UCRL 2389
UNCLASSIFIED

# UNIVERSITY OF CALIFORNIA

# Radiation Laboratory

BERKELEY, CALIFORNIA

## DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

UCRL-2389
Unclassified-Chemistry Distribution

UNIVERSITY OF CALIFORNIA

Radiation Laboratory

Contract No. W-7405-eng-48

# VAPOR-PRESSURES OF AMERICIUM TRIFLUORIDE AND AMERICIUM METAL

Stephen Charles Carniglia

(Thesis)

November, 1953

Berkeley, California

# TABLE OF CONTENTS


| | | Page |
|---|---|---|
| | List of Illustrations | 3 |
| | ABSTRACT | 4 |
| I. | INTRODUCTION | 5 |
| II. | THE KNUDSEN EFFUSION METHOD | 8 |
| | A. Choice of Method | 8 |
| | B. Description of the Method | 8 |
| | C. Equations | 14 |
| III. | THE APPARATUS | 18 |
| | A. Description of the Apparatus | 18 |
| | B. Constants of the Apparatus | 33 |
| | C. Preliminary Experiments | 35 |
| IV. | DATA | 39 |
| | A. Plutonium Trifluoride | 39 |
| | B. Americium Trifluoride | 45 |
| | C. Americium Metal | 53 |
| V. | UNCERTAINTIES | 59 |
| | A. General | 59 |
| | B. Plutonium Trifluoride and Americium Trifluoride | 64 |
| | C. Americium Metal | 66 |
| VI. | DISCUSSION OF RESULTS | 68 |
| | A. Plutonium Trifluoride | 68 |
| | B. Americium Trifluoride | 69 |
| | C. Americium Metal | 71 |
| VII. | ACKNOWLEDGMENTS | 73 |
| VIII. | REFERENCES | 74 |

## LIST OF ILLUSTRATIONS


| Figure | | Page |
|---|---|---|
| 1. | Essential Parts of the Radiochemical Knudsen Effusion System | 11 |
| 2. | Equipment Used in Measuring the Vapor-Pressures of $PuF_3$, $AmF_3$, and Americium | 19 |
| 3. | Furnace-Collimator Assembly | 22 |
| 4. | Twin Effusion Apparatus | 24 |
| 5. | Shutter-Receiver Assemblies | 26 |
| 6. | Effusion Vessels | 27 |
| 7. | Furnace Power Supply | 30 |
| 8. | Vapor-Pressure of Plutonium Trifluoride | 44 |
| 9. | Vapor-Pressure of Americium Trifluoride | 52 |
| 10. | Vapor-Pressure of Americium Metal | 58 |

# VAPOR-PRESSURES OF AMERICIUM TRIFLUORIDE AND AMERICIUM METAL

Stephen C. Carniglia
Radiation Laboratory and Department of Chemistry
University of California, Berkeley, California

November, 1953

## ABSTRACT

The vapor-pressures of plutonium trifluoride, americium trifluoride, and americium metal have been measured by a modification of the Knudsen effusion method. The measurements on $PuF_3$, made to provide a basis against which to refer the other data, agreed remarkably well with previously published results. The vaporization equations obeyed by this substance over the temperature range $1220^\circ$ K to $1450^\circ$ K are:

$$\log p_{(mm)} = 12.018 - 20,520/T,$$

or, assuming $\Delta C_{p(sublim)} = -14$ cal/mole/degree,

$$\log p_{(mm)} = 37.119 - 24,625/T - 7.046 \log T.$$

The data for $AmF_3$ showed a detectable curvature. The points were fitted by the equation, (assuming also $\Delta C_{p(sublim)} = -14$ cal/mole/degree),

$$\log p_{(mm)} = 36.880 - 24,650/T - 7.046 \log T,$$

over the temperature range $1120^\circ$ K to $1470^\circ$ K. The vapor-pressure of americium metal obeyed the equation,

$$\log p_{(mm)} = 7.563 - 13,162/T,$$

or, assuming $\Delta C_{p(vap)} = -2$,

$$\log p_{(mm)} = 11.092 - 13,700/T - \log T,$$

from the melting point, $1100^\circ$ K, to $1450^\circ$ K.

The apparatus, an opposed twin device permitting simultaneous vaporization of a reference substance and the substance under study, is described in detail. Derived thermodynamic quantities are presented, and uncertainties attending each measurement are discussed.

# VAPOR-PRESSURES OF AMERICIUM TRIFLUORIDE AND AMERICIUM METAL

Stephen C. Carniglia
Radiation Laboratory and Department of Chemistry
University of California, Berkeley, California

November, 1953

## I. INTRODUCTION

The desirability of accurate vapor-pressure measurements as a contribution to the data of chemical thermodynamics needs no elaboration. Both the direct results and derived quantities are put to practical use in selecting methods and conditions for preparation, handling, and separation of substances; or to theoretical use as additions to the knowledge of atomic and molecular structure and properties.

Consistent with interest of this laboratory in the chemistry of the heaviest elements, it was desired to obtain this type of thermodynamic data for americium and its compounds, to the highest degree of precision feasible under the restrictions imposed by the limited supply and by the chemical and nuclear properties of this element. In addition, it was deemed of value to design and put into operation an instrument with which continuing research might be carried on, suited to the interests and resources of this laboratory, i.e., employing radioactivity as a means of measurement.

In view of the occasional publication of vaporization data which, although consistent internally, are of untested absolute accuracy, it is sometimes hazardous to infer relative volatilities of different substances at a given temperature. Therefore it was decided to build into the instrument the capacity to make simultaneous measurements

on two substances at assuredly equal temperatures. This was accomplished by constructing the equilibrium vessel as an opposed twin, carefully machined from a single piece of metal to assure perfect symmetry. This theme of symmetry was carried out from the vessel through the surrounding furnace to the measuring equipment placed opposite each end.

Measurements made to date with the device so constructed have yielded vaporization data for the trifluorides of plutonium and americium, and for elementary americium. A brief account of previous studies follows.

Plutonium trifluoride. -- The vapor-pressure of plutonium trifluoride was reported in the open literature by Phipps, Sears, Seifert, and Simpson[1] in 1949. The authors interpreted the data as obeying the equations,

$$\log p_{(mm)} = 12.468 - 21,120/T \text{ and}$$

$$\log p_{(mm)} = 11.273 - 19,400/T,$$

in the temperature ranges $1200^{\circ} - 1447^{\circ}$ K and $1447^{\circ} - 1770^{\circ}$ K, respectively. The assumption of a negligible difference in heat capacities between the gas and the condensed phase is implicit in such expressions. They inferred a melting-point at $1447^{\circ}$ with a heat of fusion of about 8 kcal/mole. Brewer, Bromley, Gilles, and Lofgren[2] fitted the same points by a curved line, implying a $\Delta C_p$ (sublim) of -14 cal/mole/degree; they estimated the melting point as $1680^{\circ}$ K. The latter estimate was verified by Westrum and Wallmann[3] in 1951, when they found the melting point to be $1699 \pm 2^{\circ}$ K by direct measurement.

The work cited in reference 1 is generally considered to be excellent experimental work. It was felt that a repetition of the vapor-pressure measurements on $PuF_3$, verifying the earlier results, would strengthen both the existing data on $PuF_3$ and the other work reported here. This substance was used for reference in operation of the device as a comparator.

Americium trifluoride. -- The vapor-pressure of solid americium trifluoride was reported by Jones[4] in 1951, over the temperature range 1070° K to 1450° K. The author of the work suspected a systematic error, although his sublimation equation,

$$\log p_{(mm)} = 10.89 - 20,030/T,$$

was reasonably well fitted by the data. Cause for suspicion of the results lay in the calculated entropy of vaporization at the boiling point, based upon an extrapolation of the same data, which was substantially lower than that of $PuF_3$ and lower than that predicted by Trouton's rule.

Americium. -- The vaporization of americium from a dilute solution of americium in plutonium was reported in 1950 by Erway and Simpson,[5] the data extending over the temperature range 1450° K to 1820° K. They calculated the equation,

$$\log p_{(mm)} = 7.02 - 11,300/T,$$

on the assumption that the plutonium-americium composition used by them could be regarded as a perfect solution.

## II. THE KNUDSEN EFFUSION METHOD

### A. Choice of Method

The minute quantities available and the physico-chemical properties of americium rendered a microchemical method of measurement not only appropriate but inescapable. Technical difficulties associated with static methods on this scale were prohibitive; in addition, vapor-pressures expected were too low for manometric detection. Of the flow methods in use (transpiration, Langmuir evaporation, effusion) only the Knudsen effusion method,[6] modified so as to employ radiochemical techniques of estimation,[1] gave promise of absolute reliability as well as economy.

### B. Description of the Method

In the Knudsen effusion method of vapor-pressure measurement, a small fraction of the gas molecules in an equilibrium chamber are allowed to escape through a pinhole into a highly evacuated space, the number effusing per unit time through a hole of known area being related to interior partial pressure, temperature, and molecular weight of the gas by the laws of the Kinetic Theory. In consequence of this flow, the Knudsen vessel does not enclose a system truly at equilibrium; however the departure is under suitable conditions completely negligible.

In its simplest form, measurement of vapor-pressure by means of this device consists in maintaining a chamber at uniform known temperature for a measured time interval, the total number of molecules effusing at all angles through the orifice being computed from weights of the chamber and contents taken before and after the

experiment. In addition to requiring relatively large amounts of sample and prolonged experiments for detectable weight differences, this total effusion method relies upon near-idealization of the orifice. The condition demanded by the total effusion equation, an infinitely thin-edged orifice in a flat wall, is difficult to realize; moreover, departures from the ideal are not easily compensated for quantitatively. This and other aspects of the theory have been treated by Knauer and Stern,[7] Clausing,[8,9] Whitman,[10] and Johnston and Speiser.[11]

The critical nature of the orifice condition has prompted some workers to collimate and collect only a small portion of the effusant, in a cone about the normal to the orifice. Theory and experiment both indicate that moderate deviations from the ideal orifice have only a small effect on effusion within such a cone, the effect increasing with increasing angular departure from the axis.[8,12] Use of a collimating system has, of course, a pronounced influence on the means available and appropriate for determining the amount of material effusing per unit time. Some typical measurements and typical effusion equipment may be cited for reference and comparison.[13-17]

The radiochemical modification described by Simpson and co-workers,[1] which has been employed in a number of determinations in several laboratories,[4,5,18-20] is made feasible by the fact that extremely small amounts of radioactive substances may be estimated with precision by counting the decay events. This quality permits the use of small samples and brief periods of exposure of each collector, as well as collimation to a very narrow beam.

Fundamentally, the equipment for this modified Knudsen method includes a thermostatted equilibrium vessel with the effusion orifice,

a collimator to define the beam geometry, a shutter to define the time of exposure, a receiver upon which the beam of molecules is condensed, and an envelope maintained at high vacuum which surrounds all these units. Receivers are later placed in a suitable device for counting the radioactive decay of the condensate. The equipment is shown schematically in Fig. 1.

Applicability of the working equation for this type of measurement depends upon adherence to a mountainous list of conditions, although in practice it is not difficult to realize them all within a stipulated error limit, nor to evaluate the resultant error experimentally for a number of cases. The conditions are:

1. Temperature uniformity. -- The vessel should be truly uniformly heated. In approaching this ideal it is desirable to have the location of the sample cooler than the end bearing the orifice rather than the reverse, so as to avoid distillation and subsequent reduction in apparent volatility. On the other hand, it is difficult to maintain the relatively thin orifice-bearing wall at the temperature of the vessel in general, since this wall cannot be shielded to prevent radiation losses and must rely on its own conduction to replace the radiated heat.

It is possible to measure the temperature difference resulting from this condition; one may also evaluate its influence on distillation by observing whether the sample has condensed around the orifice during an experiment. In its effect on achievement of equilibrium inside the vessel, the entire "cold" area around the orifice may be regarded as pertinent under Condition 2.

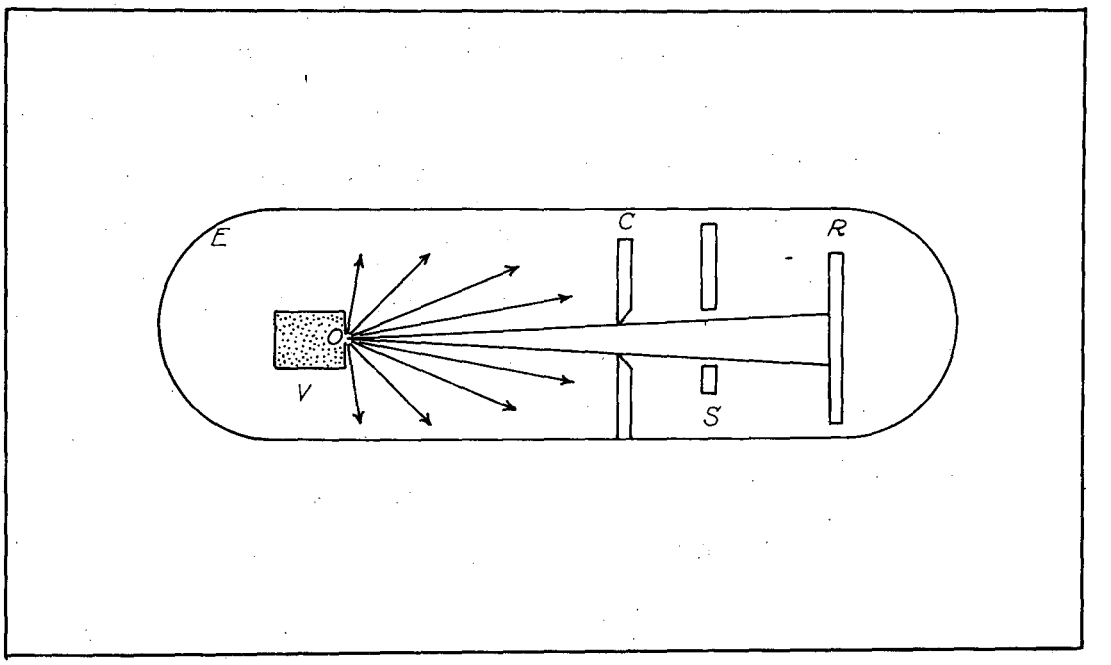


Fig. 1: Essential parts of the radiochemical Knudsen effusion system.

2. Evaporation surface area. -- Interior equilibrium is disturbed by effusion through the orifice; hence the orifice area should be small as compared to the extent of evaporating surface. Different individuals have suggested different limiting values of this ratio, ranging somewhere near the value 1:10 for unit accommodation coefficient of the surface;[9, 21] however, uniform results from experiments employing different values of the ratio provide empirical evidence of satisfaction of the condition in a given case.

3. Orifice condition. -- The orifice should be reasonably thin-edged. For angles of divergence of the collected beam of 5 degrees, the length-to-diameter ratio of a cylindrical orifice may be as high as 1:1 with only about 1% effect on the effusion rate.[8]

4. Mean free path within vessel. -- The mean free path of the molecules within the vessel should be larger than the dimensions of the orifice. Departure from this condition changes the nature of the flow through the orifice from molecular streaming to hydrodynamic flow,[22] rendering the kinetic equation used inaccurate. Although it is possible to adjust data taken at higher pressures, operation in this region was considered impractical in the present case because the rate of transport becomes so large as to exhaust the small samples available.

