1
ARGONNE NATIONAL LABORATORY
P. O. Box 299
Lemont, Illinois

200, 11219

VAPOR PRESSURE OF URANIUM

by

E. G. Rauh and R. J. Thorn

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ABSTRACT

The vapor pressures and the heat of vaporization of liquid uranium have been measured by collecting a known fraction of the vapor effusing from a Knudsen cell. The deposits were "weighed" by comparing the number of fissions upon thermal neutron irradiation with the fissions from a standard. The measured rate of vaporization is extremely sensitive to the residual pressure of oxygen in the vacuum at background pressures of the order of 10^{-7} mm Hg. With the aid of a theoretically derived expression the effusion rate can be extrapolated to zero oxygen pressure to yield for the vapor pressure the result that

$$\log p \text{ (mm)} = -\frac{(23330 \pm 21)}{T} + (8.583 \pm 0.011),$$

over the temperature range 1630 to 1970°K. This expression, together with heat capacity data for solid uranium, yield a value of 116.6 kcal/mole for the heat of sublimation at 0°K and predict a value of about 4.7 kcal/mole for the heat of fusion.

I. INTRODUCTION

An inspection of a summary⁽¹⁾ of the determinations of the vapor pressure of uranium revealed that a more careful and complete investigation of this property was necessary before its value could be established. The most recent measurements by Derge and Cefola⁽²⁾ are subject to error for the following reasons: (1) No accurate determination of the weights of uranium deposited on the targets from the effusion oven could be made because the α -counts of the deposits were about the same as the background count. (2) The residual pressure in the system was of the order of 10^{-4} mm Hg. (3) No correction was made for the solubility of the crucible material in liquid uranium. (4) The authors did not examine their data for internal consistency. Such an analysis would have shown that their data predict an unreasonable value for the heat of fusion.

Since techniques are now available which permit the elimination of these sources of error, the vapor pressure has been redetermined over a temperature range from 1630 to 1970°K. As in the previous measurements the Knudsen effusion method⁽³⁾ was used, but refinements giving greater precision were employed. First, a more sensitive method which is independent of any quantity such as half-life was employed to "weigh" the deposit. This method of weighing the deposit involved fission counting and resulted in 10^4 times greater sensitivity. Second, the experimental conditions were more nearly ideal. Not only was the residual pressure in the vacuum system lower (10^{-7} mm Hg or better) but a quantitative determination of the effect of oxygen was made. Third, the data were analyzed for internal consistency with the aid of recently reported auxiliary data pertaining to the entropies of the vapor and solid.

II. EXPERIMENTAL MEASUREMENTS

A. Method

1. Vapor Pressure - The vapor pressure was determined by collecting a known fraction of the vapor effusing from a Knudsen cell. In this method the vapor pressure is found, from the kinetic theory and the cosine law,⁽⁴⁾ to be related to the weight collected, $\underline{W}$, by the relation,

$$p = (2\pi RT/M)^{1/2} (d/\rho)^2 (W/\pi r^2 t) \quad (1)$$

in which $\underline{d}$ is the orifice-to-collimator distance, $\underline{r}$ is the radius of the collimator, $\underline{\rho}$ is the radius of the orifice, $\underline{t}$ is the time of collection, and $\underline{R}$, $\underline{T}$, $\underline{M}$, have their usual significance. In the derivation of this expression the assumptions are made that the area of the orifice is small compared with the area of the collimator, and the square of the collimator radius is small compared with the square of the orifice-to-collimator distance. Since $r^2/d^2 \cong 0.001$ for all the measurements, the second assumption is certainly justified. The value of $\pi\rho^2/\pi r^2$ for Exposure Series 1 through 3 was about 0.002. Hence the first assumption introduces no appreciable error in these experiments. In Exposure Series 4 and 5, however, $\pi\rho^2/\pi r^2$ was about 0.2 and 0.1, respectively, but as shown later even these values lead to inconsequential errors. The quantities $\underline{d}$ and ρ were measured at room temperature and corrected for the expansion of the effusion cell at the temperature and corrected for the expansion of the effusion cell at the temperatures of effusion.

The deposits of uranium metal on the targets were weighed by comparing the number of fissions upon thermal neutron irradiation in the thermal column of the Argonne heavy water reactor with the fissions from a standard, both plates being counted simultaneously in a twin chamber counter. The data obtained thus were analyzed according to the following procedure.

The number of fissions per unit time is related to the weight of uranium on a given plate by the relation

$$F = \frac{(nv) \sigma f W N_0}{M}, \quad (2)$$

in which (nv) is the neutron flux, σ is the cross section for fission, f is the fractional weight of U^{235} in the weight W , N_0 is Avogadro's number, and M is the molecular weight of uranium. If two plates are counted simultaneously, then $(nv) \sigma f/M$ can be eliminated, and one finds that

$$W_i = (F_i/F_s) W_s.$$

If C is the gross count and if B is the background count, then

$$W_i = \frac{(C_i - B_i)}{(C_s - B_s)} W_s. \quad (3)$$

Since the background is proportional to the neutron flux, if the neutron flux during some particular counting period is taken as an arbitrary "standard pile level," the background for some other counting period is given by the expression,

$$B_i = B_\ell \frac{F_m}{F_{m\ell}}$$

or

$$B_i = B_\ell \frac{C_m}{C_{m\ell}}, \quad (4)$$

in which the subscript ℓ refers to the standard pile level and m refers to the monitor plate (which was also one of the standard plates). If the value of B_i given by Eq. (4) is substituted into Eq. (3), the resulting equation is

$$W_i = \left[\frac{C_i - B_\ell (C_m/C_{m\ell})}{C_s - B_\ell (C_m/C_{m\ell})} \right] W_s. \quad (5)$$

Eq. (5) is used (a) to interrelate all the standard plates and (b) to relate the vapor pressure plates to the standard plates. Standard plate No. 9 was selected as the monitor plate in both of these cases. The weight of uranium on this plate relative to the other standard plates is found from Eq. (5) to be given by the relation,

$$W_m = \left\{ \frac{C_m[1 - (B_\ell/C_{m\ell})]}{C_s[1 - (B_\ell C_m/C_{m\ell} C_s)]} \right\} W_s. \quad (6)$$

Although $\underline{C}$ and $\underline{B}$ are, by definition, counts per unit time, they can be taken as total counts if corresponding plates are counted simultaneously.

