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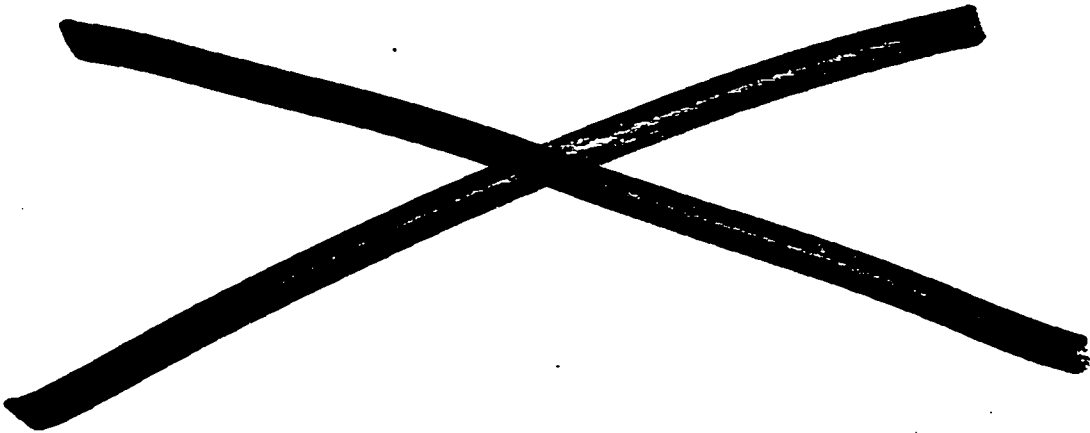
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VAPOR PRESSURE OF PLUTONIUM TRICHLORIDE



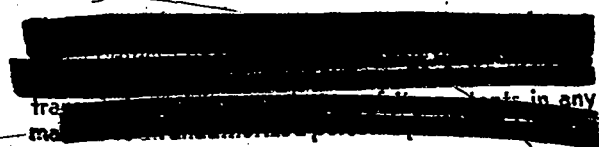
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ABSTRACT

The vapor pressures of plutonium trichloride in the temperature range 659° C to 762° C are reported, as determined by Knudsen's method of molecular effusion. At 663° the pressure above the solid chloride is 4.6×10^{-5} mm Hg while at 741° it is 4.2×10^{-3} mm Hg. The pressure at 762°, at which the chloride is thought to be fused, is 7×10^{-3} mm Hg. The melting point is probably $760^\circ \pm 5^\circ$ C. The vapor pressure above the solid chloride between 650° and 750° C can be represented by the equation:

$$\log_{10} P = - (2.1 \times 10^4/T) + 18.6$$

where

P = pressure in mm Hg

T = absolute temperature

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VAPOR PRESSURE OF PLUTONIUM TRICHLORIDEINTRODUCTION

This report presents some measurements on the vapor pressure of plutonium trichloride. The experimental work was discontinued before its completion because of the pressure of other work.

Experimental Method

The vapor pressure of PuCl_3 was measured by Knudsen's method of molecular effusion¹). In this method the vapors are permitted to effuse through an orifice whose diameter is less than the mean free path of the gas molecules in the chamber. The vapor pressure can then be calculated from the equation:

$$P = (m/a.t)(2\pi RT/M)^{1/2}$$

where

P = vapor pressure in dynes/cm²

m = amount of condensed salt in gms

a = area of hole in cm²

t = time of distillation in seconds

R = gas constant in ergs/mole/° C

T = absolute temperature

M = molecular weight.

Apparatus and Experimental Procedure

The apparatus is shown in Fig. 1. It consisted of a flat bottomed quartz tube with a pyrex cold finger. The quartz-to-pyrex connection was made by

1) Knudsen, Ann. d. Physik, 47, 697 (1915).


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means of 40/50 standard-taper ground joints. The ground joint and cold finger were kept cool by means of circulating water. A #22 gauge chromel-p₀alumel thermocouple was used to measure the temperature; it was brought into the apparatus through a tungsten pressed seal. The apparatus was attached to the pumping system by means of a ball joint. The pumping system consisted of a two-stage mercury diffusion pump backed by a mechanical pump and included appropriate traps. The pressure in the pumping line was measured with a McLeod gauge.

