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The Vapor Pressure of Americium*

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(Received February 21, 1950)

The vapor pressure of americium from a dilute solution in plutonium has been measured by a modification of the Knudsen effusion method. The resulting vapor pressure for pure americium in the temperature range 1450°K to 1820°K is given by the equation $\log_{10} p_{\text{mm}} = 7.02 - (11,300)/T$. The vapor pressures are probably accurate to a factor of two or three. Relative values are much more precise.

INTRODUCTION

IN the Knudsen¹ effusion method for the determination of vapor pressures the substance to be studied is placed in an oven having a small thin-edged orifice. The oven is maintained at constant known temperature in a vacuum and measurement is made of the amount of vapor effusing from the orifice in a known period of time. The rate of effusion of vapor is a function of the partial pressure of vapor in the oven, the size of the orifice, the oven temperature, and the molecular weight of the vapor molecule. In order that the partial pressure of vapor in the oven be equal to the saturation vapor pressure at the oven temperature, it is essential that the evaporation surface be very large compared to the total area of the orifice and any leaks in the oven. Since the orifice must be large enough to permit effusion of a measurable amount of vapor and since there is also a lower limit to the size of orifice which may be used in practice, it is in general desirable to have at least a few milligrams of material available for vapor pressure measurements.

When only tracer amounts of material are available, it is possible to meet the above requirement of large evaporation surface by using a dilute solution of the desired material in a second substance. If the two substances are sufficiently similar, it may be assumed that an ideal solution is formed. Thus a large evaporation surface may be obtained and the vapor phase in the oven will be saturated with respect to each component of the solution. The desired vapor pressure may be calculated from the measured partial pressure and the mole fraction of the constituent in the solution.

The relatively short² half-life of Am^{241} with its correspondingly high specific activity permits the detection and measurement of very small amounts of this isotope. Therefore it is possible to measure very small partial pressures of americium by the effusion method and consequently to use very dilute solutions of americium to charge the effusion oven.

In this investigation plutonium metal was used as the solvent for the tracer amount of americium. Since

these two metals are neighboring elements in the actinide series, it is reasonable to assume the applicability of perfect solution laws.

APPARATUS

To prevent oxidation of the surface of the metal sample it was desirable that the apparatus permit the sample to be kept in a high vacuum throughout the entire series of measurements. The apparatus which was used is shown in Fig. 1. Except for the type of oven and oven support, this apparatus is similar to that described by Phipps, Sears, Seifert, and Simpson.³ In this apparatus a calculable fraction of the vapor which effuses from the orifice passes through a collimator and is collected on a cooled platinum target.

The oven and oven support are shown in detail in Fig. 2. The oven was machined from 0.75-in. tantalum rod. The fact that molten metals will creep over hot, clean tantalum surfaces is an advantage in that the resulting thin layer of metal offers a large evaporation surface. However, the creepage may be a disadvantage if it occurs to too great an extent. In such a case the oven orifice may be partially closed or some metal may even creep onto the outside of the orifice plate. To combat this possibility, the oven had a set of two nested cups. To utilize the hindering effect that sharp edges have on creepage, each cup had a sharp upper edge. The sample was placed in the innermost cup.

The oven orifice was formed at the center of a disk of 0.005-in. tantalum foil, which was then spot-welded to the top of the oven. The top section of the oven was force-fitted to the bottom section by a perfect fitting taper joint. At the oven temperatures used, the two pieces cohered strongly to each other, thereby preventing any leakage of vapor. The lower section of the oven had a threaded 0.15-cm hole drilled in its center. This hole was of the proper depth and diameter to simulate blackbody conditions. The temperature of the oven was determined by observation of this "blackbody" hole with a calibrated Leeds and Northrup optical pyrometer.

The oven was supported by three 0.040-in. tungsten legs, spaced equilaterally in its base. These three legs rested respectively in a conical hole, a V-groove, and a

* This investigation was carried out under Contract No. W-7401-eng-37 for the Manhattan Project at the Metallurgical Laboratory, University of Chicago.