From Eq. (6) and a number of other standard plates on which the weights of uranium are known, an average value $\overline{W_m^1}$ can be calculated. The weight of uranium on any vapor pressure plate is then calculated from the relation,

$$W_i = \frac{[C_i - C_m(B_l / C_{ml})]}{[C_m - C_m(B_l / C_{ml})]} \overline{W_m^1} \quad (7)$$

The standard plates were prepared from standard solutions of uranyl nitrate (acidic). These solutions were made according to two procedures. In the first one 20 mg of the same material used for the vapor pressure determination was dissolved in nitric acid, and this solution was then diluted to a known weight in a weight buret (60 cc capacity). This solution was further diluted twice more, each time 1 gm solution being diluted to about 60 gm of solution (by weight). In the second method the wire was also dissolved in nitric acid (10 cc of concentrate), but the resulting solution was diluted to one liter in a volumetric flask. A weighed amount (approximately 1 gm) of this solution was diluted again to one liter. In a third standard solution the last step was altered slightly by adding 10 cc of concentrated nitric acid before the dilution. The amount of the standard solution placed on the platinum plates was determined both by the weight of solution transferred from a specially prepared weight pipette and by the weight of solution on the plate which was placed in a special weighing bottle. In all cases these two weights were the same within 0.4%. The solutions on the plates were evaporated to dryness in a dessicator, and thereafter the plates were heated to about 200°C for a few seconds.

A summary of the interrelation between the standard plates is given in Table I. These data were analyzed statistically by assuming that, if in a number of observations the number of errors numerically greater than some error $\underline{a}$ is less than one half, then an observation with an error greater than $\underline{a}$ should be rejected. The value of $\underline{a}$ is found from the relation

$$P = 2\pi^{-1/2} \int_0^{\rho a/r} \exp(-t^2) dt,$$

in which $\underline{P}$ is obtained from the number of observations, $\underline{n}$, and the relation

$$n - nP = 1/2 .$$

Table I
INTERCOMPARISON OF STANDARD PLATES

Plate No.	Solution No.	Weight of Uranium (10 ⁻⁹ gm)	Calculated Weight on Monitor (10 ⁻⁹ gm)
8	I	7.09	6.51
11	II	1.16	5.51
12	II	1.39	5.79
13	I	9.11	7.85 ^b
14	I	6.35	8.31 ^b
15	II	1.06	5.98
16	II	1.21	1.92 ^b
17	II	1.88	3.97 ^b
18	III	2.54	6.12
19	III	1.12	5.98
20	I	7.80	6.49
21	I	7.20	6.38
50λ	a	1.45	6.07
9	I	6.26	6.26
			Average = 6.109 ± 0.067

^aSolution and plate prepared by Gray Pyle of the Chemistry Division.

^bRejected on statistical basis.

2. Heat of Vaporization (and Sublimation) - In addition to the usual interest in the heat of vaporization, in this case this quantity provides a means of examining the data for internal consistency. This is made possible by comparing the value obtained from the Clapeyron equation,

$$\Delta H_V = -RT \frac{d \ln p}{d (1/T)} \quad (8)$$

with that obtained from the second and third laws of thermodynamics.

From statistical mechanical relations one finds for the heat of sublimation (at 0°K) of a crystalline solid to a perfect monatomic gas

$$\Delta H_0^0 = T \left\{ -R \ln p + R \ln \left[\frac{(2\pi k)^{3/2}}{h^3 N_0^{5/2}} \right] + R \ln T^{5/2} M^{3/2} \right. \\ \left. + R \ln RQ + \frac{H_s^0}{T} - S_s^0 - 1/T \int_p^1 V_s dp \right\}, \quad (9)$$

in which p is the vapor pressure at a temperature T , Q is the electronic partition function for the gas, H_s^0 is the heat content of the solid, S_s^0 is the entropy of the solid, and the other symbols have their customary significance. From the heat of sublimation and the heat of fusion one can then calculate a heat of vaporization to compare with that calculated from Eq. (8). At the melting point, 1406°K, Eq. (9) becomes

$$\Delta H_0^0 = 1.406 (-R \ln p_m + 46.280) \text{ kcal/mole} . \quad (10)$$

In the evaluation of the constant in this equation the last term in Eq. (9) was neglected. The partition function was evaluated from data by Kiess, Humphreys, and Laun⁽⁵⁾ and the heat content and entropy of the solid have been calculated from data reported by Ginnings and Corruccini.⁽⁶⁾ These data also interrelate the heat of sublimation at the melting point, ΔH_{1406} , and that at 0°K.

$$\Delta H_{1406} = \Delta H_0 - 5.2 \text{ kcal/mole} .$$

Since $\Delta H_{1406} = \Delta H_v + \Delta H_f$, in which ΔH_f is the heat of fusion, one finds that the heat of sublimation can also be calculated from Eq. (8) by the expression

$$\Delta H_0 = \Delta H_v + 5.2 + \Delta H_f . \quad (11)$$

B. Apparatus and Procedure

Aside from some minor alterations, the apparatus was identical to that used by Erway and Simpson.⁽⁷⁾ A shutter was provided to protect the optical window between pyrometer readings. A variable leak was provided at the throat of the divergent nozzle mercury vapor pump. This consisted of a brass Hoke needle valve controlled by a 600:1 reducing drive; with this control the pressure at the ion gauge could be changed by as little as 10% at 10^{-7} mm Hg with a full atmosphere of pressure behind the valve. The position of the drive was not reproducible, but the pressure remained constant for a given setting for long periods of time. The tantalum effusion cell was also the same as that described by Erway and Simpson⁽⁷⁾, except

that the inner nested cups were drawn from sheet tantalum. Unfortunately, even tantalum may not be the most desirable material to use for a crucible to contain uranium. Although there is no evidence that the two materials form solid solutions, tantalum is soluble in liquid uranium. However, the solubility has been determined⁽⁸⁾ as a function of temperature, and, as shown later, the correction for the solubility is not sufficiently large to cause an appreciable error in either the vapor pressure or the heat of vaporization.

The platinum disks (0.75 x 0.005 in.) on which the vapor condensed were cleaned chemically with nitric acid and then heated to about 500°C just prior to their introduction into the apparatus. As determined by actual measurement the target in situ attained a temperature of less than 200°C with the oven at the highest temperature. Although this would appear to be a sufficiently low temperature to condense all of the uranium, a further test of the fraction condensing was carried out. A 0.5-in. hole was drilled through one target holder, and this holder was loaded with 2 platinum disks with 0.25-in. holes through their centers. The target behind the altered holder was then also exposed to the uranium beam; any atoms reflected from the third target would condense on the back of the second. As shown by fission counting there was no uranium on the middle target. Hence all of the uranium arriving at a target must have condensed.

The temperature was measured with a disappearing filament pyrometer which was standardized against a calibrated band lamp. All readings were corrected for the transmissivity of interposed window and prism.

The uranium in the form of wire containing about 93% U^{235} was cleaned anodically in an electrolyte of 46% concentrated sulfuric acid and 6% glycerine. Within one hour after the metal was cleaned it was placed in the apparatus and the latter was evacuated.

III. EXPERIMENTAL DATA

A. Exposure Series 1

The data obtained in the initial series of exposures are given in Table II and in Fig. 1. The least squares analysis of the $\log p$ vs $1/T$ values yields the values given in the first row of Table VII. It is observed that the results predict a negative value for the heat of fusion and hence indicate a discrepancy. An examination of exposures 4, 5, and 6 shows that these values have positive deviations from the corresponding values calculated from the least squares equation which are more than five times the probable errors at these points. This does not mean, however, that these exposures are in error. A more complete examination reveals that some other factor besides temperature may have influenced the effusion rate during the experiment.