5. Effusing species. -- The effusing species must be known, both for correct molecular weight assignment and for correct translation of radioactive counting data. For the simplest interpretation of experimental results, it is desirable that the effusant be a single species, independent of temperature.

6. Mean free path outside vessel. -- The external molecular beam must be free from scattering, i.e., the free path of molecules outside the orifice must be larger than the dimensions of the outer envelope. The mean free path may be estimated as a function of total pressure in the system; in addition, the actual amount of scattering occurring may be evaluated by experiment.

7. Condensation. -- All effusant molecules must be condensed upon their first impingement on a solid surface. This is an obvious requirement for the receiver surface; reflection from the collimator or from the envelope is also undesirable since it increases the effects of scattering.

This requirement restricts the use of over-lying furnace coils, radiation shielding, or other obstruction in view of the orifice, hot enough either to reflect molecules or to evaporate those condensed at some previous time. An example of a failure due to such cause has been reported by Simpson, et al.[1]

Scattering from the receiver may be detected by placing a second target close to and facing it but outside of the beam. Scattering from the envelope may be similarly disclosed. Use of overlying obstructions close to the effusion vessel is simply avoided.

8. Collimator condition. -- For the form of the effusion equation employed here, the defining collimator must be nearly circular. The orifice may be of any shape provided it is very small relative to the collimator and provided Condition 3 is met.

9. Alignment. -- The orifice and collimator should both be perpendicular to the line joining their centers. Minor deviations are tolerable and, if recognized, can be compensated. As an

example, a misalignment of the orifice or collimator plane by 3 degrees reduces the geometry of a 5 degree divergent beam by about 0.2 percent.

10. Chamber inertness. -- It hardly needs stating that the container material must not affect the activity of the substance under investigation, by either chemical interaction or solution phenomena. The use of vessels of diverse materials as a means of testing this condition is highly desirable.

11. Composition of sample. -- Other sources of contamination of the sample must be recognized, besides reaction with the vessel material. All such sources should be minimized, and their effects should be evaluated where possible.

Effects of non-conformity to the above list will be discussed under Uncertainties, Section V.

## C. Equations

1. Total effusion. -- Making the ordinary assumptions of the Kinetic Theory of Ideal Gases, one is led to the equation giving the number of molecules passing at all angles within $2\pi$ through a 1 $cm^2$ plane per second, under conditions of thermodynamic equilibrium in an enclosed space:[23]

$$n = \frac{n_o \bar{v}}{4} . \qquad (1)$$

Here, $n_o$ is the number of molecules present per $cm^3$; $\bar{v}$ is a suitable average velocity.

For a single molecular species, $\bar{v}$ is the simple mean velocity, derived from the Maxwellian distribution law as:

$$\bar{v} = \sqrt{\frac{8kT}{\pi m}} . \tag{2}$$

In equation (2), k is the Boltzmann Constant, T is the absolute temperature, and m the weight of a single molecule in grams. Combining equations (1) and (2) with the Ideal Gas Law, $p = n_o kT$, so as to eliminate $n_o$ and $\bar{v}$, yields:

$$n = \frac{p}{\sqrt{2\pi mkT}} . \tag{3}$$

If now the number N is defined as the number of moles of gas striking an element of area a $cm^2$ of the enclosing wall in time t minutes (60 t seconds), then,

$$N = \frac{60atn}{N_o} ,$$

where $N_o$ is Avogadro's number. Hence, employing equation (3),

$$N = \frac{60atp}{\sqrt{2\pi MRT}} . \tag{4}$$

If the area element a coincides with the effusion orifice, then equation (4) is the equation for total effusion under conditions of ideality and equilibrium.

2. Angular distribution. -- Thermodynamic equilibrium also defines the angular distribution of molecules passing through an ideal orifice:

$$dN = N \sin \phi \cos \phi \, d\phi, \tag{5}$$

where $\phi$ is the angle of departure from the normal to the orifice plane. Equation (5) is the Cosine Distribution Law[24] stated in such form as to include all molecules emanating in paths defining a conical region between departure angles $\phi$ and $\phi + d\phi$.

Employing a circular collimator and an orifice-collimator axis normal to the orifice plane, it is necessary simply to integrate equation (5) from $\phi = 0$ to $\phi = \phi_c$, the limiting angle cut off by the collimator. This yields:

$$N_c = N \sin^2 \phi_c;$$

which, on combining with the trigonometric relation,

$$\sin^2 \phi_c = \frac{r^2}{d^2 + r^2},$$

and with equation (4), yields:

$$N_c = \frac{60atp}{\sqrt{2\pi MRT}} \cdot \frac{r^2}{d^2 + r^2}. \tag{6}$$

Here r is the collimator radius and d the axial orifice-collimator distance. $N_c$ is the number of moles passing through the collimator in an exposure t minutes long.

3. Radiochemical assay. -- The number $N_c$ is determined in the present work by counting alpha-decay events in the condensate. Employing the fundamental law of radioactive decay,

$$\left[-\frac{dA}{dt}\right] = \lambda A; \tag{7}$$

given n, the number of radioactive atoms per molecule of effusant, i.e.,

$$A = nN_c; \tag{8}$$

and employing a "geometry factor," g, for the counting device used, i.e.,

$$cg = \left[-\frac{dA}{dt}\right]; \tag{9}$$

it follows that:

$$N_c = \frac{cg}{n\lambda}. \tag{10}$$

Consistent units are of course required: if the counting rate c is recorded in counts per minute, then the decay constant $\lambda$ must be in disintegrations per minute per mole.

4. The finished equation. -- Combining equations (6) and (10) and solving for p yields:

$$p = \frac{cg}{60an\lambda t} \cdot \sqrt{2\pi MRT} \cdot (1 + \frac{d^2}{r^2}). \qquad (11)$$

Equation (11) gives the pressure in cgs units. For practical purposes it is desirable to insert a unit conversion factor f, and to arrange the terms in groups as follows:

$$p = \left[\frac{f\sqrt{2\pi R}}{60}\right] \cdot \left[\frac{g}{a}(1 + \frac{d^2}{r^2})\right] \cdot \left[\frac{\sqrt{M}}{n\lambda}\right] \cdot \left[\frac{c\sqrt{T}}{t}\right]. \qquad (12)$$

In this equation, which was used for all work to be described, p is the partial pressure of the vapor in the vessel in dynes/$cm^2$ if f = 1, and in other units for appropriate values of f; R is the gas constant in cgs units; g is the counter geometry factor, defined as cg = (-dA/dt); a is the orifice area in $cm^2$; d is the axial orifice-collimator distance, and r is the collimator radius, both in cm; M is the gram-molecular weight of the effusant; n is the number of radioactive atoms in a molecule of the effusant; $\lambda$ is the decay constant of the radioactive element, in disintegrations per minute per gram-mole; c is the observed alpha counting rate of an exposed receiver in counts/min; T is the vessel temperature in $^{o}K$; t is the time in minutes during which the receiver was exposed to the collimated beam of effusant.

The significance of the grouping of terms is as follows: 1st bracket - numbers and general physical constants; 2nd bracket -

constants of the apparatus; 3rd bracket - constants characteristic of the substance on which measurements were made; 4th bracket - raw data taken for each individual target exposure.

## III. APPARATUS

### A. Description

The entire assemblage of equipment for measuring vapor-pressures is depicted photographically in Fig. 2.

1. Vacuum envelope. --The effusion apparatus was contained in a Pyrex air-cooled bulb 6 in. in diameter, bearing two opposed arms about 1 3/4 in. in diameter and 6 in. long and ending in tapered ground fittings. A similar arm forming a "tee" with these made connection to the vacuum line. The opposed arms carried the weight of the furnace-collimator system to be described, its axis horizontal. Caps to these arms carried the shutter and receiver systems; one cap bore also the furnace electrodes and thermocouple wires.

Following the work with $PuF_3$ and the first series of measurements on $AmF_3$, this envelope was replaced by one bearing yet another arm, hanging vertically below the bulb. This arm terminated in a charcoal trap, used to assist in maintaining the high vacuum demanded for work with americium metal. It can be seen in Fig. 2.

The vacuum line, of about 1 3/4 in. diameter Pyrex tubing, led through a 15 mm stopcock to a liquid-nitrogen trap, thence to an Eimac Model A-1, 3-stage fractionating oil-diffusion pump (Eitel-McCullough, Inc., San Bruno, Calif.), and finally to a Duo-Seal mechanical forepump (W. M. Welch Mfg. Co., Chicago, Ill.). Valves and fittings permitted the admission of argon, dried over phosphorous

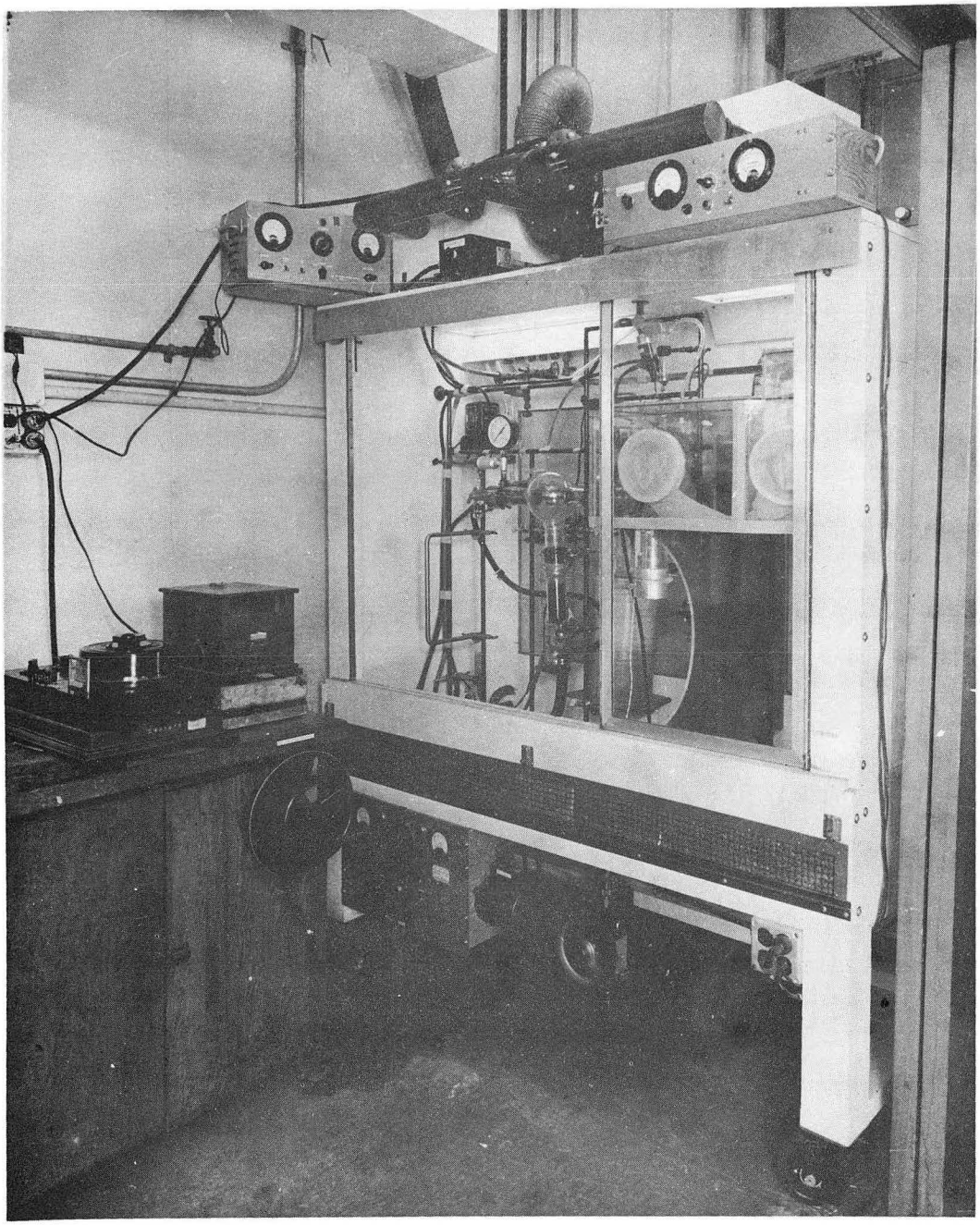

Fig. 2. Equipment used in measuring the vapor-pressures of $PuF_3$, $AmF_3$, and americium.

pentoxide and then passed over uranium shavings at $400^{\circ}$ C, for purposes of opening the line. Lubriseal high-vacuum grease and Apiezon W wax were used for stopcocks and semi-permanent joints, respectively.

The pumping system produced an ultimate vacuum in the envelope of $1 \times 10^{-7}$ mm Hg, a maximum pressure during furnace operation of about $10^{-5}$ mm without the use of a charcoal trap and $<5 \times 10^{-6}$ mm with the trap installed. Pressures were measured by means of an RCA 1949 tube placed between the furnace and the main stopcock noted above, and operated on a log ion gauge circuit designed and built by the Electronics group under Mr. H. P. Robinson.

2. Furnace-collimator unit. -- This integral unit consisted of a central cylindrical resistance-wire furnace within guides mounted on two sturdy tantalum rails 1/8 in. x 1/4 in. x 8 in. long; a defining collimator at each end of the rails; and rough collimators midway between. All parts were firmly bolted to the railway, and all were accurately machined to ensure the alignment and symmetry desired for use as a "twin" or comparator. The collimators were 1/8 in. thick disks of stainless steel, the openings drilled accurately conical.

The furnace consisted, in order from the inside out, of a thin-walled alundum sleeve, 3/16 in. I. D. x 7/8 in. long; the heating element; an alundum shell 1/2 in. O. D. x 7/8 in. long with a close-fitting cylindrical molybdenum radiation shield; and finally an outer shield also of molybdenum. The ends of the outer alundum sleeve and fitted shield were suspended by means of positioning screws inside tantalum rings which were a part of the rigid railway system. Tolerances within the outer sleeve assured permanent furnace alignment.

The heating element consisted of fourteen evenly spaced turns of 0.030 in. molybdenum wire, making a helix 1/4 in. I.D. x 7/8 in. long. The end turns and leads were etched with 8 M nitric acid to a diameter of 0.022 in. to increase their heat output: in operation the end turns were some $200^{\circ}$ - $300^{\circ}$ C above the temperature of the body of the helix, thus combating the effects of end radiation. To the leads were welded short lengths of 0.035 in. platinum wire, which were in turn spot-welded to 0.080 in. nickel bus-bars leading finally in the cooler regions of the system to bus-bars of copper. The latter passed through short porcelain insulators set in the collimator disks, and were joined at their ends by flexible, demountable connections to heavy tungsten electrodes sealed through a glass cap.

The furnace-collimator unit is shown photographed in Fig. 3.

3. Shutter-receiver systems. --Simplicity was the keynote of the shutter-receiver mechanisms employed in "twin" operation, since one unit had to share very limited space with the emerging electrodes and thermocouple leads. The devices at both ends were identical. A glass rod passing through a well-greased tapered ground fitting in the Pyrex cap was used to rotate a 1/8 in. square brass rod ending in a short round section, the tip of which rode in a cavity in the center of the defining collimator disk. Thrust and flexibility were provided by inserting the square brass rod, against a compressed light phosphor bronze helix, into a loose-fitting square brass housing which was itself firmly strapped to the glass rotator.