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¹ M. Knudsen, *Ann. d. Physik* **29**, 179 (1909).

² G. T. Seaborg, *Chem. and Eng. News* **25**, 358 (1947).

³ Phipps, Sears, Seifert, and Simpson, *J. Chem. Phys.* **18**, 713 (1950).

flat-bottom groove, which were ground to equal depth in the quartz oven support. This type of support gave a definite reproducible position for the oven. Also supported on the quartz table and concentric with the oven was a two-walled quartz radiation shield. The shield had sections of 1-mil platinum foil between its walls. As the oven was heated by induction, the sections of platinum foil were separated by small gaps in order to decrease the power loss in the radiation shield. The hole at the center of the quartz table and the optical Pyrex window at the bottom of the apparatus made it possible to observe the oven with the pyrometer.

Platinum targets (0.75 in. diameter \times 0.005 in.) were mounted in aluminum holders as previously described.³ Fifty target holders were stacked in the cassette magazine (Fig. 1) with the target side facing the collimator. As previously described,³ a shutter was

provided to interrupt the beam of vapor molecules passing from the orifice through the collimator and an ejector rod was provided to push the bottom target across the ejection table. A Pyrex tube with several flat "seal-off" constrictions was provided to collect the ejected targets and permit their removal from the apparatus.

The apparatus was attached to a vacuum line which had sufficient pumping speed to maintain a pressure of less than 10^{-6} mm of Hg in the apparatus while the oven was at its highest temperature.

PROCEDURE

A 66.97-mg sample of plutonium metal was used, which was prepared to contain tracer amounts of Pu^{241} and Am^{241} .² A tracer amount of Pu^{238} was also present. The sample was homogeneous, since the tracer isotopes