Table II

• EXPOSURE SERIES 1

Exposure Number	Exposure Time (minutes)	Oven Temp. ($^{\circ}\text{K}$) ^c	Ion Gauge Reading (mm Hg x 10^7)	Monitor Count (fissions/min) ^a	Vapor Pressure Plate Count (fissions/min) ^b	Vapor Pressure (mm Hg)
1- 1	6.07	1968	15.0	11979	2619	2.86×10^{-4}
1- 2	10.18	1917	10.0	11953	1929	1.24×10^{-4}
1- 3	36.11	1829	10.0	11956	1624	2.84×10^{-5}
1- 4	16.55	1719	2.0	11995	151	5.68×10^{-6}
1- 5	55.07	1638	1.0	11961	89	9.82×10^{-7}
1- 6	31.04	1679	1.5	11871	111	2.20×10^{-6}
1- 7	13.19	1770	3.0	11977	197	9.43×10^{-6}
1- 8	22.06	1864	5.0	11968	1834	5.38×10^{-5}
1- 9	16.06	1900	8.0	11809	2554	1.04×10^{-4}
1-10	29.36	1790	4.0	11850	613	1.32×10^{-5}
1-11	21.04	1701	2.0	11967	78	2.30×10^{-6}
1-12	11.18	1914	10.0	11869	2269	1.33×10^{-4}
1-13	22.07	1774	3.5	11968	345	9.74×10^{-6}
1-14	28.08	1671	1.0	11868	48	1.27×10^{-6}
1-15	6.36	1965	15.0	11962	2701	2.82×10^{-4}
1-16	11.23	1915	7.0	11941	2087	1.22×10^{-4}
1-17	36.05	1831	4.0	11810	1441	2.56×10^{-5}
1-18	16.09	1736	2.0	11830	110	4.28×10^{-6}
1-19	46.36	1633	0.9	12151	32	4.19×10^{-7}
1-20	41.49	1678	1.2	11846	93	1.38×10^{-6}
1-21	15.06	1769	2.0	11897	193	8.08×10^{-6}
1-22	21.35	1862	4.0	12035	1425	4.31×10^{-5}
1-23	17.09	1900	5.0	12000	2267	8.65×10^{-5}
1-24	32.03	1789	2.5	11912	565	1.12×10^{-5}
1-25	22.10	1703	1.0	11910	72	2.02×10^{-6}
1-26	8.06	1969	20.0	11889	3333	2.74×10^{-4}

Collimator area $0.22472 \pm 0.00084 \text{ cm}^2$ Oven orifice $(2.883 \pm 0.015) \times 10^{-4} \text{ cm}^2$ Orifice-to-collimator distance $7.908 \pm 0.005 \text{ cm}$

Oven charge 66 mg

^a
$$\left[C_m - C_m (B\ell / C_m \ell) \right] / t, \text{ Eq. (7)}$$

^b
$$\left[C_i - C_m (B\ell / C_m \ell) \right] / t, \text{ Eq. (7)}$$

^c Average deviation $\pm 1.0^{\circ}$.

FIGURE 1.
EXPOSURE SERIES I.

This is inferred from the fact that the first nine exposures are statistically consistent with each other and yield a positive value for the heat of fusion. In view of the observations of Phipps, Seifert, and Simpson⁽⁹⁾ one surmises that the residual oxygen in the vacuum vessel may have caused the observed decrease in the rate of effusion during the experiment.

B. Exposure Series 2

As an exploratory attempt to ascertain whether there was an appreciable amount of oxide present during Exposure Series 1, the oven from that experiment was exposed to air for about three weeks and replaced in the apparatus for another series of exposures. The results (Table III and Fig. 2) yield for the vapor pressure and the heats the values listed in Table VII. Since the values agree with those obtained in Exposure Series 1 with the first nine points excluded, one infers that oxidized metal must have been present in the first case.

C. Exposure Series 3

Since the data obtained in Exposure Series 1 and 2 indicate a possible effect of the residual gases of the vacuum, a third series of exposures was made to measure this effect quantitatively. In the first subseries of exposures the uranium was evaporated with the lowest obtainable background pressure. In three subsequent subseries (Exposure Series 3b through 3d) oxygen was admitted at successively greater pressures. These four subseries of exposures were prepared on successive days, and throughout this period liquid nitrogen was maintained in that part of the apparatus surrounding the targets and collimator. The last subseries of exposures was prepared after a lapse of three days during which time the liquid nitrogen was not maintained in this container. The pressure in the vacuum system during the last series was about the same as during the first series. In all these experiments the pressure in the system was sufficiently low so that scattering of the beam could be neglected.

The data which are presented in Table IVa through Table IVe and in Fig. 3 give the values summarized in Table VII.

D. Exposure Series 4

If an appreciable fraction of the metal in the crucible is either oxidized or coated with oxide, then the area of clean metal evaporating may be small. To examine this possible source of error, vapor pressure measurements were made from an oven having a larger orifice (approximately 100 times greater area) than those employed previously. (See Tables V and VI and Fig. 4.) Examination of exposures 4-11 and 4-17 shows that these have positive deviations which are greater than five times the probable errors at these points and are not included in calculating the results shown in Table VII.

Table III
EXPOSURE SERIES 2

Exposure Number ^d	Exposure Time (minutes)	Oven Temp. (°K) ^c	Ion Gauge Reading (mm Hg x 10 ⁷)	Monitor Count (fissions/min) ^a	Vapor Pressure Plate Count (fissions/min) ^b	Vapor Pressure (mm Hg)
2- 1	11.11	1947	40.0	65230	6011	1.35 x 10 ⁻⁴
2- 3	11.20	1947	14.0	64828	6007	1.34 x 10 ⁻⁴
2- 5	10.07	1944	9.0	65471	5081	1.26 x 10 ⁻⁴
2- 7	10.09	1944	9.0	65606	5123	1.27 x 10 ⁻⁴
2- 9	10.02	1943	8.0	65603	4792	1.19 x 10 ⁻⁴
2-10	14.37	1862	3.0	65344	1759	3.00 x 10 ⁻⁵
2-11	30.02	1773	1.6	65496	736	5.85 x 10 ⁻⁶
2-12	32.02	1674	1.0	65368	113	8.20 x 10 ⁻⁷
2-13	30.19	1723	1.0	67874	255	1.99 x 10 ⁻⁶
2-14	30.50	1809	3.0	72101	1261	9.96 x 10 ⁻⁶
2-15	11.02	1904	7.0	67290	2628	5.90 x 10 ⁻⁵

Collimator area $0.22472 \pm 0.00084 \text{ cm}^2$

Oven orifice $(2.883 \pm 0.015) \times 10^{-4} \text{ cm}^2$

Orifice-to-collimator distance $7.909 \pm 0.004 \text{ cm}$

Oven charge 66 mg

$$^a [C_m - C_m (B\ell/C_m \ell)] / t, \text{ Eq. (7)}$$

$$^b [C_i - C_m (B\ell/C_m \ell)] / t, \text{ Eq. (7)}$$

^c Average deviation $\pm 1.0^\circ$

^d Exposures 2-2, 2-4, 2-6, 2-8 were made on fused silica targets which are to be used for nuclear studies.