The effusion box containing the salt was made of 15 mil platinum sheet and consisted of a platinum cylinder welded to a platinum disc. The cover, which fitted precisely, was removable for admitting the sample. A hole of 1.027 mm diameter was drilled in the top through which the gas could effuse. The size of the hole was measured directly by means of a micrometer microscope.

In assembling the apparatus care was taken to have the thermocouple pressed firmly against the platinum box. The system was then pumped down to a "stick vac" and the furnace brought gradually to the desired temperature. At the elevated temperatures, the pressure in the system was generally lower than 10^{-5} mm Hg. Particular care was taken (by lowering the temperature) not to permit the pressure to become greater than 10^{-4} mm Hg. This was done to avoid undue reaction of the trichloride with the residual gas in the system.

The amount of distillate was determined by removing the platinum box and dissolving the material from the system. Three series of washings were made; the first was with water, and the other two with con. HCl. These solutions were diluted to a definite volume and assayed by the α -counting technique. The accuracy of the assays was given as 5 percent. The final washing contained generally less than 1 percent of the amount of material in the first washing.



A calculation was made for the amount of distillation occurring before the system reached the desired temperature, and the total distillate was corrected by that amount. This correction was generally of the order of 10 percent. While the temperature was changing rapidly, it was recorded every two minutes. When the system was at temperature, the reading was checked every 15 minutes. The temperature was kept constant to about 8° C at the desired value and a time weighted average of these readings taken.

Experimental Results

The apparatus was tested with NaCl before attempting PuCl_3 . At 639° C, a vapor pressure of 4.23×10^{-3} mm Hg was obtained. This value was considered in satisfactory agreement with the value of 4.09×10^{-3} mm Hg obtained by Mayer and Kentner²⁾ at this temperature.

The results obtained for PuCl_3 are tabulated below and the data plotted in Fig. 2 as the log of the vapor pressure against the reciprocal of the absolute temperature. The molecular weight of 345.4 (PuCl_3) was assumed for the salt in the vapor phase for purposes of calculation.

TABLE I. VAPOR PRESSURE OF PuCl_3

$t^{\circ}\text{C}$	P mm Hg	Position of Thermocouple	Condensed Phase
659	1.1×10^{-4}	0	Solid
663	4.6×10^{-5}	0	"
665	5.3×10^{-5}	A	"
701	6.7×10^{-4}	□	"
702	2.5×10^{-4}	0	"

2) Mayer and Kentner, J. Chem. Phys., 6, 301 (1938)

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TABLE I. VAPOR PRESSURE OF PuCl₃ (cont'd)

t°C	P mm Hg	Position of Thermocouple	Condensed Phase
736	1.6×10^{-3}	O	Solid
741	4.2×10^{-3}	Δ	"
762	7.0×10^{-3}	Δ	Liquid

O thermocouple against the bottom of the box
 Δ thermocouple on the top of the box
 □ thermocouple against a ridge in the center of the box
 (These symbols are used also in Fig. 2)

A temperature gradient of about 25° C was found between the top and bottom of the box. This was corrected for by assuming that the vapors were midway between the upper and lower temperature. Hence measurements made with the thermocouple against the bottom of the box were decreased by 13° C; with the thermocouple on the lid, they were increased by 13° C; and no correction was made with the thermocouple in the center.

During the course of the measurements the material in bottom of box condensed on the under surface of the lid due to the large temperature gradient present. There was the danger in this process of the solid bridging across the orifice but in no case was this observed to have happened.

The data for 762° C were probably measurements of liquid-vapor equilibrium. At the end of that run, the material remaining in the box was observed to have the shape of solidified droplets of liquid which had fallen down from the lid.