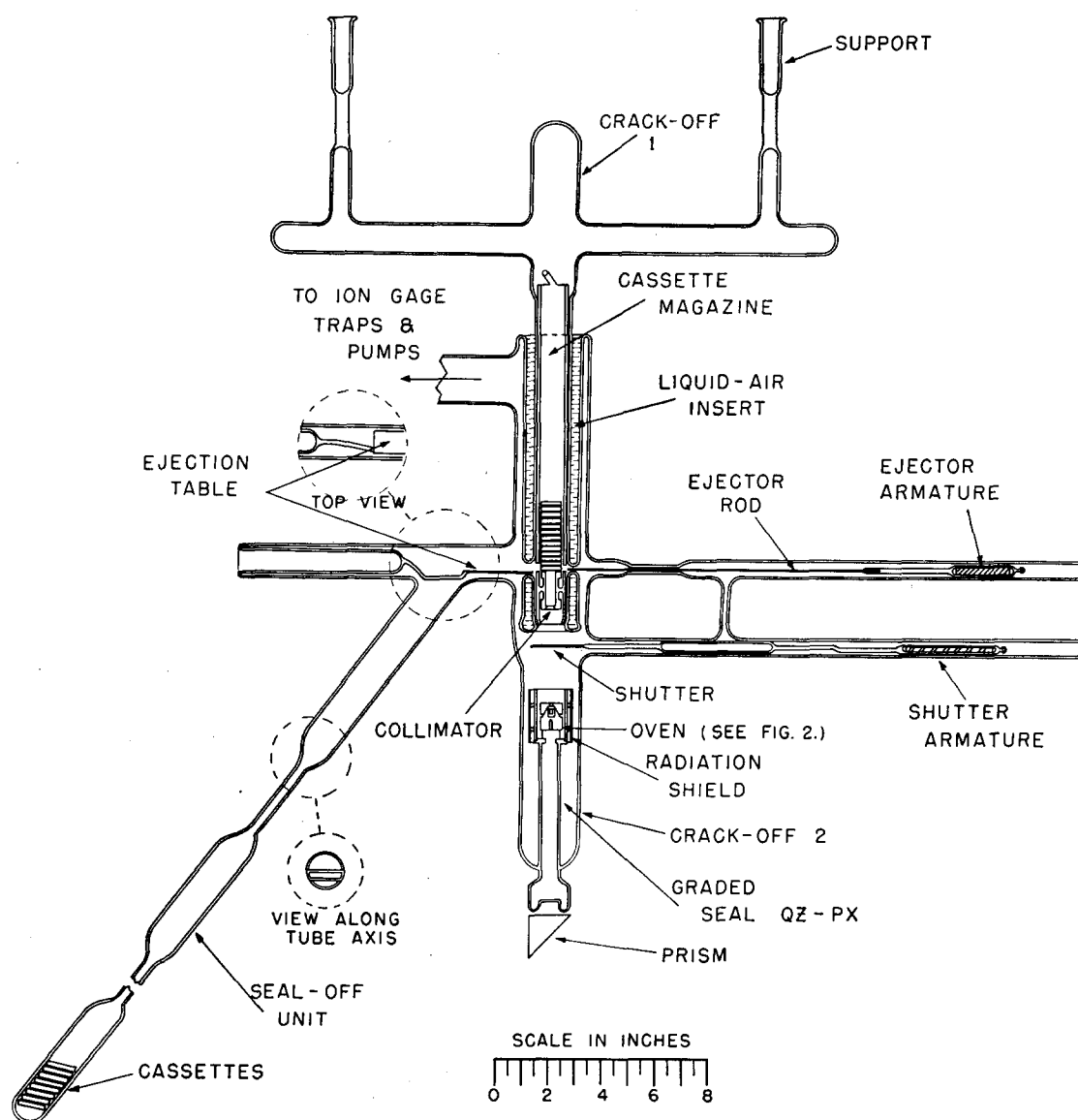


Fig. 1. Apparatus for the measurement of the vapor pressure of americium metal.

were present in the plutonium sample when it was reduced to metal. The cleaned sample of metal was sealed in an evacuated ampoule until the time it was placed in the oven.

The two sections of the oven were thoroughly outgassed by induction heating in an auxiliary vacuum system to a temperature of 2000°C for a period of 10 hr. After the oven was outgassed by this treatment, the vacuum in the system was broken with helium which had been dried by passage through a liquid air cooled trap. The oven was then removed and loaded in a stream of helium. After the charge had been placed in the oven base, the top section was forced on with a hydraulic press at a pressure of 2000 lb in⁻². While the oven was being loaded, the vapor pressure vacuum system, which had previously been evacuated and thoroughly torched, was opened at "crack-off 1" (Fig. 1) and dried helium was allowed to flow through the system. The oven was placed in position on the quartz table and the target magazine was replaced above it. The system was evacuated to a pressure of 8×10^{-7} mm of Hg. During the initial heating of the oven the temperature was raised slowly, so as to maintain a low pressure in the system.

With liquid nitrogen in the "liquid air insert" (Fig. 1) and the shutter in place under the collimator, the oven was heated by induction to a constant temperature. Then the shutter was opened and the target was exposed to effusing vapor for a measured length of time. The oven temperature was determined every 30 sec. during the exposure. At the end of the exposure the shutter was closed and the power output of the induction heater was altered to raise or lower the temperature of the oven for the exposure of the next target. The exposed target was ejected as previously described³ and the next target was allowed to fall into position. After a desired number of targets had been exposed, they were removed from the apparatus by sealing off the compartment of the "seal-off unit" (Fig. 1) which contained the exposed targets. The exposed targets were removed from the aluminum holders and the amount of americium deposited on each was determined by radiochemical assay.

