. By constant adjustment of the Geneva control of the RF generator it was possible to keep the temperature constant within $\pm 5°$ and usually within $\pm 2°$ as indicated by the thermocouple.

Targets were successively exposed to the effusing vapour at various measured temperatures for appropriate times. The cassettes containing the exposed targets were successively ejected and fell into a tube attached to the apparatus by a cone-and-socket joint. At the end of the run, all the targets were removed from the apparatus before the pot was disturbed and were removed from the glove box, which surrounded the whole apparatus, as quickly as possible to avoid accidental alpha-contamination.

The cassettes themselves were always found to be inactive and the targets were removed from them in the open laboratory. The activity was counted on a scintillation-counter with a low background. During the run, blank trays were pushed out at intervals and these were also counted. This served to check the freedom of the trays from accidental cross-contamination. This was extremely important because, at the lowest temperatures at which vapour pressures were measured, exposure to the effusing beam for upwards of one hour resulted in only 5—50 measured counts per minute being found on a tray. In some of the earlier runs,

TABLE 1. *Nickel pot; diameter of orifice* 0·0073 *cm.*

T	$10^5/T$	p	$\log_{10} p$	T	$10^5/T$	p	$\log_{10} p$
1069°	93·55	$1{\cdot}216 \times 10^{-4}$	$\bar{4}{\cdot}0849$	1245°	80·32	$6{\cdot}576 \times 10^{-3}$	$\bar{3}{\cdot}8180$
1137	87·95	$3{\cdot}842 \times 10^{-4}$	$\bar{4}{\cdot}5845$	1317	75·93	$1{\cdot}630 \times 10^{-2}$	$\bar{2}{\cdot}2122$
1197	83·54	$2{\cdot}113 \times 10^{-3}$	$\bar{3}{\cdot}3249$	1377	72·62	$7{\cdot}631 \times 10^{-2}$	$\bar{2}{\cdot}8826$

In this run an earlier model of the apparatus was used (D 0·784 cm., *r* 15·1 cm.).

TABLE 2. *Diameter of orifice* 0·0108 *cm.*

T	$10^5/T$	p	$\log_{10} p$
1153°	86·7	$1·067 \times 10^{-3}$	$\bar{3}·0281$
1150	87·0	$1·629 \times 10^{-3}$	$\bar{3}·2121$
1164	85·9	$2·364 \times 10^{-3}$	$\bar{3}·3738$
1208	82·8	$4·923 \times 10^{-4}$	$\bar{4}·4923$
1247	80·2	$3·023 \times 10^{-3}$	$\bar{3}·4804$
1288	77·6	$1·071 \times 10^{-2}$	$\bar{2}·0299$
1336	74·8	$1·628 \times 10^{-2}$	$\bar{2}·2114$
1363	73·2	$3·917 \times 10^{-2}$	$\bar{2}·5930$
1463	68·2	$2·135 \times 10^{-1}$	$\bar{1}·3295$
1492	67·0	$6·607 \times 10^{-1}$	$\bar{1}·8200$
1534	65·2	$1·078 \times 10$	1·0328
1589	62·9	$1·390 \times 10^{2}$	2·1429

TABLE 3. *Diameter of orifice* 0·0234 *cm.*

T	$10^5/T$	p	$\log_{10} p$
968°	103·3	$1·923 \times 10^{-5}$	$\bar{5}·2840$
997	100·3	$9·234 \times 10^{-5}$	$\bar{5}·9654$
1026	97·5	$1·736 \times 10^{-4}$	$\bar{4}·2396$

Run discontinued; pusher jammed.

TABLE 4. *Diameter of orifice* 0·0110 *cm.*

T	$10^5/T$	p	$\log_{10} p$
1014°	98·4	$7·658 \times 10^{-5}$	$\bar{5}·8841$
1028	97·3	$3·196 \times 10^{-5}$	$\bar{5}·5045$
1036	96·5	$1·487 \times 10^{-4}$	$\bar{4}·1722$
1075	93·0	$1·528 \times 10^{-4}$	$\bar{4}·1840$
1099	91·0	$3·538 \times 10^{-4}$	$\bar{4}·5488$
1128	88·6	$3·741 \times 10^{-4}$	$\bar{4}·5729$

Run discontinued; cassette fell off sloping platform on to pot.