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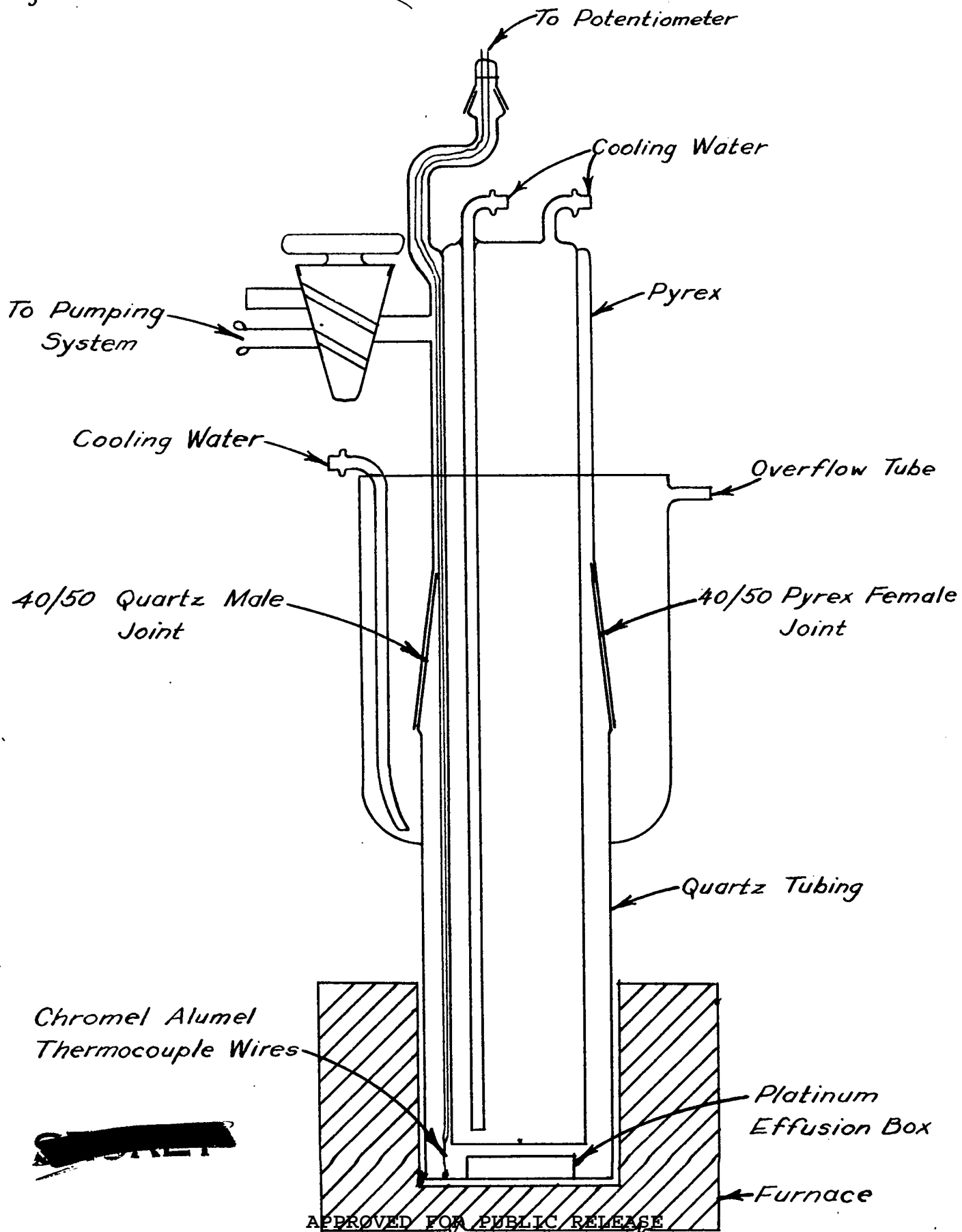
Discussion and Conclusions

The results obtained are good to a factor of two, which corresponds to an uncertainty of 10° C in the temperature measurement. This accuracy is within the limits aimed at in undertaking this work, but is not sufficient to warrant a reliable calculation of the heat of sublimation. By having the distilling chamber at a more uniform temperature, the results could be improved a good deal. By using a smaller diameter platinum box which could fit into a quartz well, this could probably be achieved.

The trichloride used in this work was prepared by Johns, Bakes, and Moulton. The radio-chemical assays were done by the assay group. The author also wishes to thank Wichers for the purification of the NaCl used, Garner for the use of the platinum box and the measurements of its orifice, and Cpl. Luft for his assistance in some of the measurements.