The shutter consisted of a circular opening in one quadrant of a brass disk, the disk being mounted by a friction bearing in its center

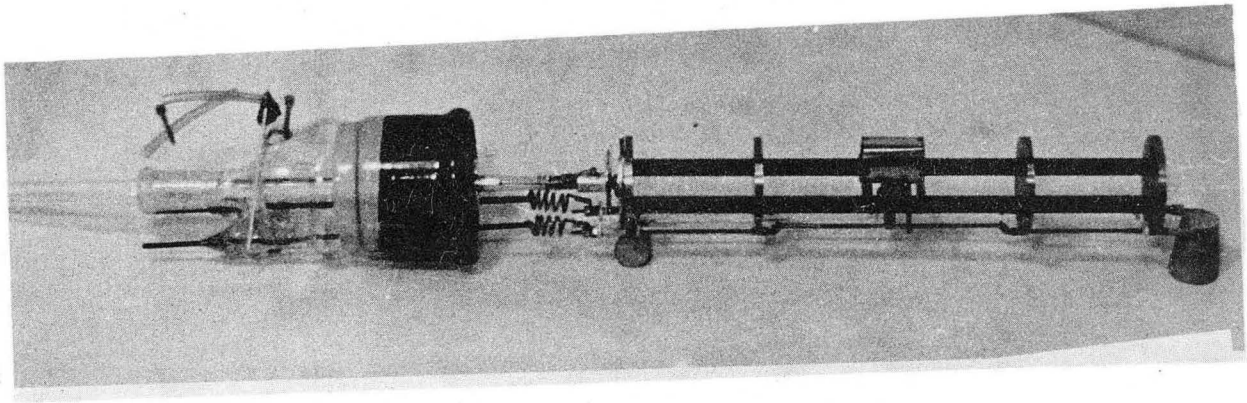

Fig. 3. Furnace-collimator assembly.

over the cylindrical section of the brass driving shaft. The shutter disk was thus rotated close behind the collimator piece, its motion constrained by a pin on the latter to exactly one-quarter turn from "full-closed" to "full-open" position.

The receiver was a 0.005 in. platinum disk, marked into quadrants and provided with a 1/8 in. square hole to fit the driving shaft; this disk was clamped to the shaft immediately behind the shutter, after washing, rinsing, and flaming.

In operation, rotation of the glass rod a quarter-turn in either direction served to turn both receiver and shutter together to "open" or "closed" position; continued rotation with the shutter against its stop served to bring different receiver quadrants into line behind the shutter opening. In this manner it was possible to make four timed exposures to the effusant from each end of the twin Knudsen vessel, between shutdowns for receiver replacement. Receivers were later cut into separate quadrants with a razor for alpha particle counting.

Fig. 4 gives the external appearance of the assembled "twin" system, including furnace, collimators, shutters, and receivers.

For conventional operation with only one end of the effusion apparatus in use it was possible to employ a more elaborate receiver magazine. In this unit the shutter and its operation were the same as described above; however, the driving shaft was entirely of round brass rod, passing out of the vacuum envelope through a Wilson seal. The housing for the latter was seated by means of a groove bearing a greased "O-ring" against the end of a brass tapered fitting, which was in turn waxed onto the end of its glass arm.

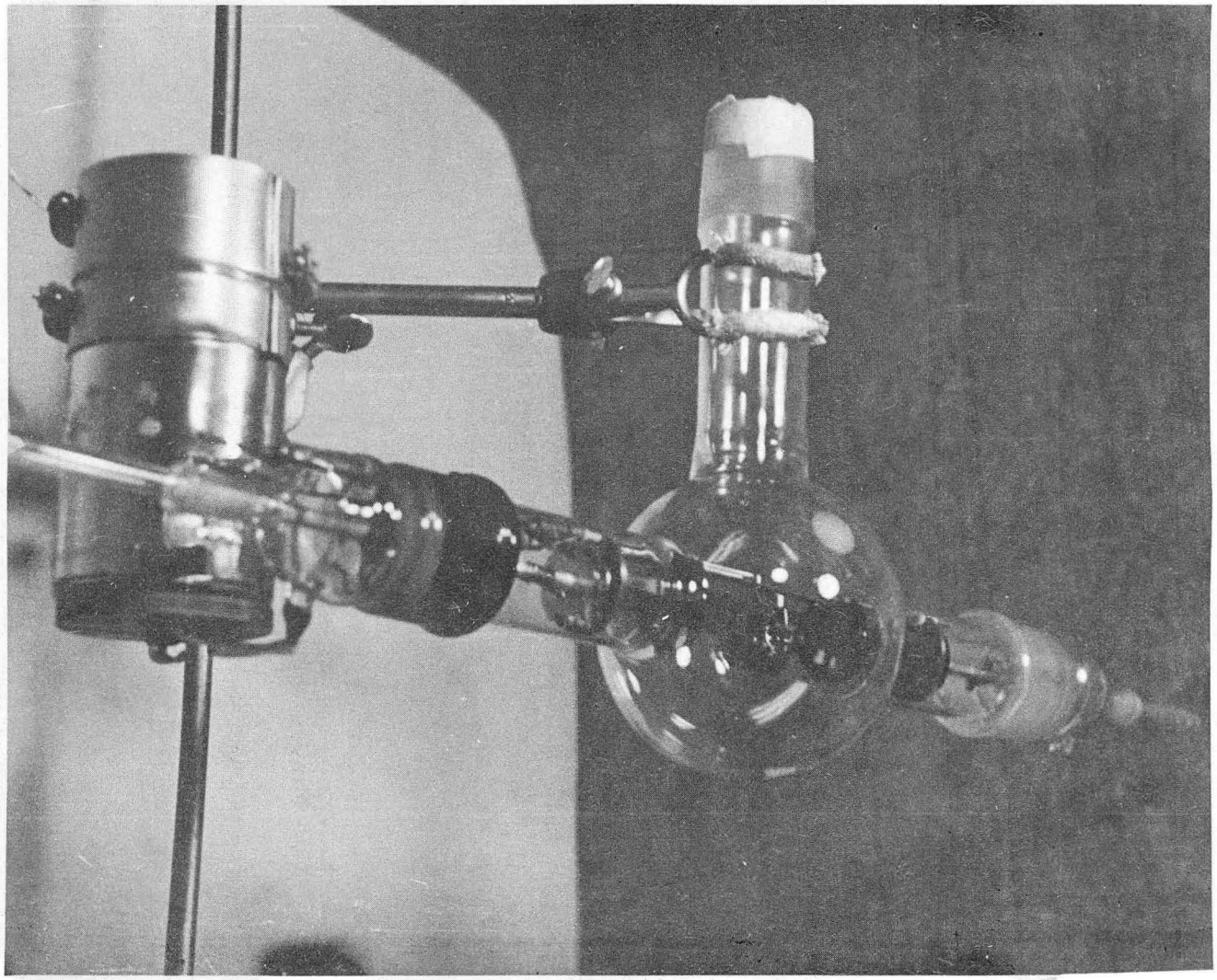

Fig. 4. Twin effusion apparatus.

Targets consisted of small disks of 0.005 in. platinum, drilled very near to the edge. A packet of fifteen to twenty-five of these were washed, rinsed, and flamed, then threaded over the driving shaft, which was provided with a 1/80 in. pitch, left-hand thread. Guides and a rider were employed which, when the shaft was rotated in one direction, caused the disks to pass one at a time over a knife-edge, whereupon they swung down freely and hung below the shaft and in line with the collimator opening. A quarter-turn of the shaft in the other direction then opened the shutter for exposure.

The shaft thread changed from 1/80 in. pitch to 1/20 in. pitch at the position of the knife-edge, so that used targets were slightly separated as they passed down the threads and were successively replaced from the pack. Contact between exposed disks was thus restricted to their outermost edges, which were beyond the limits of the beam. The disks were removed singly with forceps for counting subsequent to a completed series of exposures.

Both twin- and single-type shutter-receiver systems are sketched in Fig. 5.

4. Effusion vessel. -- Three types of crucible were used, one "twin" and two "single" modifications. The three types are sketched in Fig. 6. All parts were of tantalum, except for platinum gaskets.

In order to ensure exact positioning of the crucible along its axis, a centering pin of 1/16 in. alundum rod was passed through matched holes in the furnace and into a shallow cavity in the crucible. The pin rode in a split tantalum tube fixed to the railway system, and was held under pressure by a very light tungsten wire helix backed by a tantalum collar screwed onto the end of the tube. An additional

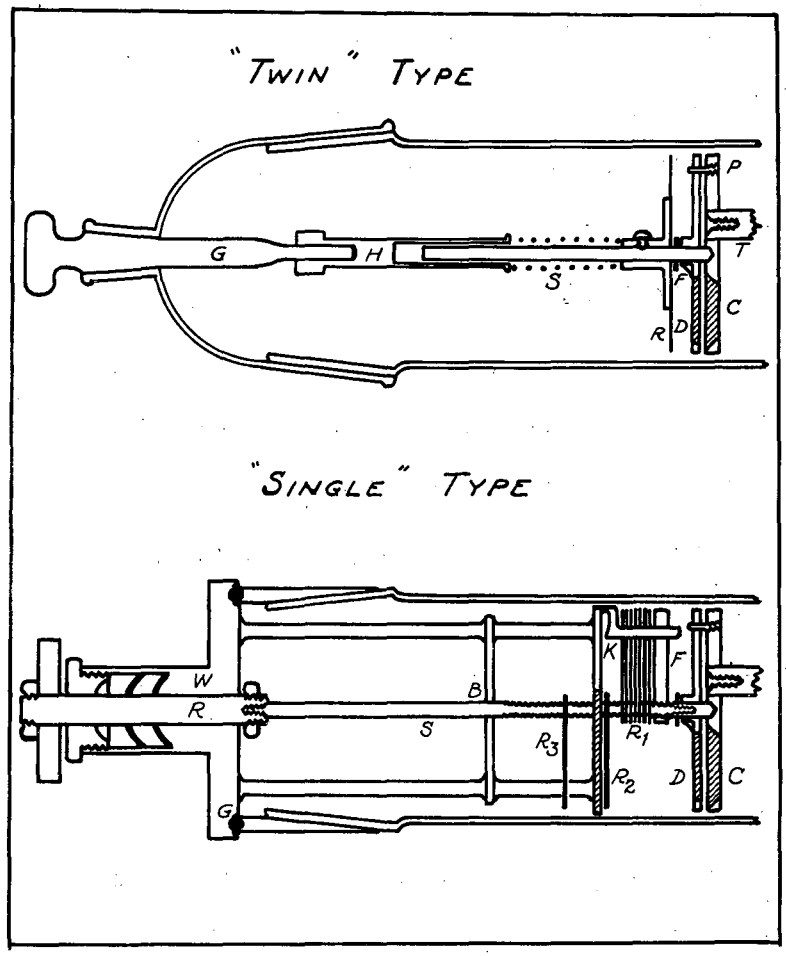


Fig. 5. Shutter-receiver assemblies.

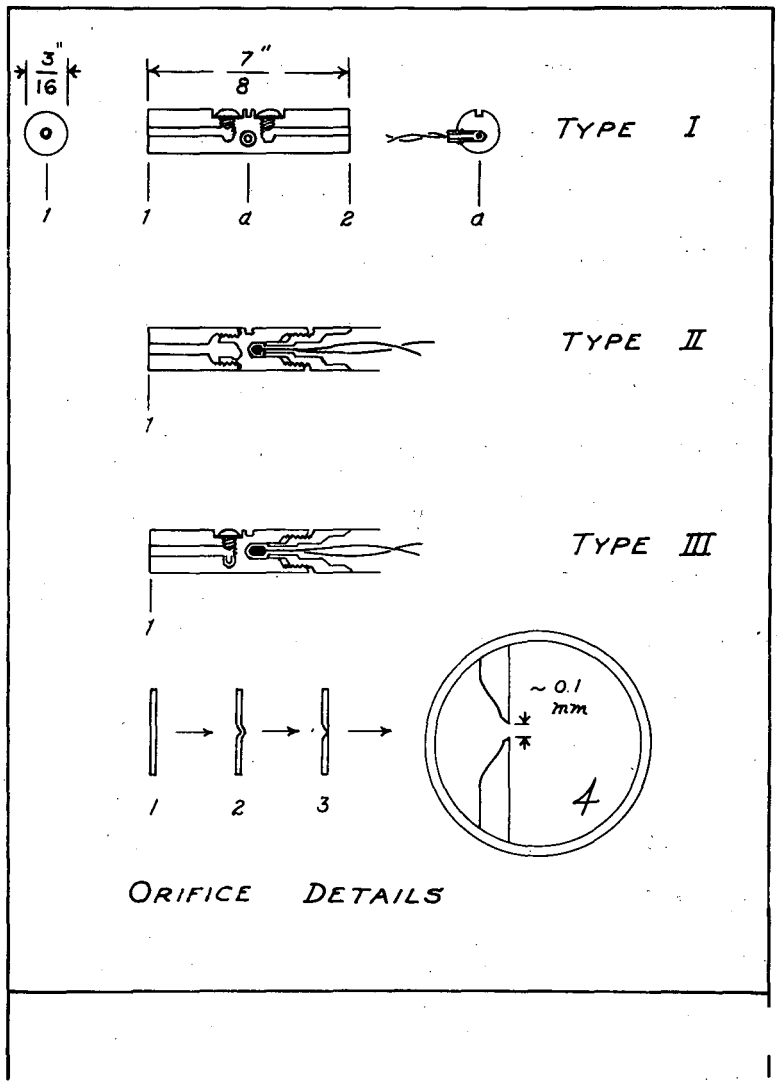


Fig. 6. Effusion vessels.

function of the centering pin was to drain heat off from just behind the sample, preventing it from attaining a temperature higher than that of the orifice wall.

In early experiments orifice foils of 0.0003-in. tantalum, welded under a heavier ring to the front face of the crucible, were used. This type of closure has been employed by Jones[4] and others. It was abandoned, however, after measurements on $PuF_3$ yielded very low results and appearance of sublimate on the interior of the foil indicated gross transport of the sample by distillation. The type of closure used throughout the work related here was similar to that described by Phipps, Sears, Seifert, and Simpson:[1] a piece of 0.006 in. tantalum sheet was dimpled with an awl, then filed flat on the outside face; subsequent alternating operations with a sharp steel needle from the inside and with fine crocus cloth on the outside produced a nearly round, fairly smooth-edged orifice. The sheet was spot-welded over the entire face of the crucible to ensure maximum thermal contact as well as an hermetic seal. Orifice details are included in Fig. 6.

5. Thermocouple. -- For measuring temperature, platinum vs. 90-platinum, 10-rhodium thermocouples were used with all crucible types, differing only in mode of insertion. A tantalum sleeve 1/16 in. O.D. x 1/8 in. long pressed the junction into the side of the twin type, the sleeve being inserted by one-half to one turn of conventional machine thread. The aftermost section of the single-type crucibles pressed the thermocouple junction into place in a similar manner, except that in the latter case the leads emerged out the after end of the furnace instead of transversely out the side.

Fig. 6 shows the details of thermocouple insertion in the three crucible types.

