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Vapor Pressures of Americium Trifluoride and Plutonium Trifluoride, Heats and Free Energies of Sublimation

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The vapor pressures of solid AmF_3 and PuF_3 were measured in the temperature range ~1100–~1300°K. by the Knudsen method. Separate free energy of sublimation equations, yielding calculated pressures in agreement with observation within $\cong \pm 5\%$ were derived for each of the four samples examined. The experimental data, together with an assumed ΔC_p of sublimation of -14 cal. mole^{-1} deg.$^{-1}$, yield: AmF_3 sample D-1, ΔF (cal.) $= 112{,}650 + 32.24T \log T - 155.55T$; AmF_3 sample E, $\Delta F = 112{,}690 + 32.24T \log T - 155.45T$; PuF_3 sample C-2, $\Delta F = 111{,}340 + 32.24T \log T - 155.61T$; PuF_3 sample D-2, $\Delta F = 113{,}180 + 32.24T \log T - 157.13T$. Samples D-1 and D-2 were run simultaneously in a double chambered, "twin" effusion vessel, and the results suggest that the greater volatility of PuF_3 at elevated temperatures as compared with AmF_3 is due to a slightly more positive entropy of sublimation rather than to a smaller heat.

Introduction

The vapor pressures of plutonium trifluoride, trichloride and tribromide were measured at elevated temperatures by Phipps, Sears, Seifert and Simpson[2,3] who used a modification of the Knudsen[4] effusion method adapted for radiometric assay of the vapor condensates.

The work of Phipps, *et al.*, is notable for its precision and for the wide range of pressures investigated. The data represent a significant contribution to the body of basic thermodynamic information concerning the actinide elements and are of practical application in connection with the purification of plutonium halides by sublimation, as well as in preparing thin uniform samples of plutonium for nuclear studies, by vapor condensation.

The vapor pressure measurements reported here were undertaken as part of a continuing program of investigation of the basic thermodynamics of americium. More broadly, however, the data were sought in connection with our general interest in the comparative chemistry of the 5f series of elements. In particular, we have been concerned with three basic aspects of heavy element chemistry: (a) trends in the heats of analogous reactions of successive elements associated with progressive changes in crystal energy originating from the "actinide" contraction; (b) entropy variations among similar oxidation-reduction reactions attributable to variable ground state multiplicity changes; (c) possible entropy effects due to Starke splitting of the ground states of the cations in ionic compounds.

Some comparative studies on the heats and entropies of analogous reactions of americium and a number of the 4f elements have been reported previously.[5–8]

Since, as a rule, the effects in which we are interested are expected to occur as relatively small variations imposed upon much greater over-all heat and entropy differences we feel that it is essential that comparison between different elements be made by methods and techniques which are held as nearly identical as possible. In the present work on the vapor pressures of americium trifluoride and plutonium trifluoride, it was not possible for us to duplicate the elegant apparatus used by Phipps, *et al.*,[2,3] in their studies of the plutonium halides. In order that our measurements might have high relative, if not absolute, accuracy, we chose to construct a "twin" Knudsen device, in which measurements on plutonium trifluoride and americium trifluoride were made simultaneously under conditions which we hoped would largely diminish systematic errors by cancellation. It turned out that absolute values of the vapor pressure of plutonium trifluoride computed from our observations agreed rather well with those of Phipps, *et al.*,[2,3] leading us to conclude that such systematic errors could not be much greater than the error of the reference measurements. Subsequently some measurements were made with our apparatus in "single" operation.