FIGURE 2.
EXPOSURE SERIES 2.

Table IVa

EXPOSURE SERIES 3a

Exposure Number	Exposure Time (minutes)	Oven Temp. ($^{\circ}\text{K}$) ^c	Ion Gauge Reading (mm Hg x 10^7)	Monitor Count (fissions/min) ^a	Vapor Pressure Plate Count (fissions/min) ^b	Vapor Pressure (mm Hg)
3- 1	6.83	1965	15.0	70322	18735	5.27×10^{-4}
3- 2	10.45	1921	9.0	68560	15134	2.76×10^{-4}
3- 3	32.29	1834	4.0	59377	10774	6.22×10^{-5}
3- 4	30.23	1723	1.0	68357	1998	1.20×10^{-5}
3- 5	56.43	1641	0.6	66778	975	3.06×10^{-6}
3- 6	30.10	1686	0.7	67237	1015	6.05×10^{-6}
3- 7	30.37	1772	1.4	67205	4291	2.59×10^{-5}
3- 8	19.05	1864	3.5	68080	12014	1.19×10^{-4}
3- 9	13.03	1903	5.0	66251	15344	2.23×10^{-4}
3-10	25.11	1792	1.5	67947	4094	3.01×10^{-5}
3-11	30.56	1705	0.8	69712	943	5.56×10^{-6}

Collimator area $0.22472 \pm 0.00084 \text{ cm}^2$

^a $\left[C_m - C_m (B\ell / C_m \ell) \right] / t, \text{ Eq. (7)}$

Oven orifice $(3.7291 \pm 0.0002) \times 10^{-4} \text{ cm}^2$

^b $\left[C_i - C_m (B\ell / C_m \ell) \right] / t, \text{ Eq. (7)}$

Orifice-to-collimator distance $7.8829 \pm 0.0051 \text{ cm}$ ^c Average deviation $\pm 1.0^{\circ}$

Oven charge 77.6 mg

Table IVb

EXPOSURE SERIES 3b

Exposure Number	Exposure Time (minutes)	Oven Temp. ($^{\circ}\text{K}$) ^c	Ion Gauge Reading (mm Hg x 10^7)	Monitor Count (fissions/min) ^a	Vapor Pressure Plate Count (fissions/min) ^b	Vapor Pressure (mm Hg)
3-12	6.05	1968	11.0	63876	17336	5.18×10^{-4}
3-13	11.09	1922	7.0	63976	14492	2.49×10^{-4}
3-14	30.11	1835	3.0	63835	8449	5.23×10^{-5}
3-15	31.08	1725	1.5	63814	1042	6.06×10^{-6}
3-16	59.95	1640	3.5	63975	341	1.00×10^{-6}
3-17	30.10	1685	3.5	63973	412	2.45×10^{-6}
3-18	30.99	1773	4.0	64016	2458	1.46×10^{-5}
3-19	25.06	1865	6.0	64386	10629	7.98×10^{-5}
3-20	16.11	1905	7.0	64020	13900	1.64×10^{-4}
3-21	30.01	1794	4.0	63994	3445	2.12×10^{-5}
3-22	31.30	1705	3.5	63941	601	3.46×10^{-6}

Collimator area $0.22472 \pm 0.00084 \text{ cm}^2$

^a $\left[C_m - C_m (B\ell / C_m \ell) \right] / t, \text{ Eq. (7)}$

Oven orifice $(3.7291 \pm 0.0002) \times 10^{-4} \text{ cm}^2$

^b $\left[C_i - C_m (B\ell / C_m \ell) \right] / t, \text{ Eq. (7)}$

Orifice-to-collimator distance $7.8829 \pm 0.0051 \text{ cm}$ ^c Average deviation $\pm 1.0^{\circ}$.

Oven charge 77.6 mg

Table IVc

EXPOSURE SERIES 3c

Exposure Number	Exposure Time (minutes)	Oven Temp. ($^{\circ}\text{K}$) ^c	Ion Gauge Reading (mm Hg x 10^7)	Monitor Count (fissions/min) ^a	Vapor Pressure Plate Count (fissions/min) ^b	Vapor Pressure (mm Hg)
3-23	7.33	1968	19.0	63377	17005	4.47×10^{-4}
3-24	12.70	1922	9.0	63733	13635	2.04×10^{-4}
3-25	30.59	1833	6.0	63979	6709	4.09×10^{-5}
3-26	30.13	1724	10.0	63946	752	4.52×10^{-6}
3-27	—	—	—	—	—	used as blank
3-28	30.02	1681	10.0	64211	283	1.69×10^{-6}
3-29	30.31	1774	10.0	63077	1880	1.14×10^{-5}
3-30	22.34	1867	12.0	63407	8191	6.89×10^{-5}
3-31	15.07	1907	14.0	62987	11103	1.40×10^{-4}
3-32	30.00	1793	10.0	63686	2717	1.67×10^{-5}
3-33	32.00	1708	10.0	63382	792	4.46×10^{-6}

Collimator area $0.22472 \pm 0.00084 \text{ cm}^2$ Oven orifice $(3.7291 \pm 0.0002) \times 10^{-4} \text{ cm}^2$ Orifice-to-collimator distance $7.8829 \pm 0.0051 \text{ cm}$

Oven charge 77.6 mg

^a $\left[C_m - C_m (B \ell / C_m \ell) \right] / t, \text{ Eq. (7)}$

^b $\left[C_i - C_m (B \ell / C_m \ell) \right] / t, \text{ Eq. (7)}$

^c Average deviation $\pm 1.0^{\circ}$

Table IVd

EXPOSURE SERIES 3d

Exposure Number	Exposure Time (minutes)	Oven Temp. ($^{\circ}\text{K}$) ^c	Ion Gauge Reading (mm Hg x 10^7)	Monitor Count (fissions/min) ^a	Vapor Pressure Plate Count (fissions/min) ^b	Vapor Pressure (mm Hg)
3-34	7.01	1965	40.0	63311	13302	3.65×10^{-4}
3-35	11.02	1923	40.0	63096	9707	1.68×10^{-4}
3-36	31.03	1836	40.0	63476	5636	3.39×10^{-5}
3-37	30.42	1724	40.0	63271	495	2.94×10^{-6}
3-38	—	—	—	—	—	used as blank
3-39	30.02	1683	40.0	63375	185	1.10×10^{-6}
3-40	31.07	1771	40.0	63823	1305	7.70×10^{-6}
3-41	22.53	1866	40.0	62740	6154	5.14×10^{-5}
3-42	17.76	1907	40.0	62586	9710	1.04×10^{-4}
3-43	30.04	1796	40.0	63082	1962	1.20×10^{-5}
3-44	34.04	1707	40.0	63086	336	1.78×10^{-6}

Collimator area $0.22472 \pm 0.00084 \text{ cm}^2$ Oven orifice $(3.7291 \pm 0.0002) \times 10^{-4} \text{ cm}^2$ Orifice-to-collimator distance $7.8829 \pm 0.0051 \text{ cm}$