No protective tubing was permitted in the immediate vicinity of the furnace, because local operating temperatures exceeded the safe limits for the available ceramics in vacuo. Suitable means were employed to prevent sagging and "shorting". Where the wires were cooler, standard porcelain protective tubes were used. Passing out of the vacuum envelope, the thermocouple wires were sealed through a glass bead, the latter being waxed into a tubulation in the same Pyrex cap which bore the furnace electrodes. A conventional ice-water bath cold junction was employed. Radio pin-jacks connected the wires on one side of the cold junction to twisted copper leads which conducted the emf to a potentiometer.

The associated measuring equipment consisted of a Leeds and Northrup Model 7552 slide-wire potentiometer (Leeds and Northrup Co., Philadelphia, Pa.), a Rubicon Model 3402 HH galvanometer (Rubicon Co., Philadelphia, Pa.) giving a sensitivity of about 0.5 mm deflection per microvolt, and a standard cell of 1.01887 volt emf (manufactured by the Eppley Laboratory, Inc., Newport, R.I.).

6. Furnace power supply and control. -- The power for the resistance-wire furnace was supplied as indicated schematically in Fig. 7. Variac "A" was used to fix the input approximately; the operator used Variac "B" to maintain constant temperature, keeping the galvanometer in the thermocouple circuit as near as possible to the "zero" position. By this means exposure times were varied from 1 minute to 100 minutes, yet maintaining less than $\pm 0.5^{\circ}$ to $1.0^{\circ}$ temperature variation during any exposure. In addition, the operator could balance an occasional fluctuation by a deliberate one of opposite

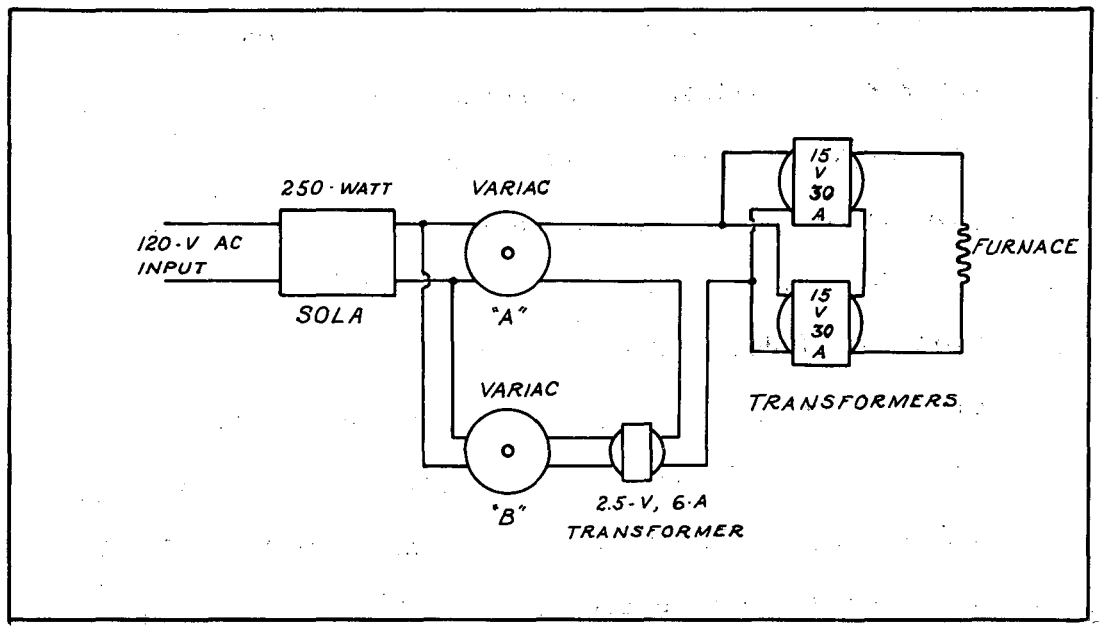


Fig. 7. Furnace power supply.

sign and similar duration, thus reducing to a minimum the scattering of points due to random temperature changes.

Air cooling of the external electrodes and of the bulb and arms was provided by suitably placed fans.

7. Dry-box. -- At the conclusion of twin operation, when the charcoal trap, new receiver unit, and single-type crucibles were installed, a gloved dry-box was built and fitted over one arm of the Pyrex furnace envelope. This box was equipped with hose to the purified argon supply. An airlock for entry and exit of materials, which could also be swept with argon, prevented admission of gross amounts of air and moisture. In addition, a fan within the box circulated the contained atmosphere through a large duct system which included a trap cooled by a dry-ice-acetone bath. Thus moisture from the surfaces of newly introduced materials, or intruding by diffusion through the gloves, was effectively frozen out. This system was in continuous operation for over a month before the measurements on americium metal were made.

8. Safety. -- The dry-box served as the point of concentration of activity going into and out of the vacuum system; it was operated and treated in much the same manner as a "Berkeley Box." The entire vacuum system and the dry-box were contained in a large housing designed and built by Messrs. W. G. Ruehle, W. D. Phillips, and others in the Health Chemistry group under Mr. N. B. Garden. This box was provided with three sliding safety-plate glass doors in front and three separate wooden doors in back, for access. A heavy-duty exhaust and filter system gave about as much draft as a fume hood,

although with the doors shut protection in case of implosion would have been nearly complete.

Figure 2 shows this housing with two of the front doors removed; the dry-box is prominent among the contents.

9. Equipment for measuring other variables. -- The fourth bracket in Equation II-(12) contains all variables pertaining to a given exposure, namely T, the absolute temperature of the sample during exposure of the target; t, the duration of the exposure; and c, the alpha-particle counting rate of the exposed target. The equipment used in measuring and controlling the temperature has been described in a preceding paragraph.

Exposure times were clocked with a newly-adjusted watch which was checked against an electric timer of extremely high precision.

Alpha-particle counts were registered with a standard high-geometry parallel plate, argon-filled ionization chamber of local design, employing standard amplifying and scaling circuits and mechanical registers. Counting time was clocked with an electric timer. Counting equipment was supplied and serviced by the Electronics group under Mr. H. P. Robinson.

Coincidence corrections were made to the alpha-particle counting rates of plates carrying 5000 c/m and higher.

10. Auxiliary equipment. -- Much additional equipment was employed in the many operations preliminary to the actual vaporization experiments. These devices included other vacuum lines, furnaces, microscopes, optical pyrometers, etc. Being incidental items, they will be described only briefly and in connection with the operations in which they were employed.

## B. Constants of the Apparatus

The accepted numerical values of the general physical constants, as well as the values of the constants of the equipment, may be grouped for convenience in this section.

It was indicated following the presentation of the Effusion Equation II-(12) that the units in which the vapor-pressure p is expressed fix the value of the conversion factor f. It will be convenient to state the pressure in millimeters of mercury, hence,

$$f = 0.750_1 \times 10^{-3}.$$

The value used for R, the molal gas constant, is:

$$R = 0.831_4 \times 10^8 \text{ c.g.s. units.}$$

The alpha-particle counter geometry factor was taken as:

$$g = 1.92,$$

corresponding to the accepted counting efficiency of 52 percent for this type of chamber and thin radioactive sources.

The orifice area a was measured at room temperature with the aid of a camera lucida attachment (Spencer Lens Co., Buffalo, N.Y.) on a microscope using a 44x objective and 10x eyepiece (Bausch and Lomb Optical Co., Rochester, N.Y.). A stage micrometer with 0.010 mm subdivisions (Bausch and Lomb) permitted the tracing of rectangles of known area through the same optical system.

In practice, a tracing of the orifice image was made on a piece of clean semi-gloss paper, then internally and/or externally tangent rectangles were traced on the same sheet. Making accurate cutouts to these lines and weighing the pieces gave enough information, with the known areas represented by the rectangles, for calculation of the orifice area. Numerous trials indicated that the method was

reliable to better than ±1.0 percent. The orifices used were traced at least twice in the fashion described, the average computed area being adopted. The room temperature values so obtained are listed in Table I.

The value of the orifice area actually employed for a given exposure was corrected to the vessel temperature measured during that exposure. The temperature correction was computed according to the following expression, based upon a linear expansion coefficient for tantalum of $7 \times 10^{-6}$:

$$A_T = A_{298} \left(\frac{996 + 0.014\ T}{1000}\right).$$

Table I

Orifice Areas, Room Temperature Values

| Orifice Designation[a] | | Area, $A_{298}$ | | Run[b] |
|---|---|---|---|---|
| C-2 | (I) | $(1.02_4 \pm 0.005) \times 10^{-4}$ cm$^2$ | $PuF_3$ | V and VI |
| D-1 | (I) | $(1.16_2 \pm 0.005) \times 10^{-4}$ cm$^2$ | $AmF_3$ | I - IV |
| D-2 | (I) | $(2.96_8 \pm 0.012) \times 10^{-4}$ cm$^2$ | $PuF_3$ | I - IV |
| E | (II) | $(1.83_2 \pm 0.010) \times 10^{-4}$ cm$^2$ | $AmF_3$ | V |
| K | (III) | $(0.722 \pm 0.003) \times 10^{-4}$ cm$^2$ | Am | II |
| L | (III) | $(0.771 \pm 0.002) \times 10^{-4}$ cm$^2$ | Am | I |

[a]Crucible type is designated by (I), (II), or (III), in accordance with the notation in Fig. 6; crucibles were assigned letters A, B, C, etc., in order as fabricated; orifices on Type I vessels were numbered 1 and 2 to match the end-designation given in Fig. 6 and in the ensuing text.

[b]Runs were assigned numbers corresponding to sample loading, or to each receiver set using the same loading in "twin" operation.

The axial orifice-collimator distances were determined as follows. The total collimator-to-collimator distance was measured at least twice at each of five different operating temperatures, using a 12-in. Vernier caliper (L. S. Starrett Co., Atholl, Mass.) and aligning the jaws visually from outside the vacuum envelope. All crucibles were machined to close tolerances and were accurately positioned as previously described. When the temperature-corrected vessel lengths were subtracted from the measured overall dimension, the difference was found to be substantially independent of temperature. The two ends of the unit, designated as "1" and "2", did, however, have slightly different orifice-collimator distances:

$$d_1 = 9.10 \pm 0.01 \text{ cm},$$

$$d_2 = 9.08 \pm 0.01 \text{ cm}.$$

The collimator diameters were measured to extreme precision at room temperature, using a calibrated traveling microscope (Pantechnical Mfg. Co., Berkeley, Cal.). Their images were circular within ±0.13 percent. Mean values were taken of five different diameters, each one measured twice. These gave for radii,

$$r_1 = r_2 = 0.553_3 \pm 0.0002 \text{ cm}.$$

No temperature correction was necessary, since the defining collimator disks were protected from excessive heating.

## C. Preliminary Experiments

A number of investigations were carried out parallel with the development of the equipment in its final form.

The design of the furnace and of the effusion vessels was arrived at following many observations with the optical pyrometer of the temperature at various locations in dummy crucibles. Because of

difficulties in obtaining optimum conditions for optical pyrometry, it was not possible to rely heavily on the observations; however, it appeared that temperature variations over the length of the crucibles used were not more than a few degrees. Similarly, apparent temperatures of the orifice-bearing face and of the interior read through the orifice gave, upon correction for emissivity, values which were close together.

Thermocouple performance was exhaustively investigated. The absence of protective tubing near the point of emergence from the crucible exposed the thermocouple wires to poisoning by materials evaporated from the furnace at very high temperatures, which effect actually fixed the upper temperature limit of operation of the equipment. Thermocouples used after these trials were completed were not subjected to temperatures within 200° of that at which emf deterioration was observed.

The thermocouples were calibrated in place by the use of standard melting point substances. In the process it was learned that the emf-temperature relation was constant (within ±5 microvolts, or ±0.5° C) with time, with removal and re-insertion of the thermocouple, with replacement of the crucible, with replacement of the hot junction by welding, and even with replacement of whole lengths of platinum or platinum-rhodium wire from stocks on hand. A standard ice-bath cold junction was used as previously noted; the resulting emf values fell rather consistently about 10 μv or 1° below the values in the standard reference table quoted from Roeser and Wensel[25] by Weber.[26]

In order to establish this conformity to the tabulated values, melting points of gold, silver, aluminum, and tin were taken. Subsequent

calibrations were made employing only gold and aluminum or gold alone, the conformity over a range of a few hundred degrees being assured.

Crucibles employed for the calibration were regular effusion vessels but with the orifice foil left off; thermocouple insertion was exactly the same as in later vapor-pressure work. Pure graphite thimbles 0.060 in. O.D. x 0.030 in. I.D. x 1/8 in. long were used to contain tiny pieces of the standard metals formed into an "L"-shape. The thimble with its metal strip was placed far back in the tantalum crucible in the position of the vapor-pressure sample, then the temperature was raised gradually (about $1^{\circ}$/minute in the vicinity of the melting point) while an operator kept the thermocouple potentiometer circuit constantly in balance. Melting of the standard metal was observed with the aid of a small telescope, a window temporarily replacing one of the shutter-receiver units and suitable illumination being supplied by a 100-watt spotlight.

Since observed melting rather than thermal arrest was taken for the melting point, NBS-calibrated metal samples were not required; nor are such samples supplied in the form of sheets suitable for this micro-scale method. Therefore the best metals available in this laboratory were used, and were handled with extreme care to avoid contamination. The freezing points as tabulated by Weber[27] were adopted as melting temperatures.

Data pertinent to these metals are assembled in Table II. The sample "Observed E.M.F.'s at Melting", taken from the calibration data for the Type I crucible, is included to indicate the reliability of the method.

Of the metals used, the silver was not of as high purity as desired, although its melting characteristics appeared normal. Aluminum appeared heavily encrusted after melting, presumably with oxide; hence its apparent melting temperature is not necessarily reliable. This difficulty was never entirely overcome, even loading within the argon-filled equipment; it may be attributed to outgassing of the graphite thimble.

Scattering and incompleteness of condensation of the effusant were investigated by placing extra targets outside of the beam but in key positions to indicate these types of interference. Counting of the targets always indicated alpha particle activity insignificant in comparison with the amounts of material collected during exposures. A conservative limit of 0.5 percent may be placed on the error so caused.

Table II
Standard-Melting-Point Metals Used in Thermocouple Calibration

| Metal | Gold | Silver | Aluminum | Tin |
|---|---|---|---|---|
| Source | S.S. White Dental Mfg. Company | Handy-Harmon | Johnson-Matthey | Hilger |
| Purity (Original Anal.) | 99.99+% | 99.99% | 99.99+% | 99.995% |
| Purity (Spectrographic Anal.* on Prepared Strips) | 99.99+% | 99.9%; 0.1% Cu | 99.99+% | 99.99% |
| Melting Point[27] | 1063° C | 961° C | 660° C | 232° C |
| Thermocouple E.M.F. at M.P., Ref. Table[26] | 10.300 mv | 9.120 mv | 5.840 mv | 1.710 mv |
| Thermocouple E.M.F. at Meltings Observed--Example | 10.285<br>10.293<br>10.295 | 9.095<br>9.110 | 5.860<br>5.860 | 1.707 |

*Spectrographic analyses were performed on the prepared strips, or solutions made from them, by the Spectrochemical Group under Mr. J. G. Conway.

# IV. DATA

## A. Plutonium Trifluoride

All of the data reported in this section were obtained from two samples of plutonium trifluoride, which are most conveniently identified by reference to the crucible and chamber into which each was loaded, viz.,

Sample C-2,

Sample D-2.