Figure 1

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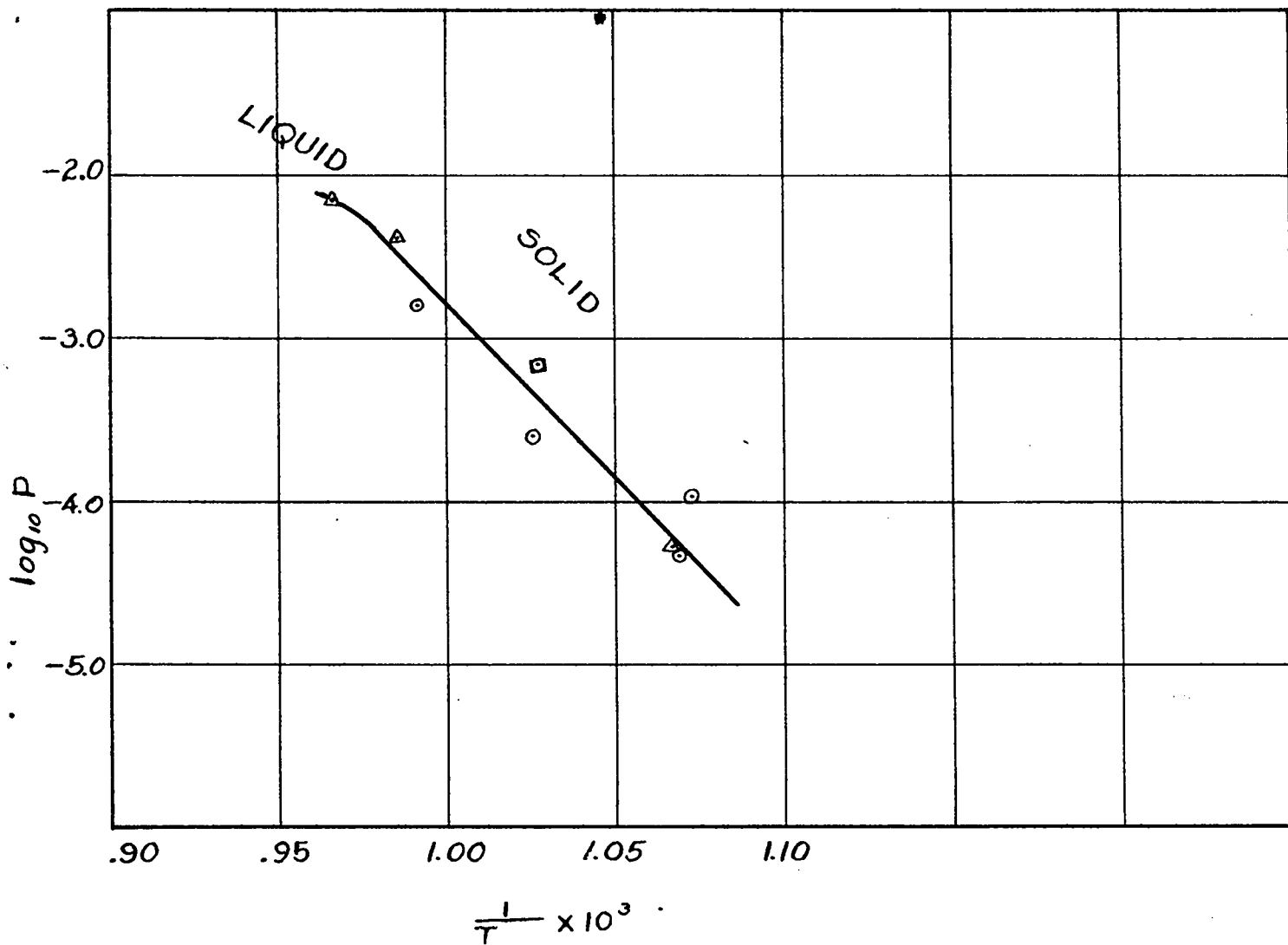


Figure 2

VAPOR PRESSURE OF PuCl_3

$$\text{(Solid)} \quad \log_{10} P = -\frac{2.1 \times 10^4}{T} + 18.6 \quad \text{for } 650^\circ - 750^\circ \text{C.}$$

P = Vapor pressure in mm Hg

T = Absolute temperature

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