Experimental

Vapor Pressure Apparatus.—Constructional details of the twin effusion apparatus are given in full elsewhere[9] and will be mentioned here only briefly. The double chambered effusion vessel of tantalum was of symmetrical construction formed by drilling $^3/_{64}$ in. diameter holes to a depth of $^3/_8$ in. in each end of a cylindrical rod $^7/_8$ in. long by $^3/_8$ in. diameter. A smaller hole, perpendicular to the main axis of the cylinder, penetrated part way into the central septum and was used to accommodate a platinum, 90% platinum-10% rhodium thermocouple. The ends of the cylinder were covered by discs of tantalum foil spotwelded in place, in which 0.1 mm. diameter effusion orifices had been prepared by the method of Phipps, *et al.*[2] Threaded ports through the side of the crucible provided access to the cavities for loading; during operation these ports were closed with tantalum screws fitted with ring gaskets of soft platinum.

The effusion vessel was contained in a cylindrical sleeve of Alundum wound with evenly spaced turns of 30-mil molybdenum wire; end turns were etched with acid to a diameter of 22 mils to increase their heat output. Thermal decomposition of the Alundum at an effusion vessel temperature of about 1300° caused thermocouple poisoning and imposed this upper limit to the temperature range of the equipment.

The heating coil was surrounded by two concentric radiation shields of thin molybdenum foil.

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[1] Westvaco Mineral Products Division, Food Machinery and Chemical Corporation, Newark, California. Abstracted in part from the Ph.D. dissertation of Stephen C. Carniglia, Nov., 1953.

[2] T. E. Phipps, G. W. Sears, R. L. Seifert and O. C. Simpson, "The Transuranium Elements: Research Papers," McGraw-Hill Book Co., Inc., New York, 1949, National Nuclear Energy Series, Plutonium Project Record, Vol. 14B, p. 682.

[3] T. E. Phipps, G. W. Sears, R. L. Seifert and O. C. Simspon, *J. Chem. Phys.*, **18**, 713 (1950).

[4] M. Knudsen, *Ann. Physik*, **29**, 179 (1909).

[5] C. W. Koch and B. B. Cunningham, THIS JOURNAL, **76**, 1471 (1954).

[6] C. W. Koch and B. B. Cunningham, *ibid.*, **76**, 1470 (1954).

[7] C. W. Koch and B. B. Cunningham, *ibid.*, **75**, 796 (1953).

[8] C. W. Koch, A. Broido and B. B. Cunningham, *ibid.*, **74**, 2349 (1952).

[9] S. C. Carniglia and B. B. Cunningham, *Rev. Sci. Instr.*, in press.

The assembly described was supported in a horizontal position on two tantalum rails (which were part of a rigid rectangular framework) and fixed in place by a positioning pin. The rails also supported steel collimating discs at distances of about two inches and four inches from each of the effusion orifices.

Temperature control to within ±0.5° was maintained during exposure by manual operation of a supplementary power supply to ensure minimum deflection of a sensitive galvanometer (Rubicon Model 3402 H H; 0.5 mm. per microvolt) included in the thermocouple circuit.

Absolute temperatures were evaluated from preliminary experiments in which "in place" calibration of the thermocouple was carried out against the melting points of pure samples of gold, silver, tin and aluminum contained in graphite crucibles inside a "dummy" effusion vessel.

In special observations prior to vapor pressure measurements it was established that the maximum difference in temperature between different parts of the effusion vessel was less than three degrees at operating temperatures and that the asymmetry of the temperature profile of the vessel was less than one degree.

In "twin" operation manually operated shutter-receiver systems were mounted immediately behind the two collimators in extreme position; during exposure the vapor passing through the collimator openings condensed in a circular area well within the boundaries of one quadrant of a large platinum disc which could be rotated through successive 90° turns. In runs in which high levels of activity were vaporized no significant scattering of material from the collecting surface was detected. The quantity of vapor condensed in a known period of time was determined by standard methods of alpha radiometric assay. Half-lives used for Am^{241} and Pu^{239} were those given by Hollander, Perlman and Seaborg.[10]

The apparatus was contained in a vacuum envelope of Pyrex glass connected to a conventional high vacuum system. Evacuation was aided by a supplementary trap containing absorbent charcoal cooled with liquid nitrogen. The following pressures were noted: ultimate, 8×10^{-8}; maximum (transient), 2.5×10^{-6}; steady operating 1×10^{-6}.