(It will be noted that these designations coincide with those of orifices listed in Table II)

Sample C-2 was employed in exposure series V and VI of a group of vapor-pressure runs originally designed to verify proper operation of the equipment, and series I-IV with sample D-2 were made subsequently. While both samples were run in "twin" equipment, only sample D-2 was involved in comparative measurements: $AmF_3$ sample D-1, referred to in a following section, was run simultaneously.

Each run designation, e.g., "III", refers to a particular twin-type platinum collector disk, the furnace having been cooled and the vacuum broken between runs for replacement of disks. Each individual exposure is denoted by reference to the particular quadrant of the collector which was placed in line with the beam, e.g., "III-2."

1. Preparation and purity. --The samples used were taken from a batch of several hundred milligrams of $PuF_3$ prepared by Mr. R. D. McLaughlin from a carefully purified Pu(IV) stock solution. The trifluoride was precipitated from the aqueous system with hydrogen fluoride, after reduction of the plutonium to Pu(III) with sulfur dioxide. The precipitate was air-dried after washing with acetone, then finally

vacuum-dried at room temperature and stored under cover in ordinary atmosphere.

Spectrochemical analysis, performed under the direction of Mr. J. G. Conway, indicated that the material was 99.9+ percent pure as regards cations. Approximately 0.02 percent aluminum, 0.01 percent lanthanum, and 0.02 percent magnesium were detected.

A powder sample was sent to the X-ray Diffraction group under Dr. D. H. Templeton. The diffraction pattern indicated a single phase, with normal lattice parameters for $PuF_3$ (hexagonal).

2. Preparation for measurement. -- Both samples were handled and measurements were executed in the same manner, as follows.

The tantalum crucible, after prolonged boiling in aqua regia and rinsing in water, was placed in a vacuum furnace and held at about 1500° C for an hour. After a suitable cooling period, the crucible was removed to the device set up for orifice measurement, and two tracings were made as described previously. Earlier experiments had indicated that orifice dimensions did not change subsequent to a single firing.

The sample, an estimated 1 milligram of $PuF_3$ powder, was loaded into the crucible in air, and the gasket and set-screw were assembled firmly. Exterior surfaces were checked for alpha activity. The furnace-collimator assembly was removed to a fume-hood from the vacuum line, the latter under a continuous flow of dried argon while open. The crucible was fixed into place in the furnace, the thermocouple junction was installed, then the assembly was returned

to the vacuum line and swept with argon. After a brief pumping down, the system was flushed a second time with argon before the final evacuation was begun.

Following prolonged pumping, ordinarily overnight, the furnace was heated very gradually to operating temperatures. This operation normally required four hours or more. Equilibration from a few minutes to half an hour preceded each recorded exposure.

Manipulations for making exposures have been described in an earlier section. After the four quadrants had been exposed, the system was allowed to cool at least two hours before opening for removal and replacement of receivers. Pumping down for subsequent runs followed the same routine.

Receivers were cut into separate quadrants and counted for alpha activity as previously noted. Over 10,000 counts were recorded for all samples, many times this number for the most active ones.

3. The numerical equation. -- In addition to physical constants and constants of the equipment, the Effusion Equation II-(12) contains certain numbers pertaining to the sample itself, namely the molecular weight and composition of the effusant and the alpha decay constant of the plutonium.

Brewer, et al.[2] have employed thermodynamical calculations to show that $PuF_{3(g)}$ is stable against decomposition at temperatures far in excess of the maximum encountered here. The extended temperature range covered by Simpson, et al.[1], with no anomalous curvature in the plot of log p vs 1/T, indicates that the composition of the effusing species does not vary detectably with temperature; nor is the existence of a dimer at these high temperatures energetically very reasonable.

Hence the molecular formula $PuF_3$ for the effusant may be assumed with confidence.

This formula fixes the number n in Equation II-(12): $n = 1$.

The plutonium employed may be regarded, to a close approximation, as pure isotope 239. Taking the atomic weight of this isotope as 239.1, and that of fluorine as 19.0, gives:

$$M_{PuF_3} = 296.1 \text{ grams.}$$

The best value for the half-life of $Pu^{239}$ is taken from Hollander, Perlman, and Seaborg[28] as:

$$T_{1/2} = 24,400 \text{ years.}$$

From this is calculated the value of the decay constant:

$$\lambda_{Pu^{239}} = 3.253 \times 10^{-3} \text{ disint/min/g-mole.}$$

Inserting all appropriate constants into Equation II-(12), and including the temperature-correcting function for orifice area, yields,

$$\text{(C-2): } p_{(mm)} = 7.65 \times 10^{-7} \cdot \frac{c\sqrt{T}}{t} \cdot \left[\frac{1000}{996 + 0.014T}\right];$$

$$\text{(D-2): } p_{(mm)} = 2.638 \times 10^{-7} \cdot \frac{c\sqrt{T}}{t} \cdot \left[\frac{1000}{996 + 0.014T}\right].$$

4. Data and results. -- Table III includes for each exposure the measured counting rate, the measured exposure time, and the absolute temperature as computed from the thermocouple emf by the use of the table supplied by Weber[26] and the appropriate calibration correction. Shown also are the values of the vapor-pressure computed by the equations given in the preceding paragraph, and the corresponding values of $\log_{10} p_{(mm)}$ and $10^4/T$ for purposes of plotting the data.

A conventional plot of log p vs. $10^4/T$ for $PuF_3$ is given in Fig. 8. The experimental points obtained from Table III have been numbered in chronological order, no other distinction appearing justified.

The solid curve is the best-fitting straight line. The straight line fitted by Simpson, et al.[1] to their data over the same temperature range coincides almost perfectly with this curve.

Derived quantities will be presented under Discussion of Results, Section VI.

Table III

The Vapor-Pressure of Plutonium Trifluoride: Data and Results

| Exposure | c(c/m) | t(min) | T(°K) | p(mm) | log p | $10^4/T$ |
|---|---|---|---|---|---|---|
| (Sample C-2) | | | | | | |
| V-1 | 999. | 10.00 | 1413 | $2.827 \times 10^{-3}$ | -3 + .451 | 7.08 |
| V-2 | 333.9 | 20.00 | 1338 | $4.61 \times 10^{-4}$ | -4 + .664 | 7.47 |
| V-3 | 176.6 | 50.00 | 1280 | $9.53 \times 10^{-5}$ | -5 + .979 | 7.81 |
| V-4 | 47.7 | 100.00 | 1214 | $1.255 \times 10^{-5}$ | -5 + .099 | 8.24 |
| VI-1 | 245.7 | 50.00 | 1292 | $1.332 \times 10^{-4}$ | -4 + .124 | 7.74 |
| VI-2 | 329.0 | 20.00 | 1335 | $4.53 \times 10^{-4}$ | -4 + .656 | 7.49 |
| VI-3 | 683. | 10.00 | 1393 | $1.921 \times 10^{-3}$ | -3 + .283 | 7.18 |
| VI-4 | 1031. | 5.00 | 1444 | $5.90 \times 10^{-3}$ | -3 + .771 | 6.92 |
| (Sample D-2)* | | | | | | |
| I-1 | 1105. | 5.00 | 1392 | $2.143 \times 10^{-3}$ | -3 + .331 | 7.18 |
| II-1 | 1579. | 5.00 | 1414 | $3.084 \times 10^{-3}$ | -3 + .489 | 7.07 |
| II-2 | 911. | 10.00 | 1360 | $8.73 \times 10^{-4}$ | -4 + .941 | 7.35 |
| II-3 | 267.3 | 14.50 | 1302 | $1.730 \times 10^{-4}$ | -4 + .238 | 7.68 |
| III-1 | 2615. | 15.00 | 1385 | $1.686 \times 10^{-3}$ | -3 + .227 | 7.22 |
| III-2 | 819. | 30.00 | 1311 | $2.572 \times 10^{-4}$ | -4 + .410 | 7.63 |
| IV-1 | 143.0 | 15.00 | 1274 | $8.86 \times 10^{-5}$ | -5 + .947 | 7.85 |
| IV-4 | 1369. | 4.00 | 1412 | $3.340 \times 10^{-3}$ | -3 + .524 | 7.08 |

*Certain quadrant numbers are not included, either because technical difficulties prevented making the exposures, or because the temperature was set so low as to render accumulation of countable amounts of activity impractical.

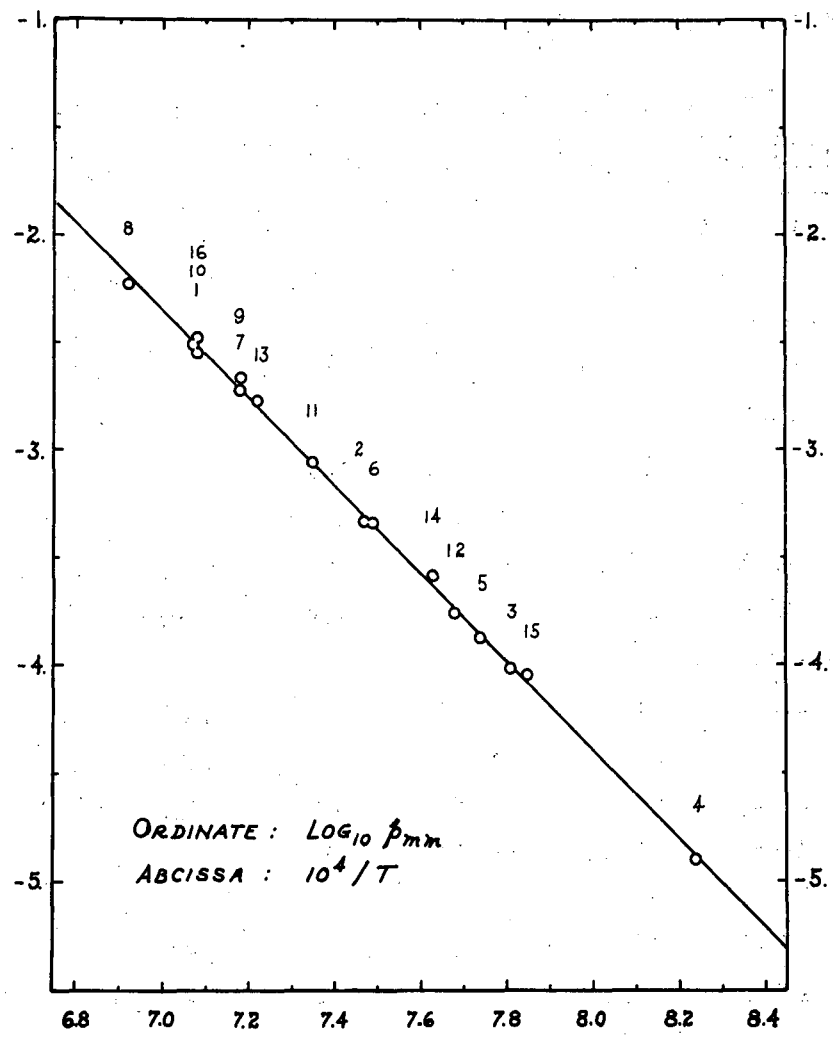


Fig. 8. Vapor-pressure of plutonium trifluoride.

## B. Americium Trifluoride

The data on $AmF_3$ are also based upon two samples. The first, designated as sample D-1, was run simultaneously with $PuF_3$, sample D-2, in use of the equipment as a twin, in exposure series I-IV.

The second sample of $AmF_3$, designated as sample E, was run after the equipment was modified to include the single-chamber effusion crucible, the multiple receiver unit, the charcoal trap and dry-box, all described in Section III of this paper. All exposures to Sample E were taken in a single heating, in series V.

Exposure numbers in series I-IV refer to quadrants as before. In series V the numbers refer to receiver plates stacked consecutively in the magazine.

1. Preparation and purity. -- Americium trifluoride and americium being the principal subjects of this work, their preparation and characterization will be described in detail.

According to Hollander, Perlman, and Seaborg,[28] the isotope $Am^{241}$ accompanies plutonium in prolonged neutron-irradiation of uranium:

$$U^{238}\ (n, \gamma)\ U^{239};$$
$$U^{239} \xrightarrow[23\ m]{\beta^-} Np^{239};$$
$$Np^{239} \xrightarrow[2.3\ d]{\beta^-} Pu^{239};$$
$$Pu^{239}\ (n, \gamma)\ Pu^{240};$$
$$Pu^{240}\ (n, \gamma)\ Pu^{241};$$
$$Pu^{241} \xrightarrow[14\ y]{\beta^-} Am^{241}.$$

The americium so produced is essentially isotopically pure.

A solution of americium nitrate, separated from the bulk of the accompanying plutonium, but containing some Pu(IV), $La^{+++}$, $Fe^{+++}$, and other impurities, was received by this laboratory in 1951. Its purification was undertaken at the time of receipt by Dr. B. B. Cunningham, Dr. J. C. Wallmann, and Mrs. R. Heppler, employing a combination of precipitation and ion-exchange reactions. The americium trichloride solution which resulted has served as stock for both nuclear and chemical experimentation, and is the source of the americium used in the present measurements.

A recent spectrographic analysis of a sample taken from this stock indicated the americium to be 94.6 percent pure, indicating contamination of the solution since its purification in 1951. Impurities of aluminum (0.1 percent), calcium (0.1 percent), iron (0.02 percent), lanthanum (0.2 percent), and plutonium (5 percent) were found, in addition to an estimated trace of the $Np^{237}$ daughter of $Am^{241}$.

The solution remaining on hand at the time this work was undertaken contained approximately twenty-three milligrams of americium. The estimated purity being somewhat below that desired for physical measurements, a repurification program was drawn up for the entire stock.

After conversion to the nitrate, the Am(III) was oxidized electrolytically to Am(VI), this step being performed by Dr. S. R. Gunn in a system developed by him.[29] Overall efficiency of the oxidation was about 65 percent, as judged by the americium hold-up on a Dowex-50 (Dow Chemical Co., Midland, Mich.) cation-exchange resin column employed next. The column, operated at 2-3 $\underline{M}$ $HNO_3$, effects a clean

separation of tripositive ions such as $La^{+++}$ and $Am^{+++}$ from Am(VI).

In order to hold americium losses to a minimum, all of the wastes from the oxidation and first column pass were combined, converted to the chloride in 12.5 M HCl, placed on a second Dowex-50 column, and washed through with 12.5 M HCl. The elutriant was carefully monitored for americium, so as to effect a separation from lanthanum based upon the different elution rates.

The americium fractions were combined and subjected to further chemistry for isolation from plutonium and neptunium. The final product was assayed spectrographically and radiochemically.

The overall yield of americium was 95.3 percent, considering analysis samples as losses. The purity of the final product was 99.8+ percent as regards cations, the impurities detected being aluminum (0.1 percent) and iron (0.05 percent).

An estimated 10.8 mg of the remaining 21.8 mg of purified americium was precipitated as $AmF_3$, using aqueous hydrogen fluoride. After several washes with dilute hydrogen fluoride and water, the product was washed twice with acetone and let stand in air to dry. About 1 percent of the americium was lost in the precipitation and washes. Estimated purity was 99.8 percent.

The X-ray diffraction pattern obtained on a sample of the product indicated a single phase, the lattice parameters being normal for $AmF_3$ (hexagonal).