The analysis involved the determination of the total alpha-activity on the platinum targets by counting in a standard parallel plate alpha-chamber and a determination of the percentage of the total activity which was due to the Am²⁴¹ alpha-particles. The latter determination was made in an alpha-pulse analyzer.⁴

The small amount of Pu²³⁸ which was present in the oven charge made necessary a small correction on the measurement with the pulse analyzer, since the range of the alpha-particles⁵ from Pu²³⁸ is sufficiently near

the range of alpha-particles from Am²⁴¹ that the pulse analyzer did not distinguish between the particles originating from these two isotopes. The range of the Pu²³⁸ alphas⁵ is sufficiently less than that of the other alpha-particles to permit good separation by the pulse analyzer method. Since the percentage of Pu²³⁸ in the plutonium was known, it was possible to correct for its presence and to obtain an accurate value for the Am²⁴¹ activity on each target.

The greatest uncertainty was in the determination of the Am-Pu composition in the oven at the time of each exposure. The amount of each isotope removed from the oven during each exposure could be calculated very accurately from the analysis of the material on the target and the geometry of the apparatus. However, that removed during the intervals between exposures had to be estimated. The periods of time involved were known. However, the temperature of the oven was being changed between exposures. The temperature of the oven was measured frequently during these intervals and the total period of time between exposures was kept small compared to the length of the exposures. As a result it was possible to determine within one or two percent the total amount of each isotope removed from the oven prior to each exposure.

Corrections were made for the growth of americium from Pu²⁴¹⁶ during the experiment, which covered a period of several days. Thus the net loss of each isotope from the oven prior to the midpoint of each exposure was known. The average mole fraction of americium in the oven during each exposure could then be calculated if the initial mole fraction were known.

The initial mole fraction of americium in the metal sample could not be obtained with accuracy from analysis of a sample of the original mixture of salts because of the uncertainty as to relative loss of americium and plutonium by volatilization during reduction to metal. Loss by volatilization during the reduction step or during a remelting of the sample would result

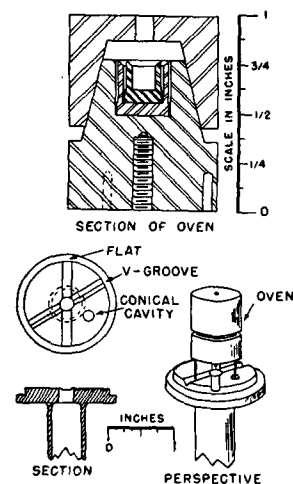


FIG. 2. Tantalum effusion oven and quartz support.

⁴ Ghiorso, Weissbourd, and Robinson, "The multi-channel pulse analyzer," MDDC-23, Technical Information Division, Oak Ridge, Tennessee.

⁵ Chamberlain, Gofman, Segrè, and Wahl, Phys. Rev. 71, 529 (1947).

⁶ G. T. Seaborg, Chem. and Eng. News 26, 1902 (1948).

TABLE I. The vapor pressure of americium metal.

Target No.	Temp. $T^{\circ}\text{K}$	Exposure time τ (min.)	Registered disintegrations of Am c (dis./min.)	Mole fraction of Am $N \times 10^5$	Vapor pressure p (mm Hg)	Recip. temp. $\frac{1}{T} \times 10^3$
1	1412	30.00	14.9	1.90	0.0301	70.8
2	1462	150.00	300	1.90	0.123	68.4
3	1500	65.00	308	1.78	0.316	66.7
4	1565	25.00	193	1.55	0.603	63.9
5	1614	10.00	113	1.43	0.977	62.0
6	1666	5.00	95.4	1.31	1.82	60.0
7	1709	3.00	82.7	1.19	2.95	58.5
8	1761	2.00	47.2	0.69 ₈	4.37	56.8
9	1818	1.00	15.8	0.32 ₇	6.31	55.0
10	1454	150.00	80.7	0.29 ₄	0.214	68.8
11	1810	1.00	13.6	0.28 ₈	6.17	55.3
12	1501	65.00	46.0	0.26 ₆	0.316	66.6

in a surface concentration of americium which was different from that in the body of the metal sample. Therefore it was not possible to obtain a truly representative sample of the reduced metal.