To protect the operator against the hazards of working with high levels of alpha radioactivity the entire system was mounted in a closed box provided with special ventilation.

Conversion of the "twin" system described above to "single" operation involved only minor changes in the design of the effusion vessel. It then became possible, however, to employ a collecting system which permitted about twenty successive exposures to be made on separate 1 in. diameter platinum discs.

Materials.—The trifluorides of plutonium and americium were precipitated from aqueous solution by the addition of hydrofluoric acid, and were dried in air. Their identity was established by X-ray diffraction analysis (powder patterns) and purities were checked by spectrographic analysis, using copper spark excitation. Impurities found in the plutonium trifluoride were: Al, 0.02%; La, 0.01%; and Mg, 0.02%. The americium trifluoride contained 0.1% Al and 0.05% Fe. About 1 mg. of trifluoride was used for each set of measurements.

The trifluorides were subjected to further drying by long exposure to high vacuum prior to heating. An effort was made to remove all oxygen from the effusion system by repeated flushing with pure dry argon. In spite of these precautions, it was found that material taken from the effusion crucibles following a set of pressure measurements contained in all cases a substantial amount of oxyfluoride. This observation is consistent with the experience of Phipps, *et al.*,[2,3] with other plutonium halides. Oxyfluoride would introduce significant errors in the vapor pressure measurements if: (1) its vapor pressure is comparable to that of the trifluoride, or (2) it is appreciably soluble in the trifluoride. The first possibility was tested in an experiment in which a sublimate collected from a mixture of plutonium oxyfluoride and plutonium trifluoride heated *in vacuo* was examined by X-ray diffraction and found to consist only of PuF_3, with lattice constants identical with those of authentic pure samples of the trifluoride. It was concluded that the volatility of the oxyfluoride is negligibly small compared with that of the trifluoride.

That the extent of solid solution formation between the oxyfluoride and the trifluoride is slight at room temperature was shown by lattice constant measurements on the trifluoride phase which was present in the trifluoride-oxyfluoride residue following the completion of vapor pressure runs.

One other aspect of the solid trifluoride vapor pressure measurements was examined briefly. A sample of PuF_3 was melted on a thin platinum filament *in vacuo* and cooled to room temperature within a few seconds. The cold melt consisted of the normal hexagonal room-temperature-stable phase only, with no evidence of a high temperature form "frozen in" by the rapid cooling. Thus, there is no direct evidence for the occurrence of a phase transformation in PuF_3 at 1440°K. as is suggested by the break in the log P *versus* $1/T$ curve drawn by Phipps, *et al.*[2,3] The absence of any such transformation having a molal enthalpy greater than about 2 kcal. was proved by Westrum and Wallmann[11] during their determination of the melting point of PuF_3 (1698°K.).

Computations.—Vapor pressures were computed from the relation

$$P_{\text{mm Hg}} = \left[\frac{7.501\sqrt{2\pi R} \times 10^{-4}}{60}\right] \left[\frac{g}{a}\left(1 + \frac{d^2}{r^2}\right)\right]\left[\frac{\sqrt{M}}{n\lambda}\right]\left[\frac{c\sqrt{T}}{t}\right] \quad (1)$$

where 7.501×10^{-4} converts dynes cm.$^{-2}$ to mm. Hg, R is the molar gas constant, T the absolute temperature, g the reciprocal of the counting yield of the alpha counter, a the area of the effusion orifice, d the axial orifice-collimator distance and r is the radius of the collimator opening. M, the molecular weight of the effusing vapor, was taken as 296.1 for PuF_3 and 298.1 for AmF_3, assuming sublimation to monomeric vapor; whence n, the number of radioactive atoms per molecule, is one. The values taken for λ, the decay constant, were 1.671×10^{15} and 3.253×10^{13} dis. min.$^{-1}$ mole^{-1} for isotopically pure Am^{241} and Pu^{239}, respectively.[8]

Alpha counting rates, c, of the exposed receivers were recorded in counts min.$^{-1}$, the temperature, T, in degrees Kelvin, and the exposure time, t, in minutes.