This material was not vacuum dried as was the plutonium trifluoride. Instead, efforts were directed at vacuum drying each sample in the early stages of each vapor-pressure run and of each metal-production run described in a following section. Americium trifluoride samples

D-1 and E, of an estimated 1 milligram each, were taken directly from this stock.

2. Preparation for measurement. -- $AmF_3$ sample D-1 was handled in essentially the same manner as was its mate, $PuF_3$ sample D-2, described previously.

Sample E required some changes in technique occasioned by the changes in equipment. The newly installed charcoal trap was baked at 400° C under high vacuum for several days, and the glass envelope was then flamed with a hand torch. After the furnace-collimator unit was degassed by heating, it was never again exposed to atmosphere other than dried argon, either in the vacuum line or when in the attached dry-box for loading and unloading. During storage periods between runs the furnace was kept in the vacuum line with the pumps operating continuously.

Crucibles of Type II were designed and built, the final form adopted as the result of further experiments with thermocouple insertion and protection. Vapor-pressure measurements were resumed after satisfactory performance was indicated by the temperature calibration experiments.

Crucible E was cleaned and fired and the orifice measured as described for the $PuF_3$ runs; it was placed in the dry-box under argon, however, immediately after measurement. Loading of the $AmF_3$ sample, of an estimated one milligram or less, was executed within the dry-box. The routine of an initial pump-down, followed by an argon flushing while the receivers were installed, then a prolonged pump-down before initiating the run, was carried out as in the previous cases.

The early stages of heating were pursued with care, on account of the suspected incomplete pre-drying of the sample. The advantage in pumping speed afforded by the charcoal trap permitted a more rapid later approach to operating temperatures in spite of outgassing of the alundum furnace sleeves, so that the total warm-up required less than four hours.

Details of exposure and counting of the single-type receivers have been outlined. All plates, totalling more than 10,000 registered alpha decay events, were counted, although a group of the more active ones were permitted to accumulate over 100,000 counts in order to determine the effect of statistical variation in counting rate upon the scattering of the data. Coincidence corrections were applied to all counts of 5,000 c/m or more.

3. The numerical equation. -- The same energetic considerations which justified the assumption of the single gaseous species $PuF_3$ apply here also, since the plutonium and americium tripositive ionic radii are not far apart.

The formula $AmF_3$ fixes the number n:

$$n = 1.$$

Taking the atomic weight of $Am^{241}$ as 241.1, and that of fluorine as 19.0, yields:

$$M_{AmF_3} = 298.1 \text{ grams.}$$

The best value of the half-life for $Am^{241}$ obtainable from Hollander, Perlman, and Seaborg,[28] is:

$$T_{1/2} = 475 \text{ years.}$$

From this is computed the decay constant:

$$\lambda_{Am} = 1.671 \times 10^{15} \text{ disint/min/g-mole.}$$

The effusion equation embodying these and the other appropriate constants, reads,

$$\text{(D-1):} \quad p = 1.327 \times 10^{-8} \cdot \frac{c\sqrt{T}}{t} \cdot \left[\frac{1000}{996 + 0.014T}\right];$$

$$\text{(E):} \quad p = 0.841 \times 10^{-8} \cdot \frac{c\sqrt{T}}{t} \cdot \left[\frac{1000}{996 + 0.014T}\right].$$

4. Data and results. -- Table IV gives for americium trifluoride the same data and computed results listed in Table III for plutonium trifluoride.

The points obtained from this table are plotted in Fig. 9, series I-IV as circles, series V as crosses. The two solid curves are the best-fitting straight lines to the respective groups of points; the fit is improved by a slight downward concavity. The dashed curve is the straight line of M. E. Jones,[4] included for comparison.

Derived quantities will be presented under Discussion of Results, Section VI.

Table IV

The Vapor-Pressure of Americium Trifluoride: Data and Results

| Exposure | c(c/m) | t(min) | T($^{o}$K) | p(mm) | log p | $10^4/T$ |
|---|---|---|---|---|---|---|
| (Sample D-1) | | | | | | |
| I-3 | 7,280. | 3.00 | 1392 | $1.183 \times 10^{-3}$ | -3 + .073 | 7.18 |
| II-1 | 10,530. | 3.00 | 1414 | $1.725 \times 10^{-3}$ | -3 + .237 | 7.07 |
| II-4 | 8,246. | 7.83 | 1360 | $5.08 \times 10^{-4}$ | -4 + .706 | 7.35 |
| II-3 | 2,796. | 13.00 | 1302 | $1.038 \times 10^{-4}$ | -4 + .016 | 7.68 |
| III-1 | 24,470. | 13.00 | 1385 | $9.15 \times 10^{-4}$ | -4 + .962 | 7.22 |
| III-2 | 8,783. | 28.00 | 1311 | $1.486 \times 10^{-4}$ | -4 + .172 | 7.63 |
| III-3 | 791. | 30.00 | 1233 | $1.213 \times 10^{-5}$ | -5 + .084 | 8.11 |
| III-4 | 34.9 | 30.00 | 1140 | $5.15 \times 10^{-7}$ | -7 + .712 | 8.77 |
| IV-1 | 1,284. | 13.00 | 1274 | $4.61 \times 10^{-5}$ | -5 + .664 | 7.85 |
| IV-2 | 77.1 | 30.00 | 1160 | $1.150 \times 10^{-6}$ | -6 + .061 | 8.62 |
| IV-4 | 7,344. | 2.00 | 1412 | $1.803 \times 10^{-3}$ | -3 + .256 | 7.08 |
| (Sample E) | | | | | | |
| V-3 | 21.0 | 10.00 | 1145 | $5.90 \times 10^{-7}$ | -7 + .771 | 8.73 |
| V-4 | 805. | 5.00 | 1275 | $4.77 \times 10^{-5}$ | -5 + .678 | 7.84 |
| V-5 | 5,198. | 3.00 | 1363 | $5.30 \times 10^{-4}$ | -4 + .724 | 7.34 |
| V-6 | 36,710. | 2.00 | 1469 | $5.82 \times 10^{-3}$ | -3 + .765 | 6.81 |
| V-7 | 11,000. | 2.00 | 1414 | $1.710 \times 10^{-3}$ | -3 + .233 | 7.07 |
| V-9 | 3,284. | 5.00 | 1330 | $1.984 \times 10^{-4}$ | -4 + .298 | 7.52 |
| V-11 | 248. | 10.00 | 1216 | $7.18 \times 10^{-6}$ | -6 + .856 | 8.22 |
| V-12 | 22.3 | 20.00 | 1126 | $3.112 \times 10^{-7}$ | -7 + .493 | 8.88 |

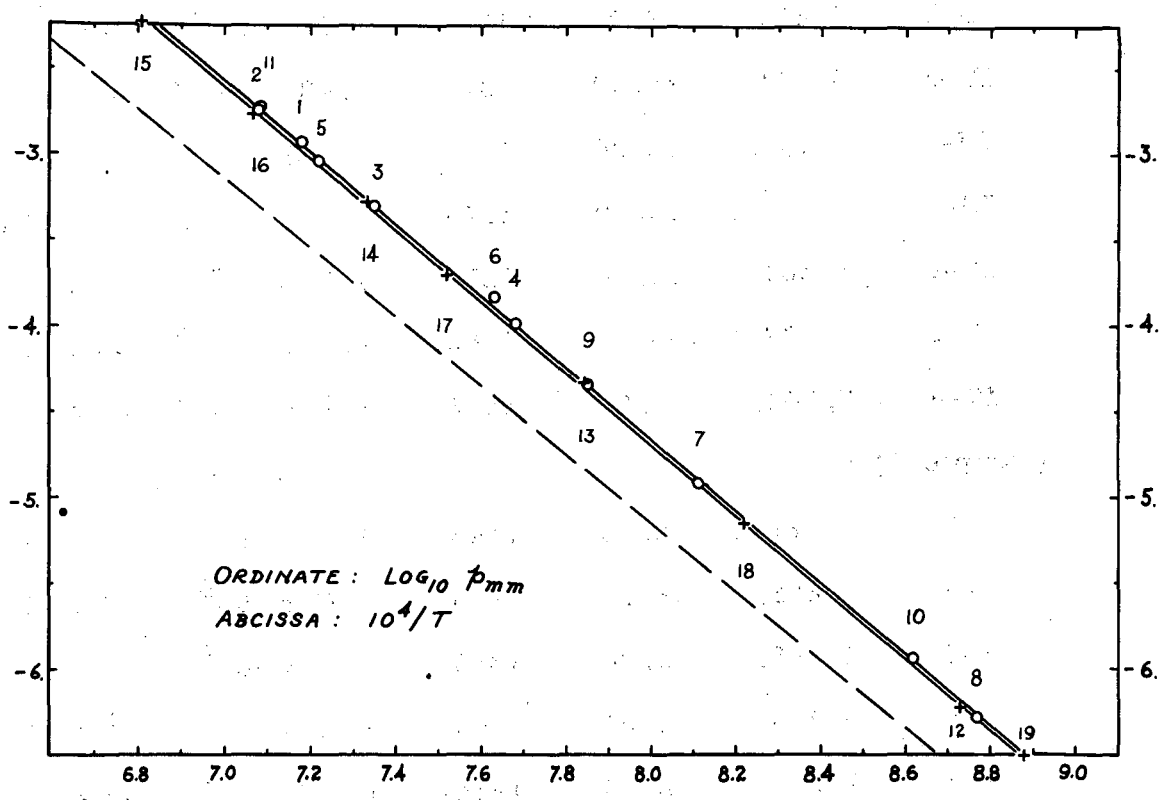


Fig. 9. Vapor-pressure of americium trifluoride.

## C. Americium Metal

Two runs with elementary americium were made, Run I on Sample L and Run II on Sample K, both in the single-type equipment.

1. Preparation and purity. -- The metal samples were prepared individually from portions of the pure americium trifluoride, by a method in common use for microgram-to-milligram-scale metal production. The technique is due to Baumbach and Kirk,[30] and is described in detail by Fried and Davidson.[31]

The $AmF_3$ reduction is effected by the following reaction, which was carried out in this work at 1100° C:

$$2AmF_3 + 3Ba \rightarrow 2Am + 3BaF_2.$$

The americium trifluoride charge was lightly tamped into a tiny crucible of sintered thoria. This, with a thin thoria plate for a lid, was placed inside a larger crucible with a piece of carefully cleaned barium; then the outer crucible was closed with a tight-fitting conical stopper, and the entire assembly was fired in a vacuum furnace. After pumping down for an hour, the loaded charges were warmed very slowly to drive off trapped moisture and gases before firing for the reduction.

The outer crucible in which Sample L was prepared was made of sintered beryllia, while thoria was used in making Sample K. The thoria behaves the same as beryllia in this application, but has far superior mechanical strength. Use of thoria inner containers has been found to yield less contamination of the product on a mole basis than is the case with sintered beryllia. The ceramics were baked at 1700° C for two hours in high vacuum immediately before use.

The americium metal appeared in each case as a single, shiny, approximately hemispherical button, adhering tightly to the

wall of the inner crucible. Measurement of the dimensions under low magnification, using an eyepiece micrometer, indicated that Sample L weighed about 400 micrograms and that Sample K was over a milligram if the density was about 10 g/cm$^3$. Because the cleaning operations were part of a carefully planned regimen preceding vapor-pressure measurement, they will be described in that connection; the purity achieved, as determined spectrographically on a piece cut from Sample K after cleaning, was 99.8 percent. Contaminants found were: aluminum (0.16 percent), calcium (0.02 percent), iron (0.02 percent), magnesium (0.02 percent).

2. Preparation for measurement. -- The entire furnace, collimator, receiver, and vacuum equipment having been maintained at high vacuum almost continuously for many days following $AmF_3$ Run V, no special preparations were undertaken beyond a brief flaming of the glass envelope. By the time of the first metal run, the charcoal trap had been cycled many times between 400$^\circ$ C under atmospheric pressure of argon and -190$^\circ$ C at high vacuum; the argon-filled dry-box had been in continuous operation for over a month.

The two runs were conducted in essentially the same manner. The tantalum effusion vessel was prepared and the orifice measured as described previously; this time, however, the vacuum firing was of more than four hours' duration, and was followed, after the orifice measurement, by a second firing for over one hour. The vessel was stored in high vacuum until loading time, when it was transferred quickly to the argon atmosphere of the dry-box.

Cleaning of the americium sample was performed manually, using steel forceps and sharpened tungsten wire for scraping under toluene. The operation was very painstakingly done, going over the entire surface many times, with several replacements of the immersion liquid, until the sample appeared as a flawlessly shiny bead under low magnification. Much metal was cut away where the button had been fused to its container in reduction, so as to insure against local contamination.

The sample was transferred, still under toluene, to the dry-box where it was removed, dried on lens tissue, examined, and placed in the effusion vessel. The latter was closed, the thermocouple was inserted, the apparatus was assembled, flushed, evacuated, flushed again during receiver installation, and pumped down for several hours, all essentially as described under $AmF_3$ Run V.

Initial heating was conducted with extreme caution so as to avoid reaction of the metal with traces of toluene or oxygen. Pressure was maintained at less than $10^{-6}$ mm throughout this period.

The exposures were executed without undue delay, once operating temperatures were reached, so as to minimize the period of reaction of the molten charge with even minute amounts of atmosphere. The maximum external pressure in Run I (Sample L) was $5 \times 10^{-6}$ mm; in Run II (Sample K), $3 \times 10^{-6}$ mm. In each case the average pressure throughout the run was $(1\text{-}2) \times 10^{-6}$ mm.

Counting of receivers for alpha activity was conducted as before, totalling at least 13,000 counts for every one.

3. The numerical equation. -- The effusant is regarded with confidence as monatomic americium gas. Hence,

$$n = 1;$$

$$M = 241.1 \text{ grams};$$

$$\lambda = 1.671 \times 10^{-15} \text{disint/min/g-mole}.$$

These and the other appropriate constants determine the numerical effusion equation,

$$\text{(L):} \quad p = 1.800 \times 10^{-8} \cdot \frac{c\sqrt{T}}{t} \cdot \left[\frac{1000}{996 + 0.014T}\right];$$

$$\text{(K):} \quad p = 1.920 \times 10^{-8} \cdot \frac{c\sqrt{T}}{t} \cdot \left[\frac{1000}{996 + 0.014T}\right].$$

4. Data and results. -- Table V gives for americium the same data and computed results listed in Tables III and IV for $PuF_3$ and $AmF_3$, respectively.

The points obtained from this table are plotted in Fig. 10, Run I as circles, Run II as crosses. The two solid curves are the best-fitting straight lines to the respective groups of points; the dashed curve is a linear extrapolation of the calculated curve of Erway and Simpson,[5] included for comparison.

Derived quantities will be presented under Discussion of Results, Section VI.