Oven charge 77.6 mg

^a $\left[C_m - C_m (B \ell / C_m \ell) \right] / t, \text{ Eq. (7)}$

^b $\left[C_i - C_m (B \ell / C_m \ell) \right] / t, \text{ Eq. (7)}$

^c Average deviations $\pm 1.0^{\circ}$

Table IVe

EXPOSURE SERIES 3e

Exposure Number	Exposure Time (minutes)	Oven Temp. ($^{\circ}$ K) ^c	Ion Gauge Reading (mm Hg x 10^7)	Monitor Count (fissions/min) ^a	Vapor Pressure Plate Count (fissions/min) ^b	Vapor Pressure (mm Hg)
3-45	10.01	1968	19.0	63222	15590	3.00×10^{-4}
3-46	39.04	1832	4.0	63227	5087	2.42×10^{-5}
3-47	36.01	1722	1.1	63317	507	2.54×10^{-6}
3-48	48.01	1694	0.8	62958	303	1.13×10^{-6}
3-49	57.02	1773	1.8	63363	2067	6.65×10^{-6}
3-50	21.14	1862	4.0	63445	4462	3.96×10^{-5}

Collimator area $0.22472 \pm 0.00084 \text{ cm}^2$ Oven orifice $(3.7291 \pm 0.0002) \times 10^{-4} \text{ cm}^2$ Orifice-to-collimator distance $7.8829 \pm 0.0051 \text{ cm}$

Oven charge 77.6 mg

^a $[C_m - C_m(B\ell/C_m\ell)]/t$, Eq. (7)^b $[C_i - C_m(B\ell/C_m\ell)]/t$, Eq. (7)^c Average deviation $\pm 1.0^{\circ}$

FIGURE 3.
EXPOSURE SERIES 3.

Table V

EXPOSURE SERIES 4

Exposure Number	Exposure Time (minutes)	Oven Temp. ($^{\circ}\text{K}$) ^c	Ion Gauge Reading (mm Hg x 10^7)	Monitor Count (fissions/min) ^a	Vapor Pressure Plate Count (fissions/min) ^b	Vapor Pressure (mm Hg)
4- 1	0.52	1959	7.0	63635	71668	2.87×10^{-4}
4- 2	4.05	1802	1.5	63307	43363	2.14×10^{-5}
4- 3	11.02	1665	<1.0	63610	5735	1.00×10^{-6}
4- 4	17.08	1553	<1.0	63549	650	7.10×10^{-8}
4- 5	63.02	1476	<1.0	63530	257	7.42×10^{-9}
4- 6	35.01	1589	<1.0	63431	2305	1.24×10^{-7}
4- 7	4.07	1703	<1.0	63385	5064	2.42×10^{-6}
4- 8	2.01	1839	1.0	63736	31260	3.14×10^{-5}
4- 9	1.04	1902	2.5	63377	50675	1.00×10^{-4}
4-10	4.03	1752	<1.0	63816	11050	5.41×10^{-6}
4-11	25.03	1620	<1.0	63871	19499	1.48×10^{-6}
4-12	—	—	—	—	—	—
4-13	0.51	1958	10.0	63654	67174	2.72×10^{-4}
4-14	5.05	1801	5.0	63633	34844	1.38×10^{-5}
4-15	12.06	1661	3.0	63635	4293	6.86×10^{-7}
4-16	16.02	1549	2.5	63544	346	4.02×10^{-8}
4-17	50.02	1474	2.5	63605	933	3.39×10^{-8}
4-18	73.60	1583	2.0	63747	3470	8.87×10^{-8}
4-19	5.00	1696	1.0	63674	3548	1.38×10^{-6}
4-20	2.02	1840	2.0	63807	37017	3.70×10^{-5}
4-21	1.03	1900	4.0	63725	47107	9.42×10^{-5}
4-22	5.01	1746	1.5	63592	10956	4.30×10^{-6}
4-23	25.07	1619	1.0	63987	3068	2.33×10^{-7}
4-24	45.02	1503	<1.0	63759	323	1.32×10^{-8}

Collimator area $0.22472 \pm 0.00084 \text{ cm}^2$ Oven orifice $(3.571 \pm 0.011) \times 10^{-2} \text{ cm}^2$ Orifice-to-collimator distance $8.021 \pm 0.003 \text{ cm}$

Oven charge 45.4 mg

^a $\left[C_m - C_m (B\ell / C_m \ell) \right] / t$, Eq. (7)

^b $\left[C_i - C_m (B\ell / C_m \ell) \right] / t$, Eq. (7)

^c Average deviation $\pm 1.0^{\circ}$.

Table VI
EXPOSURE SERIES 5

Exposure Number	Exposure Time (minutes)	Oven Temp. ($^{\circ}\text{K}$) ^c	Ion Gauge Reading (mm Hg x 10^7)	Monitor Count (fissions/min) ^a	Vapor Pressure Plate Count (fissions/min) ^b	Vapor Pressure (mm Hg)
5- 1	0.50	1959	6.0	64465	14492	1.25×10^{-4}
5- 2	4.21	1799	1.8	64507	11370	1.13×10^{-5}
5- 3	10.03	1652	0.7	64589	1048	4.19×10^{-7}
5- 4	45.23	1550	0.6	64623	387	3.32×10^{-8}
5- 5	35.21	1588	0.6	64767	914	1.02×10^{-7}
5- 6	5.53	1727	0.8	64496	4503	3.33×10^{-6}
5- 7	2.02	1842	2.0	64335	17241	3.60×10^{-5}
5- 8	1.03	1900	4.0	64432	24933	1.04×10^{-4}
5- 9	4.04	1744	1.0	64551	4916	5.00×10^{-6}
5-10	21.03	1625	0.7	63913	2116	4.00×10^{-7}
5-11	72.03	1499	0.5	63745	244	1.30×10^{-8}
5-12	0.55	1958	5.5	63931	31290	2.47×10^{-4}
5-13	4.04	1799	1.1	62394	13381	1.38×10^{-5}
5-14	10.03	1668	0.6	62517	2005	8.05×10^{-7}
5-15	40.03	1553	0.5	62545	421	4.10×10^{-8}
5-16	35.03	1591	0.6	62861	1099	1.23×10^{-7}
5-17	4.02	1731	0.6	66785	3354	3.42×10^{-6}
5-18	2.01	1837	1.5	66761	14284	2.99×10^{-5}
5-19	1.02	1903	3.0	66681	23360	9.80×10^{-5}
5-20	4.01	1747	0.8	67030	4678	4.80×10^{-6}
5-21	22.65	1626	0.5	65720	1727	3.04×10^{-7}
5-22	63.05	1526	0.4	65230	535	3.28×10^{-8}

Collimator area $0.22472 \pm 0.00084 \text{ cm}^2$

Oven orifice $(1.7690 \pm 0.009) \times 10^{-2} \text{ cm}^2$

Orifice-to-collimator distance $8.3429 \pm 0.0028 \text{ cm}$

Oven charge 780 mg

$$^a [C_m - C_m(B\ell/C_m\ell)]/t, \text{ Eq. (7)}$$

$$^b [C_i - C_m(B\ell/C_m\ell)]/t, \text{ Eq. (7)}$$

$$^c \text{Average deviation } \pm 1.0^{\circ}$$

FIGURE 4.
EXPOSURE SERIES 4.