For convenience, brackets are used to group terms as follows: (a) numbers and general physical constants, (b) constants of the apparatus, (c) constants of the effusing vapor, and (d) data pertaining to a particular exposure.

From statistical considerations we conclude that the standard error of our measurements is about ±6% in the vapor pressure, independent of temperature.

Results and Discussion

Vapor pressures computed from the experimental data by equation 1 are summarized in Table I.

As mentioned before, the vapor pressures given in Table I (as well as those computed by Phipps and co-workers[2,3]) are based on the assumption that the gaseous species are monomeric. This assumption is sufficiently questionable to deserve comment. If vaporization to dimeric $M_2F_{6(g)}$ actually occurred, the pressures tabulated would be uniformly high by the factor $2/\sqrt{2}$. The calculated entropy of sublimation—about +41 e.u.—is not affected by a uniform correction of the pressures. Upon comparison with the entropy of sublimation of $BiCl_{3(c)}$, where the vapor is known to be monomeric, the agreement is within two entropy units, whereas the entropy of vaporization to M_2F_6 molecules would be expected to be some six to ten entropy units more positive. For this reason we retain the assumption that the vapor is monomeric.

It is convenient to summarize the data of Table I by empirical functions which agree with observation within the limits of observational error.

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[10] J. M. Hollander, I. Perlman and G. T. Seaborg, *Rev. Mod. Phys.*, **25**, 469 (1953).

[11] E. F. Westrum, Jr., and J. C. Wallmann, THIS JOURNAL, **73**, 3530 (1951).

TABLE I

VAPOR PRESSURES OF PLUTONIUM TRIFLUORIDE AND AMERICIUM TRIFLUORIDE[a]

Temp., °K.	Vapor pressure, mm.		Temp., °K.	Vapor pressure, mm.	
	PuF_3	AmF_3		PuF_3	AmF_3
1126		5.07×10^{-7}[b]	1335	4.53×10^{-4}[d]	
1140		5.15×10^{-7}[c]	1338	4.61×10^{-4}[d]	
1145		5.90×10^{-7}[b]	1360	8.73×10^{-4}[e]	5.08×10^{-4}[c]
1160		1.15×10^{-6}[c]	1363		5.30×10^{-4}[b]
1214	1.255×10^{-6}[d]		1385	1.686×10^{-3}[e]	9.15×10^{-4}[c]
1216		7.18×10^{-6}[b]	1392	2.143×10^{-3}[e]	1.183×10^{-3}[c]
1233		1.213×10^{-5}[c]	1393	1.921×10^{-3}[d]	
1274	8.86×10^{-5}[e]	4.61×10^{-5}[c]	1412	3.340×10^{-3}[e]	1.803×10^{-3}[c]
1275		4.77×10^{-5}[b]	1414	3.084×10^{-3}[e]	1.725×10^{-3}[c]
1280	9.53×10^{-5}[d]		1414		1.710×10^{-3}[b]
1302	1.730×10^{-4}[e]	1.038×10^{-4}[c]	1444	5.90×10^{-3}[d]	
1311	2.572×10^{-4}[e]	1.486×10^{-4}[c]	1469		5.820×10^{-3}[b]
1330		1.984×10^{-4}[b]			

[a] Computed on the assumption that the gaseous species is monomeric. [b] Americium trifluoride sample E. Run singly. [c] Americium trifluoride sample D-1. Run simultaneously with plutonium trifluoride sample D-2. [d] Plutonium trifluoride sample C-2. [e] Plutonium trifluoride sample D-2. Run simultaneously with D-1.