Table V

The Vapor-Pressure of Americium Metal: Data and Results

| Exposure | c(c/m) | t(min) | T($^{o}$K) | p(mm) | log p | $10^4/T$ |
|---|---|---|---|---|---|---|
| (Sample L) | | | | | | |
| I-2 | 39,970. | 1.00 | 1453 | $2.699 \times 10^{-2}$ | -2. + .431 | 6.88 |
| I-4 | 44,390. | 2.00 | 1416 | $1.480 \times 10^{-2}$ | -2. + .170 | 7.06 |
| I-5 | 23,660. | 5.00 | 1313 | $3.044 \times 10^{-3}$ | -3. + .483 | 7.62 |
| I-6 | 15,800. | 12.00 | 1233 | $8.22 \times 10^{-4}$ | -5. + .915 | 8.11 |
| I-8 | 3,771. | 25.00 | 1151 | $9.10 \times 10^{-5}$ | -5. + .959 | 8.69 |
| I-9 | 686. | 50.00 | 1043 | $7.89 \times 10^{-6}$ | -6. + .897 | 9.59 |
| I-10 | 1,885. | 25.00 | 1103 | $4.45 \times 10^{-5}$ | -5. + .649 | 9.07 |
| I-11 | 11,380. | 15.00 | 1212 | $4.69 \times 10^{-4}$ | -4. + .671 | 8.25 |
| I-12 | 42,960. | 10.00 | 1300 | $2.75 \times 10^{-3}$ | -3. + .439 | 7.69 |
| I-15 | 73,600. | 5.00 | 1375 | $9.68 \times 10^{-3}$ | -3. + .986 | 7.27 |
| (Sample K) | | | | | | |
| II-2 | 1,599. | 5.00 | 1171 | $2.074 \times 10^{-4}$ | -4. + .317 | 8.54 |
| II-3 | 10,040. | 5.00 | 1269 | $1.354 \times 10^{-3}$ | -3. + .132 | 7.88 |
| II-4 | 16,280. | 2.00 | 1343 | $5.64 \times 10^{-3}$ | -3. + .751 | 7.45 |
| II-5 | 57,510. | 2.00 | 1422 | $2.049 \times 10^{-2}$ | -2. + .311 | 7.03 |
| II-6 | 22,270. | 2.00 | 1367 | $7.79 \times 10^{-3}$ | -3. + .891 | 7.32 |
| II-7 | 9,930. | 2.00 | 1307 | $3.399 \times 10^{-3}$ | -3. + .531 | 7.65 |
| II-8 | 3,321. | 3.00 | 1229 | $7.36 \times 10^{-4}$ | -4. + .867 | 8.14 |
| II-9 | 906. | 5.00 | 1150 | $1.166 \times 10^{-4}$ | -4. + .067 | 8.70 |
| II-10 | 5,820. | 2.00 | 1280 | $1.972 \times 10^{-3}$ | -3. + .295 | 7.81 |
| II-11 | 37,160. | 2.00 | 1399 | $1.314 \times 10^{-2}$ | -2. + .119 | 7.15 |
| II-12 | 79,560. | 2.00 | 1446 | $2.861 \times 10^{-2}$ | -2. + .457 | 6.92 |
| II-13 | 7,264. | 2.00 | 1301 | $2.481 \times 10^{-3}$ | -3. + .395 | 7.69 |
| II-14 | 1,479. | 4.00 | 1171 | $2.399 \times 10^{-4}$ | -4. + .380 | 8.54 |
| II-16 | 139. | 10.00 | 1043 | $8.53 \times 10^{-6}$ | -6. + .931 | 9.59 |

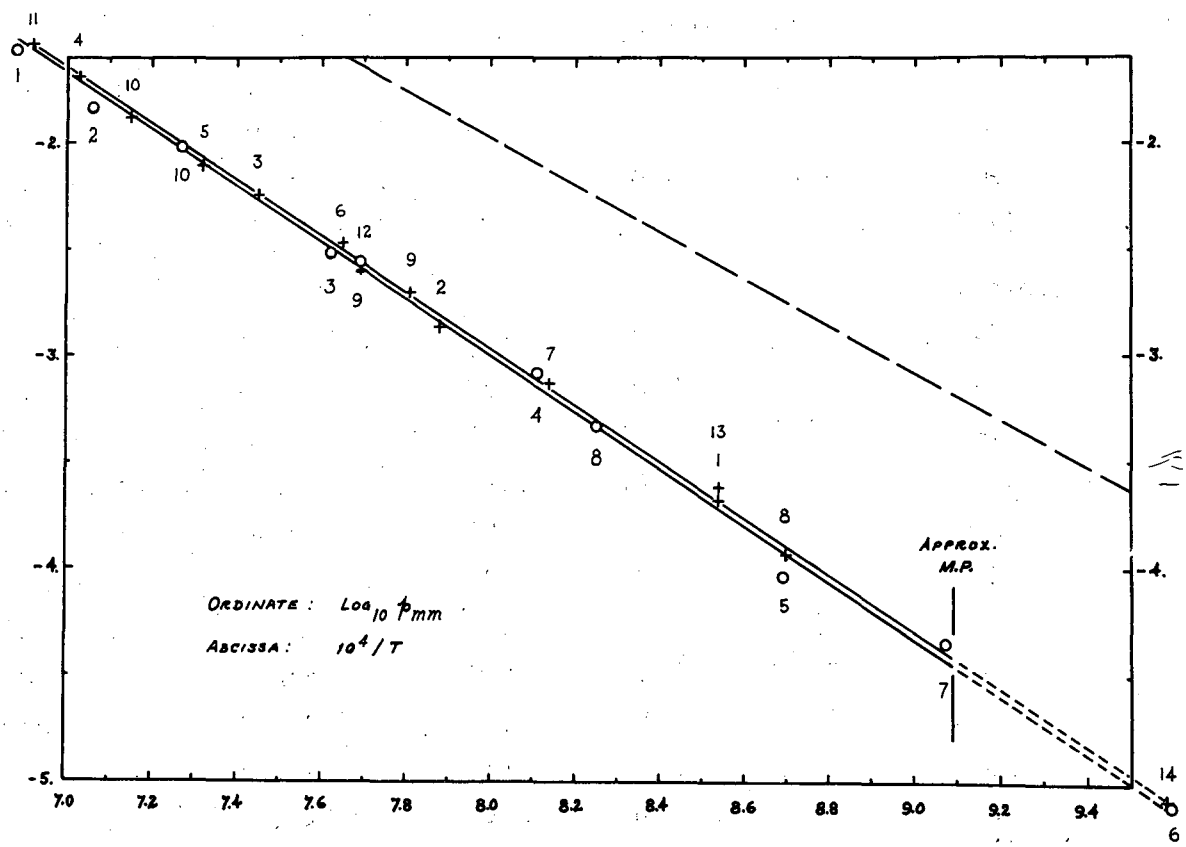


Fig. 10. Vapor-pressure of americium metal.

# V. UNCERTAINTIES

## A. General

It is convenient to consider errors and uncertainties in two groups: those arising out of failure to conform to the ideal conditions listed in Section II, and those arising out of the measurements due to fallibility of the worker and his measuring devices. Further distinction is made between errors affecting the "magnitude" of the vapor-pressure, i.e., resulting in vertical displacement of the log p vs. $10^4/T$ curve, and those affecting the "slope" of that curve and thus the heat of vaporization.

Those sources of error which were common to all the vapor-pressure measurements will be discussed in this section. Paragraphs 1 to 11 below, and their captions, conform to the listing of ideal effusion conditions in Section II. Paragraphs 12 to 14 relate to errors in the measured values of terms in the Effusion Equation II-(12).

1. Temperature uniformity. -- Efforts to maintain all parts of the effusion chamber at temperatures slightly higher than that of the sample have been described elsewhere. Failure to find evidence of transport within the crucibles upon examination subsequent to the runs may be cited in support of the optical pyrometer findings that these efforts were successful. It seems certain that the maximum temperature variation from place to place within the vessels was less than $5^\circ$ C, excepting perhaps the edges of the orifice. The resultant "magnitude" uncertainty should be considerably less than ±5 percent.

2. Evaporation surface area. -- There is different evidence relating to this condition for each of the substances measured; hence the discussions will be postponed.

3. Orifice condition. -- A systematic error in effusion of at most 0.1 percent below the ideal may be attributed to the orifice profile. This is a "magnitude" error.

4. Mean free path within vessel. -- Vapor-pressures did not exceed about $3 \times 10^{-2}$ mm in any of the experiments. At these pressures and at temperatures near $1400^{\circ}$ K, the mean free path is computed[23] to be of the order of 1 - 5 cm, far larger than the orifice dimensions.

5. Effusing species. --The possibility of vaporizing foreign species as a result of contamination will be discussed later. Phenomena such as decomposition and dimerization have been characterized as highly unlikely, rendering the molecular formulas $PuF_3$, $AmF_3$ and Am quite certain in the restricted sense intended in this paragraph.

6. Mean free path outside vessel. -- At maximum envelope pressures of about $10^{-5}$ mm Hg and at average temperatures near $400^{\circ}$ K, the mean free path is computed to be of the order of ten meters. In early experiments, targets placed so as to collect scattered molecules showed only 0 - 1 c/m alpha activity while at least $10^3$ c/m were transported in the beam. The error in vapor-pressure due to this cause is estimated to be less than 0.5 percent.

7. Condensation. -- The same experiments which denied appreciable gas-phase scattering also indicated a very high general condensing efficiency. In spite of the fact that interior metal and

glass surfaces were by physiological criteria quite hot, they were of course far below furnace temperatures and apparently reflected a negligible fraction of the incident condensible molecules.

The term "accommodation coefficient" is avoided in describing this type of condensation, since it seems desirable to reserve for that property some thermodynamic significance and to assign it a numerical value in terms of well-defined experimental conditions. Thus it is claimed that the "condensing efficiency" in this system was >99.9 percent, in the operational sense that no appreciable activity was collected on targets placed outside the collimated beam.

Condensing efficiency of the platinum targets was also high. In early experiments a secondary target was used on the back of the shutter; after the second americium metal run was made, the back of the shutter was swabbed and the swab monitored for activity. In neither case was reflection of as much as 0.1 percent from the receivers indicated. These conclusions are in agreement with the findings of others who have used clean metallic targets for condensing metals and inorganic salts.

8. Collimator condition. -- No significant error can have resulted, since the collimators were accurately circular.

9. Alignment. --Pains were taken to measure the effusion orifice under proper alignment, within about $3^{\circ}$. Alignment of the effusion device and the installed vessel was much more precise than this, although the orifice plane may have been out of line with the crucible face by up to the same amount. The resulting "magnitude" uncertainty is ±0.3 percent.

10. Chamber inertness. -- Simpson, et al.[1] have reported some early control work with tantalum and concluded that its use as a containing material for inorganic halides introduces no error.

Control experiments with americium metal were impractical on account of the limited amount of the element available; observations have been made, however, on other similar metals in tantalum,[5,16] with no contrary indications. It seems unlikely that the solubility of tantalum in molten americium is sufficient to disturb the activity of the latter by as much as 0.2 percent.

11. Composition of sample. -- There is different evidence relating to this condition for each of the three substances measured; hence the discussions will be postponed.

12. Errors in measured quantities: constants. -- The entire first bracket of Equation II-(12) is excluded as a source of appreciable uncertainty. Terms of the second bracket are next discussed one by one.

The counter geometry factor g is reliable to ±1. percent as regards counter-to-counter variation in this laboratory; its absolute certainty is not better than ±2. percent, however. The resultant error is one in "magnitude".

The uncertainty in measurement of the orifice area a due to problems of resolution and optical distortion in the making of tracings and to non-uniformity in the density of the paper images, is estimated to be ±0.7 percent. This results in a "magnitude" error in vapor-pressure.

The uncertainty in the square of d, the orifice-collimator distance, is about ±0.3 percent, including errors in measuring the length of the rail system, in fabricating the effusion vessels, and in

positioning the vessels in the furnace. Since the collimator radius r is much more precisely known, and since $d^2/r^2 >> 1$, the uncertainty in the entire term, $(1 + d^2/r^2)$ is also ±0.3 percent. This is an uncertainty in "magnitude".

13. Properties of the charge. --The square root of M, the molecular weight of the effusant, is known to better than ±0.05 percent.

The decay constant λ, derived from published half-lives, is probably accurate to ±1.0 percent in the case of americium, and even more precise than this in the case of plutonium. The resultant error in the vapor-pressure is one in "magnitude".

14. Raw data. -- In addition to an uncertainty in counter geometry, the measured counting rate is subject to a minor systematic uncertainty inherent in the coincidence correction. This is a function of the counting rate and therefore appears primarily as a small uncertainty in "slope"; its maximum effect on the computed vapor-pressure is about ±0.4 percent.

Random or statistical variation in counting rate has been held at ±0.7 percent (probable error) or less by counting more than 10,000 alpha-decay events on every plate.

Uncertainty in exposure time is estimated to be ±0.2 second, due to the human error and the time required to turn the shutter control. In the shortest exposure, of one minute duration, this random error is about ±0.3 percent; in most exposures it is much smaller.

Systematic errors in chamber temperature, as judged by the behavior during thermocouple calibrations, were of the order of $1^{\circ}$ C. Errors in measuring the thermocouple emf during runs were comparable, while temperature fluctuations averaged much less than

this. These statements apply, of course, to the temperature of the thermocouple junction. During runs, variation in external conditions might warrant putting a random uncertainty of $\pm 2^{\circ}$ C on the temperature of the sample, which translates into ±5 percent of the vapor-pressure.

It can be judged from the foregoing that the equipment should be capable, in principle, of making vapor-pressure measurements accurate in absolute magnitude to ±6 percent of the vapor-pressure; in the slope, $d \log p/d\,(10^4/T)$, to ±0.5 percent; and with scattering of points about the best curve within ±5 percent of the vapor-pressure.

B. Plutonium Trifluoride and Americium Trifluoride

X-ray diffraction patterns obtained on $AmF_3$ Samples D-1 and E after completion of the vapor-pressure runs indicated conversion to the oxyfluoride AmOF, severe in Sample D-1 but only minor in Sample E. The plutonium trifluoride samples must be regarded as having been similarly affected.

Two consequences of this contamination, its effect on composition of the sample and reduction of effective evaporating surface area, must be taken into consideration. There seems little doubt that both the $PuF_3$ and the $AmF_3$ measurements were actually made on samples saturated with oxyfluoride. These compounds are probably much less volatile than the trifluorides, hence their contribution to the vapor phase is insignificant. However, dissolving of oxyfluoride in the trifluoride lowers the activity of the latter and thus lowers the vapor-pressure. The extent to which this takes place at $1200^{\circ}$ K is unknown but must be small, probably less than 1 percent.

The depletion of evaporating surface area by coating with oxyfluoride appears negligible when the results obtained on $PuF_3$ are compared with those of Simpson, et al.[1] The latter workers employed samples twenty to forty times larger than these, and orifices essentially the same size, yet obtained the same vapor-pressures within the expected uncertainty.

The scattering of points about the best curves representing log p vs. $10^4/T$ averages approximately ±5 percent of the vapor-pressure (vertical displacement), or approximately ±2° C temperature uncertainty (horizontal displacement), for either $PuF_3$ or $AmF_3$. Prolonged counting to reduce statistical variations in counting rates improved matters but little, as might be expected. Thus the average scattering actually obtained matches the maximum scattering expected of the equipment. The discrepancy is not clearly attributable to any single cause.

The appearance of the data and the foregoing treatment of errors warrant the assignment of the following uncertainties to the $PuF_3$ and $AmF_3$ measurements: absolute vapor-pressures, ±6 percent; slope, d log p/d($10^4/T$), ±0.5 percent; average scattering of points, ±5 percent of the vapor-pressure, or ±2° C in temperature.