Table VII
SUMMARY OF RESULTS

Exposure Series	A ^a	B ^a	Heat of Vaporization ^b (kcal/mole)	Heat of Sublimation by Third Law ^b (ΔH_0^0) (kcal/mole)	Heat of Fusion (kcal/mole)
1 (all exposures)	25645 $\pm$ 335	9.433 $\pm$ 0.187	118.7	121.8	- 2.1
1 (4, 5, 6 rejected)	26752 $\pm$ 159	10.020 $\pm$ 0.088	123.8	123.0	- 6.0
1 (first 9)	23553 $\pm$ 334	8.379 $\pm$ 0.186	109.2	119.0	4.6
2	26725 $\pm$ 220	9.835 $\pm$ 0.119	123.7	124.1	- 4.8
3a	23031 $\pm$ 492	8.378 $\pm$ 0.275	106.8	116.6	4.6
3b	26846 $\pm$ 238	10.293 $\pm$ 0.133	124.2	121.7	- 7.7
3c	27069 $\pm$ 459	10.335 $\pm$ 0.253	125.2	122.5	- 7.9
3d	29376 $\pm$ 303	11.444 $\pm$ 0.167	135.8	125.9	-15.1
3e	29082 $\pm$ 106	11.211 $\pm$ 0.056	134.5	126.0	-13.7
4	26431 $\pm$ 594	9.876 $\pm$ 0.353	122.3	122.5	- 5.0
5	27459 $\pm$ 299	10.344 $\pm$ 0.174	127.0	124.2	- 8.0

^a $\log p(\text{mm}) = (-A/T) + B$.

^b Corrected for the solubility of tantalum in liquid uranium: $\log N_u = (313/T) - 0.215$.

E. Exposure Series 5.

Certain details of the data obtained in Exposures Series 3 might cause one to infer that oxygen suppressed the rate of effusion of the uranium from the cell by forming a soluble oxide. For this reason the vapor pressure was measured by the use of an oven containing a larger amount of metal than used in the previously described experiments. In addition an attempt was made to produce a lower residual pressure in the vacuum vessel. To accomplish this the oven was outgassed and subsequently loaded in situ. This necessitated an orifice larger than those used in Exposure Series 1, 2, and 3, so that the uranium wire could be inserted into the oven via the orifice. (See Figure 5 and Tables VI and VII.)

FIGURE 5.
EXPOSURE SERIES 5.

IV. DISCUSSION OF DATA

A. Internal Consistency

As stated previously, the calculation of the heat of vaporization and/or sublimation by two different procedures and a knowledge of the heat of fusion enables one to examine the measurements for internal consistency. Although the heat of fusion of uranium has not been measured, one can make an estimate of a value which is sufficiently accurate for the present purpose. Unless uranium is vastly different from the other elements it should have an entropy of fusion of about 2 or 3 eu and hence a heat of fusion of about 4 kcal/mole. Examination of the values for this quantity listed in Table VII shows that in only two cases does the calculated heat of fusion agree with this estimation. A still further inspection of the data reveals that in these two instances (Exposure Series 1, Exposures 1-9 and Exposure Series 3a) the experimental conditions were most nearly ideal for the following reasons:

- (1) Exposures 1-9 in Exposure Series 1 represent the initial part of this experiment in which the vacuum conditions were reasonably good.
- (2) In Exposure Series 3a the residual pressure in the vacuum vessel was low.
- (3) In both Exposure Series 1 and 3 an oven with a small orifice was employed whereas those in Exposure Series 4 and 5 had large orifices.

Even in the absence of a more complete analysis of the data, it would seem reasonable to reject all the measurements except these two. However, as shown below, it is possible to derive relations which describe most of the data quantitatively in such a manner that Exposure Series 3b, 3c, 3d, and 3e extrapolate to Exposure Series 3a and a reasonable value for the heat of fusion.

B. Role of Oxygen

As shown by Exposure Series 2 and 3b, 3c, and 3d the presence of both oxidized metal in the oven and oxygen in the vacuum vessel suppresses the rate of effusion of uranium from the oven. Hence it appears to be obvious that the role of oxygen present in the vacuum system is to produce an oxide of uranium. One can, however, suggest several mechanisms by which an oxide could produce the observed effect.

- (1) An oxide may form which is soluble in liquid uranium.
- (2) The uranium may become completely oxidized so that the dissociation pressure (i.e. the partial pressure of uranium over an oxide) is measured.

(3) The oxide may form a high electronic work function surface so that an appreciable number of uranium ions leaves the orifice. These may or may not be collected.

(4) An impervious oxide film may form on the liquid uranium surface and suppress the rate of evaporation of the metal.

The first mechanism seems unlikely for the following reason. For an unsaturated solution (i.e., unsaturated with oxide) the effusion rate for a given amount of oxide should depend upon the amount of metal in the effusion cell. A comparison, however, of Exposure Series 1, 2, and 4 with 5 shows that the suppression of the effusion rate is independent of the amount of metal. For a saturated solution the oxide solubility would probably increase with increasing temperature and hence would cause a decrease in the numerical value of the slope of $\log p$ vs $1/T$ with increasing oxygen or oxide, whereas the observed effect is a decrease in the slope.⁽¹⁰⁾ The second suggested mechanism is not indicated by the data since a logarithmic plot of the experimental vapor pressure vs the oxygen pressure is not linear. At present the authors are not prepared to examine the third mechanism listed above. However, it appears doubtful that there were any appreciable number of positive uranium ions collected in Exposure Series 3a, at least for reasons which will be discussed later. Although one might infer that the presence of the oxide film would not decrease the vapor pressure measured by the Knudsen method, a detailed examination of the quantitative influence of an impervious oxide layer reveals that the rate of effusion will be suppressed and that the mechanism listed last is quite plausible.

The role of the oxygen can be formulated as follows. One considers a Knudsen cell containing oxygen gas, liquid uranium, gaseous uranium, solid uranium oxide, and gaseous uranium oxide. The partial pressures are sufficiently low so that the frequency of gaseous collisions is extremely small compared with the frequency of collision at the wall. If the oxide is insoluble in the liquid, it will form a layer over a part of the metal (assumed to cover the entire inside of the cell) so that the rate of evaporation of the metal through the oxide will be negligible. (It is assumed that a monolayer is sufficient to suppress the evaporation of the metal.) One can then assume that in a relatively short time a steady-state condition is attained in which, at a given temperature and pressure of oxygen in the vacuum vessel, the number of moles of each gaseous species (i.e., O_2 , U and UO_x) and the fraction of the surface covered are constant with time. A detailed balancing of each of these molecular forms requires that

(1) the rate of change of the oxygen in the cell equals the rate of effusion into the cell from the vacuum minus the rate of effusion out of the cell minus the net rate of reaction with the liquid metal and the impervious oxide phase,

(2) the rate of change of uranium in the gas phase equals the rate of evaporation minus the rate of condensation minus the rate of effusion out of the orifice,

(3) the rate of change of the oxide in the gas phase equals the rate of evaporation minus the rate of condensation minus the rate of effusion out of the orifice, and

(4) the rate of change of a layer of the oxide in the solid phase equals the rate of formation plus the rate of condensation minus the rate of evaporation.