The initial mole fraction of americium was therefore determined by observing the partial pressure of americium above the solution for the same oven temperature at two widely separated times during the series of measurements. The ratio of observed partial pressure of americium vapor to the mole fraction of americium in the solution should be constant at a given oven temperature. A simple calculation gives a value for that initial mole fraction of americium which, when combined with the data for the net loss of all isotopes prior to the two exposures, results in the same value for the ratio of observed pressure to mole fraction for each exposure.

RESULTS

Sixteen exposures were made, during which time 5.53×10^{-9} mole of americium was removed from the oven. The last four exposures gave amounts of americium too low to detect accurately with the pulse analyzer and hence these exposures were not included in the vapor pressure calculations. The experimental data for exposures 1 to 12 are given in Table I.

The vapor pressure of americium was calculated by the following equation (cf. Eq. (4) of reference 3).

$$p_{\text{mm}} = \frac{c}{N\tau} \cdot \frac{(D^2 + 4r^2)}{aD^2} (2\pi MRT)^{\frac{1}{2}} \frac{10^{-6}}{s(241)60(1333)}, \quad (1)$$

where p_{mm} is the vapor pressure of americium in mm of Hg; c is the number of registered alpha-disintegrations per minute for the americium on the target; N is the mole fraction of americium in the oven charge at the midpoint of the time of the exposure; τ is the length of the exposure in minutes; D is the diameter of the collimator; r is the distance from orifice to collimator; a is the area of the orifice; M is the molecular weight of the americium vapor molecule; R is the molar gas

constant; T is the absolute temperature of the oven; and s is the number of registered alpha-disintegrations per minute per microgram of americium under the counting conditions used. The americium vapor was assumed to be monatomic, so that M was taken to be 241. s had the value 3.45×10^6 registered disintegrations per minute per microgram. At 25°C the experimental values of D , r , and a were, respectively, 0.5333 cm, 9.921 cm, and $2.41 \times 10^{-4} \text{ cm}^2$. The slight change in value of r and a with oven temperature was neglected, since the resulting error was negligible compared to other uncertainties. Equation (1) then reduces to the experimental equation

$$p_{\text{mm}} = \frac{3.067 \times 10^{-8} c(T)^{\frac{1}{2}}}{N\tau}, \quad (2)$$

which was used to calculate the values of p in Table I for pure americium.

The initial mole fraction of americium was calculated from the experimental data for targets 3 and 12, which were exposed at the same oven temperature within the experimental error of the temperature measurement. Unfortunately the experimental error in the analysis of the deposit on targets 13 to 16 was too great to permit this same calculation to be made with other pairs of exposures. The value arrived at by use of targets 3 and 12 was consistent with the value obtained from the initial composition of the mixture of isotopes if the history of the mixture prior to these measurements was considered.

The vapor pressure data of Table I are shown graphically in Fig. 3. The experimental points are numbered in the order in which measurements were made. The vapor pressures given by targets 1 and 2 are apparently low. This probably resulted from a lower concentration of reduced americium atoms in the surface of the sample than in the body of the sample. Equilibrium was soon attained either by diffusion or by molten metal breaking through the surface skin and spreading over the surface of the tantalum cup. The line in Fig. 3 is the most probable line as given by a least-squares calculation utilizing the data for targets

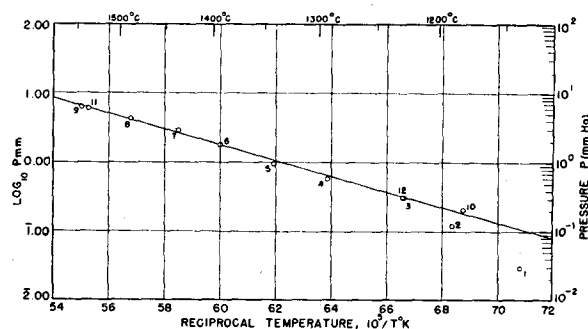


FIG. 3. Vapor pressure of americium metal.