The occurrence of oxyfluoride contaminant in the trifluoride samples prompts some reflections as to the possible cause and appropriate remedy. Oxidation of Samples D-1 and D-2 was primarily due to technical difficulties encountered during the runs. Conduct of $AmF_3$, Run V, with Sample E may be considered as representative of this type of work, however, and it is fruitful to base some comments on this run.

The amount of AmOF found in the $AmF_3$ sample may be crudely estimated as between 1 and 10 percent, containing between 0.03 and 0.3 microgram-atom of oxygen. It is calculated[23] that, at $10^{-5}$ mm external pressure of oxygen, it would take from 15 to 150 hours for the required amount of contaminant to enter the orifice; thus it is clear that the source of oxidation must have been present when the effusion vessel was loaded and closed. This corresponds to about two micrograms of oxygen or water impurity.

The admonition follows that the most impressive external vacuum cannot insure against sample contamination if the techniques of preparation of the sample and vessel are not adequate. In fact, it is instructive to note this striking contrast: to produce a monomolecular layer of oxide within a vessel of the type used here requires about ten hours' diffusion through the orifice at an external oxygen pressure of $10^{-6}$ mm, 100 hours at $10^{-7}$ mm; but may be accomplished by 0.04 microgram of oxygen as impurity in the sample. Efforts were made to minimize the possible sources of contamination in the handling of americium metal.

## C. Americium Metal

The problem of sample contamination is especially serious when the sample is a molten, extremely reactive metal. Granted that contamination was much less in the metal runs than in the trifluoride runs due to refinements in technique, it still must be supposed that some oxide was present. Assuming the oxide to have the formula AmO, the following questions arise:

Is AmO more or less volatile than americium?

Is it appreciably soluble in $Am_{(\ell)}$?

Is the reduction of evaporating surface of americium by coating with AmO serious, either by virtue of direct exclusion or through the prevention of wetting and spreading on tantalum?

The answer to the first question would appear to be; at most very little more. It is a simple matter to compute the rate of transport of material through the orifice as a function of vapor-pressure, and to show that reasonable amounts of an AmO phase would be exhausted in the higher temperature exposures, with the result that subsequent points would establish a new vapor-pressure curve at a lower level. This is not the case experimentally.

The solubility of AmO in americium at 1200° K is unknown, as is also the degree of interference with evaporation. Unfortunately, it was not possible to make any definitive observations on the samples after heating, since sticking of the set-screws prevented local access and examination down the bore of the crucibles (after cutting away the orifice foil) proved futile.

Thorn, in effusion measurements made on a larger sample of molten base metal, employing a more highly refined furnace and vacuum system and deliberately bleeding in oxygen to controlled steady-state pressures, has demonstrated a marked dependency of the apparent vapor-pressure upon degree of contamination.[32] If the americium system behaves similarly, it is not impossible that the vapor-pressures reported here be more than 100 percent low and that the slope, d log p/d ($10^4$/T), be in error by more than 5 percent. On the other hand, for measurements which are subject to such gross uncertainties, the agreement between Runs I and II would seem fortuitous.

Validity of the present americium vapor-pressures as fundamental thermodynamic data depends upon elaboration of Thorn's findings by specific experimentation on this element. It is highly desirable to obtain vapor-pressure measurements under conditions such that the evaporating surface is continuously replenished mechanically and the resulting data are essentially independent of oxygen pressure.

The requirements of such an experimental program on the americium supply will no doubt delay its execution some time, during which period the present data may enjoy at least a temporary respectability. The scattering and other aspects of the data alone warrant the following statements of uncertainty in the vapor-pressure of americium: absolute vapor-pressures, ±10 percent; slope, $d \log p/d(10^4/T)$, ±1 percent; average scattering of points, ±7 percent of the vapor-pressure, or ±3° C in temperature.

## VI. DISCUSSION OF RESULTS

### A. Plutonium Trifluoride

The agreement between the present measurements and those of Simpson, et al.[1] is gratifying. Because of the short temperature range over which the data extend, it is futile to attempt to fit other than a straight line to the points; the curve in Fig. 8 fits the equation,

$$\log p_{(mm)} = 12.018 - 20,520/T.$$

From this equation is derived a $\Delta H$ of sublimation constant with temperature:

$$\Delta H_{(sublim)} = 93.9 \text{ kcal/mole}.$$

If the data are fit by a curved line employing a $\Delta Cp$ of sublimation of -14 cal/mole/degree,[2] the equation is:

$$\log p = 37.119 - 24,625/T - 7.046 \log T.$$

This equation yields for the sublimation,

$$\Delta H_{1273^\circ K} = 94.9 \text{ kcal/mole};$$

$$\Delta H = 112.7 \text{ kcal/mole};$$

$$\Delta F_o = 112,700 - 169.9\,T - 2.303\,(-14)\,T \log T.$$

Extrapolation of this curve to the melting point, $1700^\circ$ K, yields a vapor-pressure at the melting point of 0.75 mm Hg. Assuming a $\Delta H$ of fusion of 13 kcal/mole and a $\Delta Cp$ for evaporation of the liquid of -16 cal/mole/degree, the vaporization equation is derived:

$$\log p = 39.12 - 22,500/T - 8.05 \log T.$$

The extrapolated boiling point of $PuF_3$ is obtained from the above equations as:

$$T_B = 2550^\circ \text{ K}.$$

The $\Delta H$ and $\Delta S$ of vaporization at this temperature are computed:

$$\Delta H_{(vap,\ 2550^\circ K)} = 62 \text{ kcal/mole};$$

$$\Delta S_{(vap,\ 2550^\circ K)} = 24 \text{ cal/mole/degree}.$$

B. Americium Trifluoride

The markedly higher values for the vapor-pressure obtained in this work, as compared with the data of Jones,[4] are regarded as much the more accurate. The difference is attributable mainly to the use of very thin orifice foils by Jones. Errors in the same direction and of roughly the same magnitude were discovered in the preliminary work with $PuF_3$ using the same type of foil, and are explained in terms of the observation cited of gross distillation within the effusion vessel: the very thin foil fails to maintain a temperature near that of the rest of the cavity, due to inability of its conduction to keep pace with heat loss by radiation. Jones was aware of the necessity of supplying

additional heat to combat this effect, and attempted to accomplish this by winding his heating coil more tightly near the orifice. Although this precaution sufficed to prevent gross distillation in his experiments, it now appears to have been inadequate to prevent substantial errors in his results.

The displacement of the two curves in Fig. 9 is approximately equal to the thermocouple calibration correction for crucible E, which had the abnormal value of $4^{o}$ C. In the absence of more than circumstantial evidence, however, correction of Run V on this basis is not justified; the absolute vapor-pressures on which the following calculations are based are taken as the simple average between the two best curves.

The points are best fit by curved lines. Analysis of the curvature yields an estimate of the $\Delta Cp$ of sublimation,

$$\Delta Cp_{(sublim)} = -16 \pm 8 \text{ cal/mole/degree},$$

in essential agreement with Brewer's[2] estimate for $PuF_3$.

Using the following estimated values:

$$\Delta Cp_{(sublim)} = -14 \text{ cal/mole/degree};$$
$$T_F = 1700^{o} \text{ K};$$
$$\Delta H_{(fusion)} = 13 \text{ kcal/mole; and}$$
$$\Delta Cp_{(vap)} = -16 \text{ cal/mole/degree};$$

the following equations and functions are calculated. For sublimation,

$$\log p = 36.880 - 24,650/T - 7.046 \log T;$$
$$\Delta F_{(sublim)} = 112,800 - 168.8T - 2.303\,(-14)\,T \log T;$$
$$\Delta H_{1273^{o}\,K} = 95.0 \text{ kcal/mole};$$
$$\Delta H_{o} = 112.8 \text{ kcal/mole}.$$

Vapor-pressure at the melting-point,

$$1700^{\circ}\ K;\ 0.42\ mm\ Hg.$$

For vaporization of the liquid,

$$\log p = 38.86 - 22,500/T - 8.05 \log T.$$

Extrapolated boiling point;

$$T_B = 2690^{\circ}\ K;$$

$$\Delta H_{(vap,\ 2690^{\circ}\ K)} = 60\ kcal/mole;$$

$$\Delta S_{(vap,\ 2690^{\circ}\ K)} = 22.3\ cal/mole/degree.$$

## C. Americium Metal

Erway and Simpson[5] suggested that a systematic uncertainty existed in their work with americium, owing to a lack of precise knowledge of the activity of the americium in the solutions employed. This probably explains the bulk of the displacement between their curve and that of the present work, Fig. 10, although the preceding discussion of uncertainties attendant upon the present measurements throws a shadow also on them.

While there is no experimental justification for weighting the results in favor of Run I or of Run II, the most important possible source of error causes a decrease in apparent vapor-pressure; hence it may be prudent to base estimates of thermodynamic quantities upon the second run.

The equation for the straight line determined in Run II is:

$$\log p = 7.563 - 13,162/T.$$

This equation yields a $\Delta H$ of vaporization independent of temperature:

$$\Delta H_{(vap)} = 60.2\ kcal/mole.$$

A linear extrapolation leads to estimated values of the boiling point and the entropy of vaporization:

$$T_B = 2810^\circ \text{ K};$$

$$\Delta S_{(vap,\ 2810^\circ\ K)} = 21.4 \text{ cal/mole/degree.}$$

It is less naive to estimate a $\Delta Cp$ of vaporization and base the extrapolation upon this. Assuming,

$$\Delta Cp_{(vap)} = -2 \text{ cal/mole/degree,}$$

based on tabulated value for the lower rare earths, the following are computed. For vaporization of the liquid:

$$\log p = 11.092 - 13,700/T - \log T;$$

$$\Delta F_{(vap)} = 62,690 - 50.76\ T - 2.303\ (-2)\ T \log T;$$

$$\Delta H_{1273^\circ\ K} = 60.2 \text{ kcal/mole.}$$

Vapor-pressure at the melting point, estimated to be $1100^\circ$ K:[33]

$$4.0 \times 10^{-5} \text{ mm Hg.}$$

Extrapolated boiling point:

$$T_B = 2880^\circ \text{ K};$$

$$\Delta H_{(vap,\ 2880^\circ\ K)} = 57 \text{ kcal/mole;}$$

$$\Delta S_{(vap,\ 2880^\circ\ K)} = 20 \text{ cal/mole/degree.}$$

Using the data at the melting point, and assuming a $\Delta H$ of fusion of 2.5 kcal/mole and a $\Delta Cp$ of sublimation of 4 cal/mole/degree, the sublimation equations can be estimated:

$$\log p = 15.04 - 14,700/T - 2 \log T;$$

$$\Delta F_{(sublim)} = 67,400 - 68.82\ T - 2.303\ (-4)\ T \log T;$$

$$\Delta H_o = 67.4 \text{ kcal/mole.}$$

That the data may truly be in error is indicated by the estimated entropy of vaporization at the boiling point, which is significantly lower than that predicted by Trouton's Rule. An increase in the absolute

vapor-pressure of 100 percent, or in the $\Delta H$ of vaporization of about 4 percent, would lead to a more reasonable value of the entropy.

## VII. ACKNOWLEDGMENTS

The author acknowledges gratefully the adroit direction, willing counsel, high example, and profound personal inspiration of Dr. Burris B. Cunningham, under whose guidance this work was performed.

Advice on specific matters relating to the work was received from numerous individuals, particularly Dr. Leo Brewer, Mr. Herman P. Robinson, Dr. James C. Wallmann, and Mr. Nelson B. Garden.

Assistance was contributed by the staff technical personnel in the Inorganic Chemistry, Electronics, Spectrochemical, X-ray, Inspection Technicians, and Health Chemistry groups of the Radiation Laboratory.

Portions of the equipment were built in the Machine Shop and in the Glass Shop of the Radiation Laboratory. Thanks are extended also to Mr. E. W. Hostetter, under whose instruction the author did the bulk of the fabrication and construction work.

This work was performed under the auspices of the United States Atomic Energy Commission.

## VIII. REFERENCES


1. T. E. Phipps, G. W. Sears, R. L. Seifert, and O. C. Simpson, The Transuranium Elements: Research Papers (McGraw-Hill Book Company, Inc., New York, 1949), Paper No. 6.1a, National Nuclear Energy Series, Plutonium Project Record, Vol. 14B, Div. IV. Also, J. Chem. Phys., 18, 713 (1950).
2. L. Brewer, L. Bromley, P. W. Gilles, and N. L. Lofgren, op. cit., Paper No. 6.40.
3. E. F. Westrum, Jr., and J. C. Wallmann, J. Am. Chem. Soc., 73, 3530 (1951).
4. M. E. Jones, Atomic Energy Commission Declassified Document AECD-3270 (August 1951).
5. N. D. Erway and O. C. Simpson, J. Chem. Phys. 18, 953 (1950).
6. M. Knudsen, Ann. Physik, 29, 179 (1909).
7. F. Knauer and O. Stern, Z. Physik 39, 774 (1926).
8. P. Clausing, Z. Physik 66, 471 (1930).
9. Ibid., Ann. Physik, 12, 961 (1932).
10. C. I. Whitman, J. Chem. Phys. 20, 161 (1952).
11. H. L. Johnston and R. Speiser, Trans. Am. Soc. Metals 42, 283 (1950).
12. H. Mayer, Z. Physik 52, 235 (1928).
13. H. L. Johnston and co-workers, a series of papers appearing in J. Am. Chem. Soc. under the title, "Vapor-Pressures of Inorganic Substances". The reader is referred to No. X of the series, J. Am. Chem. Soc., 75, 1830 (1953).

14. R. W. Ditchburn and J. C. Gilmour, Revs. Modern Phys. 13, 310 (1941).

15. L. Brewer, P. W. Gilles, and F. A. Jenkins, J. Chem. Phys. 16, 797 (1948).

16. A. H. Daane, Atomic Energy Commission Declassified Document AECD-3209 (December 1950).

17. E. R. Harrison, J. Appl. Chem. (London) 2, 601 (1952).

18. N. D. Erway and R. L. Seifert, Manhattan District Declassified Document MDDC-1030 (June 1947).

19. M. E. Mueller, Atomic Energy Commission Declassified Document AECD-2029 (May 1948).

20. G. Derge and M. Cefola, Metallurgical Project Report CT-2277 (October 1944).

21. R. D. J. Fraser, Molecular Rays, (Cambridge University Press, London, 1931), p. 12.

22. Ibid., p. 17.

23. The reader should consult any standard text dealing with the Kinetic Theory of Gases.

24. M. Knudsen, Ann. Physik 28, 999 (1909).

25. W. F. Roeser and H. T. Wensel, Bur. Stds. J. Res. 10, 275 (1933).

26. R. L. Weber, Heat and Temperature Measurement (Prentice-Hall, New York, 1950), p. 380.

27. Ibid., pp. 264, 268.

28. J. M. Hollander, I. Perlman, and G. T. Seaborg, Table of Isotopes, Revs. Modern Phys., 25, 469 (1953).

29. S. R. Gunn, unpublished data, 1953.

30. H. L. Baumbach and P. L. Kirk, unpublished data.

31. S. Fried and N. R. Davidson, J. Am. Chem. Soc. 70, 3539 (1948).

32. R. J. Thorn, private communication.

33. E. F. Westrum, Jr., and LeRoy Eyring, J. Am. Chem. Soc. 73, 3396 (1951).