TABLE 5. *Diameter of orifice* 0·0106 *cm.*

T	$10^5/T$	p	$\log_{10} p$
1167°	85·7	$1·888 \times 10^{-4}$	$\bar{4}·2761$
1187	84·2	$5·171 \times 10^{-4}$	$\bar{4}·7136$
1225	81·6	$7·914 \times 10^{-4}$	$\bar{4}·8984$
1248	80·1	$9·206 \times 10^{-4}$	$\bar{4}·9641$
1263	79·2	$1·191 \times 10^{-3}$	$\bar{3}·0760$
1279	78·2	$2·297 \times 10^{-3}$	$\bar{3}·3611$
1310°	76·3	$5·578 \times 10^{-3}$	$\bar{3}·7465$
1327	75·4	$8·052 \times 10^{-3}$	$\bar{3}·9059$
1337	74·8	$1·798 \times 10^{-2}$	$\bar{2}·2547$
1351	74·0	$2·937 \times 10^{-2}$	$\bar{2}·4679$
1351	74·0	$2·921 \times 10^{-2}$	$\bar{2}·4656$
1361	73·5	$3·680 \times 10^{-2}$	$\bar{2}·5658$

before the handling of the targets had been mastered, the blank trays had rather high contamination (*ca.* 100 counts/min.). In the later runs (Tables 1—5) this contamination was very small.

The furnace pot was removed from the apparatus and opened, and the *X*-ray diffraction pattern of the residue examined.

The calculation of the vapour pressure from the activity recorded on the counting trays has been formulated by Phipps *et al.*[1] The expression is:

$$p = \frac{(cT^{\frac{1}{2}})}{t}\;\frac{(D^2 + 4r^2)}{AD^2}\;\frac{(M^{\frac{1}{2}})}{239s}\;\frac{(10^{-6}\,(2\pi\boldsymbol{R})^{\frac{1}{2}})}{60}$$

where p is the vapour pressure of the material, c the absolute number of disintegrations per minute on a given target, s the specific activity of the plutonium (counts min.$^{-1}$ μg.$^{-1}$), $\boldsymbol{R}$ the molar gas constant, T the oven-temperature (°K), t the time (min.) for which the target is exposed, D the diameter of the collimator (cm.), r the distance (cm.) from the effusion orifice to the collimator, A the area (sq. cm.) of the orifice, and M is the molecular weight of the vapour molecule.

In this apparatus, the diameter of the collimator was 0·550 cm. The distance from the effusion orifice to the collimator differed slightly from run to run, but was typically 15·20 cm. The diameter of the effusion orifice is shown for each run. The calculated vapour pressures are set out in Tables 1—5 (temperatures in °K, pressures in mm. Hg).

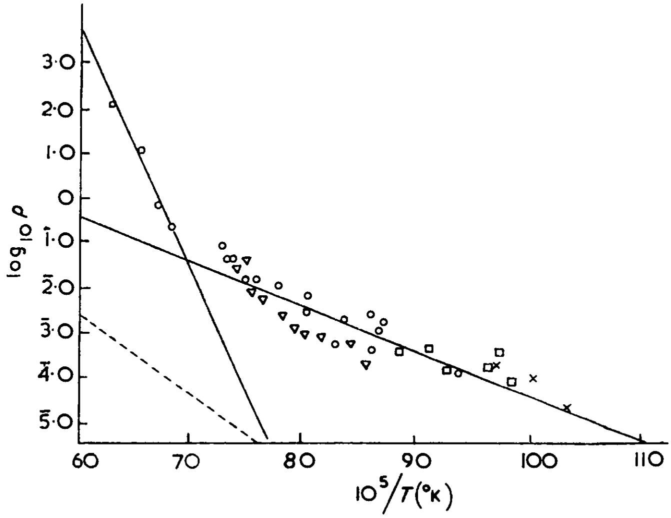
DISCUSSION

The results set out in Tables 1—5 are shown in Fig. 5. In general, the points are reasonably consistent, particularly when it is remembered that at temperatures below 1000° K, the counts on a target were very low. It is satisfactory that the points from Table 1 agree with those from Tables 2—5 since the results in Table 1 were obtained for an apparatus that differed in many respects.