3 to 12. The equation for this experimental vapor pressure curve is

$$\log_{10} p_{\text{mm}} = 7.02 - (11,300/T) \quad (3)$$

for the temperature range 1450°K to 1820°K.

The probable error in values of p calculated by Eq. (3), within the given temperature range, is less than two percent as determined by the residuals of the experimental points from the most probable line. However, the uncertainties in the initial concentrations of Am²⁴¹ and Pu²³⁸ and in possible deviations from ideal

solution laws may make the results in error by as much as a factor of 2 or 3.

On the basis of Eq. (3) the molar heat of vaporization of americium is 51.7 kcal./mole; the normal boiling point is 2460°C; and the molar entropy of vaporization at the normal boiling point is 18.9 cal./deg. mole.

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Internal Motion and Molecular Structure Studies by Electron Diffraction.

II. Interpretation and Method*

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The application of a recently developed objective procedure to the analysis of electron diffraction photographs from more complex molecules is discussed in terms of the further development of the details of some of the theoretical and experimental aspects of the procedure. The topics discussed are the physical significance of measured vibrational amplitudes, the method for drawing a background line, the calibration of photographic plates, and the computation of intensity curves by means of IBM machines.

THE theory and procedure for determining molecular structure and internal motion by an objective analysis of electron diffraction photographs have been presented in a previous paper.¹ The diffraction photographs are obtained with a rotating sector and are analyzed by means of a microphotometer. A procedure was developed for treating the molecular scattering data so that the equilibrium distances and vibrational motion can be computed directly from these data. This paper discusses refinements in interpretation and procedure which increase the accuracy and facilitate the extension of the method to the analysis of more complex molecules. The topics to be considered are the physical significance of the measured vibrational amplitude, the method for choosing the best background line representing the background scattering, a simple and accurate method for calibrating photographic plates, and the computation of intensity curves by means of IBM machines.

VIBRATIONAL MOTION, INTERPRETATION

The contribution of internal motion to scattering by gases has been evaluated in a very fine paper by R. W. James.² A brief derivation will be repeated here since the treatment differs from that given by James in a way which clarifies the physical significance of the

final result. In James' treatment, the ξ -axis of a rectangular coordinate system, ξ, η, ζ , was always placed along the line joining the pair of atoms whose motion was being considered. In the treatment to be presented, a general rectangular coordinate system is established without any restriction on its orientation and a more general expression is obtained which is suitable for application to any interatomic distance in a molecule. There may also be some advantage in having the general expression for use with spectroscopic data since it obviates the necessity for transforming the coordinate system for each pair of atoms in a molecule.

We start with the expression for the contribution to the intensity of scattering from a pair of vibrating atoms (omitting scattering factors),

$$I(s) = \int_0^\infty P(r) \frac{\sin sr}{sr} dr, \quad (1)$$

where $P(r)dr$ is the probability of finding an interatomic distance between r and $r+dr$ and $s = (4\pi \sin\theta/2)/\lambda$ where θ is the angle of scattering and λ is the wavelength of the radiation. We define a rectangular coordinate system ξ, η, ζ so that ξ^i, η^i, ζ^i are the equilibrium components of the i th atom and ξ_i, η_i, ζ_i represent its deviations from equilibrium due to the vibrational motion of the molecule. It is found that

$$r = [(\xi_i + \xi^i - \xi_j - \xi^j)^2 + (\eta_i + \eta^i - \eta_j - \eta^j)^2 + (\zeta_i + \zeta^i - \zeta_j - \zeta^j)^2]^{\frac{1}{2}} \quad (2)$$

* Presented at the Pittsburgh Diffraction Conference, November 7-8, 1949.

¹ I. L. Karle and J. Karle, *J. Chem. Phys.* **17**, 1052 (1949).

² R. W. James, *Physik. Zeits.* **33**, 737 (1932).