These statements can be written as algebraic equations if one defines:

A = the initial area of liquid metal before oxidation,

s = area of the orifice in the cell,

f = fraction of A covered with oxide,

p_u = vapor pressure of uranium metal,

p_x = vapor pressure of some oxide UO_x ,

p_o = pressure of oxygen in the vacuum vessel,

π_u = steady-state partial pressure of uranium in the cell,

π_x = steady-state partial pressure of oxide in the cell,

π_o = steady-state partial pressure of oxygen in the cell,

T_o = temperature of oxygen in the vacuum vessel, and

n = number of moles of oxide formed per mole of oxygen reacting
(i.e. $nU + O_2 = nUO_x$ or $n = 2/x$) .

In the same order as listed above the expressions are

$$\frac{dN_o}{dt} = \frac{p_o s}{(2\pi M_o R T_o)^{1/2}} - \frac{\pi_o s}{(2\pi M_o R T)^{1/2}} - \frac{\pi_o A}{(2\pi M_o R T)^{1/2}} , \quad (12)$$

$$\frac{dN_u}{dt} = \frac{p_u A(1-f)}{(2\pi M_u R T)^{1/2}} - \frac{\pi_u A}{(2\pi M_u R T)^{1/2}} - \frac{\pi_u s}{(2\pi M_u R T)^{1/2}} , \quad (13)$$

$$\frac{dN_x}{dt} = \frac{p_x A f}{(2\pi M_x R T)^{1/2}} - \frac{\pi_x A}{(2\pi M_x R T)^{1/2}} - \frac{\pi_x s}{(2\pi M_x R T)^{1/2}} , \text{ and } \quad (14)$$

$$\frac{d(UO_x)}{dt} = \frac{n\pi_o A(1-f)}{(2\pi M_o R T)^{1/2}} + \frac{\pi_x A}{(2\pi M_x R T)^{1/2}} - \frac{p_x A f}{(2\pi M_x R T)^{1/2}} . \quad (15)$$

In writing these expressions we have assumed that all reaction, condensation, and vaporization coefficients are unity. Upon comparing Eqs. (12) and (15) one might infer that a term to account for the reaction of the oxygen with the oxide has been omitted from the latter. However, since it has been assumed that a monolayer is sufficient to suppress the evaporation of the

metal, this reaction is not effective and hence should not be included. In other words the assumption is made that the oxygen reacts with the oxide without increasing the fraction of the surface covered with oxide. In view of the fact that the rate of oxidation of a metal such as uranium does not decrease appreciably until a thick coating relative to a few atomic layers has formed, it also does not appear too unreasonable to assume that the fraction of the oxygen reacting with the oxide is unity.

According to the assumption regarding the steady-state condition the left side of each of these equations is zero. Hence one can eliminate $\underline{f}$ and π_o from the expressions to obtain the relations for π_u and π_x . These are

$$\pi_u = p_u [A/(A + s) - (\pi_x/p_x)] \quad , \quad (16)$$

and

$$\pi_x = \frac{n p_o p_x (T_{M_x}/T_o M_o)^{1/2} [A/(A + s)]}{n p_o (T_{M_x}/T_o M_o)^{1/2} + p_x} \quad . \quad (17)$$

Since the experimental vapor pressures p_e were calculated on the basis of the assumption that all the uranium is in the form of atomic uranium, one writes that

$$p_e = \pi_u + (M_u/M_x)^{1/2} \pi_x \quad . \quad (18)$$

If the values of π_u and π_x as given by Eqs. (16) and (17) are substituted into Eq. (18) one finds that

$$p_e = [A/(A + s)] \left\{ p_u - [(p_u/p_x) - (M_u/M_x)^{1/2}] p_x [p_o/(p_o + P)] \right\} , \quad (19)$$

in which

$$P = (p_x/n) (T_o M_o/T_{M_x})^{1/2} \quad . \quad (20)$$

Qualitatively Eq. (19) predicts the observed data. First, if $p_u > p_x$ then the experimental vapor pressure will decrease with increasing oxygen pressure. Second, if the orifice area $\underline{s}$ is sufficiently large so that $A \gg s$, then the experimental vapor pressure will be lower than the one measured with a smaller $\underline{s}$. To find rigorously whether the data agree quantitatively with Eq. (19), a knowledge of the parameter $\underline{P}$ is required. Unfortunately, a number of the quantities contained in Eq. (20) are not known with any great accuracy. For example, the exact values of p_x , $\underline{n}$, $\underline{A}$, M_x and T_o are not known with reasonable certainty. However $\underline{P}$ can be treated as an experimental parameter which is determined from Eq. (19) for each temperature by minimizing the sum of the squares of the residuals.

To effect this analysis one must know the partial pressure of the oxygen in the vacuum vessel. Since the residual gases in a vacuum system are mostly carbon dioxide and water and/or perhaps carbon monoxide and hydrogen in the presence of hot tantalum, one cannot accept the ion gauge reading as representing the oxygen pressure. Therefore with a residual pressure of the order of 5×10^{-8} mm Hg a tenable assumption is that the partial pressure of oxygen is of the order of 10^{-8} and that this value may be considered as being zero for all practical purposes when compared with pressure of the order of 3×10^{-7} mm Hg or greater. On this basis, then, the partial pressures of oxygen in Exposure Series 3b, 3c, and 3d are obtained by subtracting the ion gauge readings in Exposure Series 3a from the corresponding readings (i.e., corresponding temperatures) in these three cases. In other words the data are analyzed on the basis of the oxygen admitted into the system.

As shown in Figure 6 the experimental vapor pressure, p_e , does appear to depend upon $p_o/(p_o + P)$ in a linear manner. Furthermore, the value of P is of the order expected since a value in the range of 10^{-6} mm Hg is indicated according to Eq. (20). In addition one can show that the values for the experimental vapor pressure obtained in Exposure Series 3e agree with the proposed mechanism. Since the vapor pressure of the oxide is less than that of the metal for all temperatures employed in this investigation and since the rate of formation of the oxide is comparable with the rate of effusion, the oxide cannot be vaporized out of the oven without also distilling out the metal. Therefore one cannot expect that the effect of the oxygen can be removed in a short time by evacuating the oxygen from the system. In view of this and the fact that the oven was exposed to the water vapor which had accumulated on the liquid nitrogen trap at the top of the apparatus (see Section III, C), further oxidation of the metal could have occurred between Exposure Series 3d and 3e. Hence the authors believe that the vapor pressures measured in Exposure Series 3e should correspond to the values for large oxygen pressure or a value of $p_o/(p_o + P)$ very close to unity. Inspecting Fig. 6, one observes that the deviations of the values for Exposure Series 3e from the extrapolated values at $p_o/(p_o + P) = 1$ for Exposure Series 3a, 3b, 3c and 3d are not unreasonable. Moreover, a statistical comparison of these values is even more satisfactory.