The values for the four highest temperatures of Table 2 are of particular interest. They appear to indicate that above 1450° K, a more volatile species is present in the vapour. The absolute value of the apparent pressure at these temperatures is uncertain, since the molecular weight of the effusing species enters into the vapour-pressure equation and, in this case, the nature of this species is unknown. Even if the molecular weight were as high as that of plutonium hexafluoride (353) or as low as the atomic weight of plutonium (239), this would make a maximum difference of ±0·4 log unit to the logarithm of the vapour pressure, and the general shape of the curve would not be greatly affected.

Dawson *et al.*[8] found that when the tetrafluoride was heated on a tantalum filament to an estimated temperature of ~900° c, a residue of trifluoride remained on the filament, and another substance was collected on a cold finger above the filament. On the basis of analyses carried out on milligram quantities of the sublimate, they tentatively suggested that it might be the pentafluoride. On the other hand, Fried and Davidson [9] stated that the trifluoride is produced from the tetrafluoride in a vacuum at ~1000° K, and that it is the trifluoride that is collected by sublimation, but this is not accepted by Brewer *et al.*[10]

FIG. 5. *Vapour pressure* [$\log_{10} p$ (mm. Hg)] *of plutonium tetrafluoride, and* (– – –) *of plutonium.*[11]



From a consideration of the heats of formation and entropies of the compounds involved, Brewer *et al.* deduce that the fluorine pressure over solid tri- and tetra-fluoride at 1000° K should only be about $10^{-8\cdot5}$ atmosphere, which would not account for the formation of trifluoride at an appreciable rate in this way; they believe that it is more likely that the formation of the trifluoride in the residue occurs by the reaction $2PuF_4 = PuF_5(g) + PuF_3$.

In the present work, when enough material for analysis remained in the effusion pot at the end of the run, it was found to be plutonium trifluoride. Evaporation of this compound could not account for the high vapour pressures found, as will be seen from the data in Table 6, where the figures for the vapour pressure of trifluoride are those given by Phipps *et al.*[1] and those for the tetrafluoride are interpolated from our work.

TABLE 6. *Vapour pressures* [log *p* (*mn. Hg*)].

Temp. (°K)	1241°	1288°	1347°	1446°	1523°	1577°
V. p. of PuF_4 (this work)	$\bar{3}$·70	$\bar{2}$·00	$\bar{2}$·35	$\bar{2}$·90	(0·75)	(1·95)
V. p. of PuF_3 (ref. 1)	$\bar{5}$·469	$\bar{4}$·073	$\bar{4}$·810	$\bar{3}$·876	$\bar{2}$·540	$\bar{2}$·991

It has been suggested that the fluoride might be reduced to plutonium metal by tantalum at this temperature and that the effusing species could be Pu. The vapour

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[8] Dawson, Elliott, Hurst, and Truswell, *J.*, 1954, 558.
[9] Fried and Davidson, N.N.E.S., Vol. XIVb, paper 6.11.
[10] Brewer, Bromley, Gilles, and Lofgren, UCRL 633 (1950).

pressure of liquid plutonium has been measured by Phipps *et al.*[11] and a line derived from their data has been added to Fig. 5. This measured vapour pressure of plutonium is too small by a factor of 10^4 to account for our results and the possibility of such a reduction must be rejected.

The vapour pressure of plutonium hexafluoride has also been measured by the present authors with others.[12] The vapour pressure of this compound is 10^2 mm. Hg at 20° C, and is far too high to account for the results under discussion.

It therefore seems most probable that the species effusing above 1450° K is PuF_5, which would be expected to be rather volatile, and may persist as such until it is condensed on the cold target. A further series of experiments was undertaken to isolate this compound on the 10 mg. scale by collecting on a cold finger the vapour from the tetrafluoride heated in a tantalum crucible. These were not successful.

Below 1450° K, the line derived by the method of least squares and plotted in Fig. 5 probably represents the vapour pressure of plutonium tetrafluoride with reasonable accuracy. The only available figures [13] for the vapour pressure of uranium tetrafluoride also lie very close to this line. It is considered that the vapour pressure of plutonium tetrafluoride can be represented by the equation given in the summary of this paper.

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[*Received, October* 28*th*, 1960.]

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[11] Phipps, Sears, Seifert, and Simpson, Proc. Internat. Conf. on the Peaceful Uses of Atomic Energy, Geneva, 1955, Vol. VII, p. 382.

[12] Mandleberg, Rae, Hurst, Long, Davies, and Francis, *J., Inorg. Nuclear Chem.*, 1956, **2**, 358.

[13] Mueller, A.E.C.D. 2029 (1948).