The data may be so represented by free energy functions of the form

$$\Delta F^0_{\text{sub}} = \Delta H^0_0 - 2.3\,\Delta C_p T \log T + IT \qquad (2)$$

where values of ΔH^0 and I are chosen to give the best fit with free energies calculated from the observed pressures. We use a ΔC_p value of -14 cal. mole^{-1} deg.$^{-1}$, consistent with the treatment of the data of Phipps, *et al.*,[2,3] by Brewer, Bromley, Gilles and Lofgren,[12] even though our experimental results are represented equally well by functions which ignore the ΔC_p of sublimation. However, an equation which includes a ΔC_p term is unquestionably more reliable for calculating pressures well outside the rather limited range of measurement. The free energy functions calculated independently for each of the four samples are: AmF_3, sample D-1, $\Delta H_0 = 112{,}650 \pm 146$ cal. mole^{-1}, $I = -155.55$ cal. mole^{-1} deg.$^{-1}$; AmF_3, sample E, $\Delta H_0 = 112{,}690 \pm 105$ cal. mole^{-1}, $I = 155.45$ cal. mole^{-1} deg.$^{-1}$; PuF_3, sample C-2, $\Delta H_0 = 111{,}340 \pm 79$ cal. mole^{-1}, $I = -155.61$ cal. mole^{-1} deg.$^{-1}$; PuF_3, sample D-2, $\Delta H_0 = 113{,}180 \pm 157$ cal. mole^{-1}, $I = -157.13$ cal. mole^{-1} deg.$^{-1}$.

For the four sets of observations calculated and observed pressures agreed within the following standard deviations in percentage: ±3, ±6, ±5, and ±4, respectively.

For comparison, we give the constants derived from the observations of Phipps, *et al.*, on PuF_3 (series I measurements): $\Delta H_0 = 115{,}500$ cal. mole^{-1}, $I = -158.7$ cal. mole^{-1} deg.$^{-1}$

The agreement between the two sets of measurements on AmF_3 is very gratifying, but the runs on PuF_3 are in rather poor accord. The results from sample D-2 (run simultaneously with AmF_3 sample D-1) are more like those obtained by Phipps and co-workers although our calculated heats and entropies are both somewhat smaller.

There is no doubt, however, that within the temperature range of our investigation, the vapor pressure of plutonium trifluoride is about twice that of americium trifluoride.

Consideration of the four sets of results as independent observations of equal validity gives somewhat contradictory answers to the question as to whether the higher volatility observed for plutonium trifluoride is due to a less positive heat or to a more positive entropy of sublimation.

The question may be resolved by making two assumptions which appear to us to be quite reasonable: (1) the discrepancy between the two sets of results on plutonium trifluoride is due primarily to thermocouple errors, and (2) in any exposure in the "twin" run the two trifluoride samples were always at a virtually identical temperature irrespective of uncertainties as to the exact value of this temperature. If these assumptions are valid, the small but generally positive temperature coefficient of the ratio of the pressure of $PuF_{3(g)}$ to that of $AmF_{3(g)}$, noted in the "twin" run, is an indication that the heat of sublimation of plutonium trifluoride is more positive than that of americium trifluoride. This conclusion is independent of any reasonable uncertainties as to the temperature measurements themselves, but is dependent upon the earlier assumption of the identity of the ΔC_p functions for the sublimation of PuF_3 and AmF_3. It then follows from the experimental data that the higher vapor pressure of PuF_3 relative to AmF_3 at the experimental temperatures must be due to an entropy of vaporization which is more positive—apparently by about 1.5 entropy units.

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(12) L. Brewer, L. Bromley, P. L. Gilles and N. Lofgren, "The Transuranium Elements: Research Papers," McGraw-Hill Book Co., Inc., New York, N. Y., 1949, National Nuclear Energy Series, Plutonium Project Record, Vol. 14B, p. 861.