To effect this comparison one must answer the following question. How does the deviation of the Exposure Series 3e value from the extrapolated value compare with the error at $p_o/(p_o + P) = 1$ (i.e., a_1) calculated from the deviation from the straight line of some other experimentally determined vapor pressure? In answering this question one can then state whether the experimental value for Exposure Series 3e is more or less consistent with the data than the value of p_e with the largest residual is with the data. It is important to notice that this question can be answered independently of the probability of occurrence of the error in p_e . If r_x is the probable error (or some other error such as the 95-5 error) at some particular value of $p_o/(p_o + P) (\neq 1)$, then in a single measurement the probability of obtaining an error within the limits of $\pm a_x$ is

$$P_x = \frac{2}{\pi^{1/2}} \int_0^{\rho a_x / r_x} \exp(-t^2) dt \quad (21)$$

FIGURE 6.

TEST OF EQUATION (19).

IS

Likewise, if r_1 and a_1 are the corresponding quantities at $p_o/(p_o + P) = 1$, then

$$P_1 = \frac{2}{\pi^{1/2}} \int_0^{\rho a_1/r_1} \exp(-t^2) dt \quad (22)$$

Since one wishes to compare a_x and a_1 under the same probability of occurrence, $P_x = P_1$ and

$$a_x/r_x = a_1/r_1 \quad (23)$$

From the least squares principle and the relation for the propagation of errors one finds that

$$a_1 = a_x \left[\frac{\sum_i (F_i - 1)^2}{\sum_i (F_i - F_x)^2} \right]^{1/2}, \quad (24)$$

in which F_i represents the value of $p_o/(p_o + P)$ at some experimentally determined value of p_e and F_x represents the same quantity at the value of p_e giving the largest deviation from the straight line. A list of the values of a_x and a_1 is given in Table VIII. In every case except one the calculated error is greater than the deviation at $p_o/(p_o + P) = 1$. Therefore Exposure Series 3e agrees with Exposure Series 3a, 3b, 3c, and 3d on the basis of the proposed mechanism.

Table VIII
COMPARISON BETWEEN EXPOSURE SERIES
3e and 3a, 3b, 3c, and 3d

Temperature (°K)	Largest Deviation of p_e from Theoretical Line (a_x)	Corresponding Deviation at $F(p_o) = 1$ (a_1)	Deviation of Subseries 3e from Extrapolation
1684	0.26×10^{-6}	0.31×10^{-6}	0.16×10^{-6}
1709	0.45	0.53	0.31
1724	0.59	> 0.59	0.39
1773	0.13×10^{-5}	> 0.13×10^{-5}	0.11×10^{-5}
1794	0.18	> 0.18	0.17
1834	0.31	0.41	0.38
1866	0.39	> 0.39	0.38
1905	0.04×10^{-4}	0.07×10^{-4}	0.05×10^{-4}
1922	0.04	0.07	0.10
1966	0.04	> 0.04	0.02

In view of the agreement discussed above, the authors believe that the theory is a reasonably correct one, and therefore the partial pressure of uranium above a solution of uranium and tantalum is given by the extrapolated value of p_e at $p_o/(p_o + P) = 0$. The least squares equation for these values is

$$\log p_e(\text{mm}) = -\frac{(23017 \pm 21)}{T} + (8.3683 \pm 0.011) \quad (25)$$

Some of the difficulties involved in the determination of the vapor pressure of an easily oxidized metal which has a low volatility at temperatures of measurement can be more readily ascertained now by the mechanism described. For example, as shown in Fig. 7, the experimentally measured vapor pressure is extremely sensitive to the oxygen pressure if the vapor pressure is as small as ten times the oxygen pressure. Even if the vapor pressure is 10^3 times the oxygen pressure, the measurements are affected by the residual oxygen in the vacuum system. It is important to observe that the sensitivity decreases with increasing oxygen pressure, so that at a pressure in the range of 10^{-6} to 10^{-5} mm Hg the effect is not great. These statements are true if the vapor pressure of the oxide is less than that of the metal, as is usually the case for the lower oxides such as UO or UO_2 . At higher oxygen pressures the higher oxides, such as UO_3 , may form, and since in the case of uranium, tantalum, and tungsten, at least, these have a vapor pressure which is higher than the metal, $p_u/p_x > (M_u/M_x)^{1/2}$, and as shown by Eq. (19) the experimental vapor pressure will increase with increasing oxygen. This explains the fact that the vapor pressures reported by Derge and Cefola⁽²⁾ were in general larger than the ones reported here. To completely circumvent these difficulties in the case of uranium it would be desirable to make measurements at a temperature of about 2200°K in a vacuum of 10^{-8} mm Hg.

C. Correction for Tantalum.

As stated previously, Schramm, Gordon and Kaufmann⁽⁸⁾ have determined the solubility of tantalum in liquid uranium. Since one would not expect the logarithm of the mole fraction of the uranium in the solution to be a linear function of reciprocal temperature, the presence of the tantalum should have introduced a curvature in the $\log p_e$ vs. $1/T$ curves. However, as shown below, the total effect is so small compared with the scatter of the data that one can not expect to detect this curvature. This fact enables one to make a first order correction without correcting the individual vapor pressure measurements. A plot of experimental values for $\log N_u$ vs. $1/T$ (Fig. 8) is actually linear in the region of interest. The authors believe, however, that this is a "fortuitous" accident caused by an experimental error in the second point. Nevertheless we accept the experimental curve so that the solubility of tantalum in uranium is represented by the equation

$$\log N_u = 313/T - 0.2145 \quad .$$

FIGURE 7.

EFFECT OF OXYGEN ON EXPERIMENTAL
VAPOR PRESSURE.

FIGURE 8.
SOLUBILITY OF TANTALUM IN URANIUM.

Since the vapor pressure of the uranium can be estimated by Raoult's law,

$$p_e = N_u p_u \quad ,$$

one finds that

$$\log p_u = \log p_e - 313/T + 0.2145 \quad . \quad (26)$$

Comparing this equation with the values of the slope and intercept in Table VII, one observes that the corrections for the tantalum solubility are of the same order as the errors. Therefore a more accurate correction is not necessary.

D. Positive Ion Emission

There now remains one more possible source of error, namely, the occurrence of positive uranium ions. The more complete system which should be considered in these experiments is as follows:

$$U_s = U_g \quad .$$

$$e_s = e_g \quad .$$

$$U_g = U_g^+ + e_g \quad .$$

If one collects on the platinum plates only the neutral uranium atoms, U_g , then one needs no knowledge concerning the positive ions and one calculates the true vapor pressure and heat of vaporization. On the other hand, if one collects both neutral atoms and positive ions, then the ratio of their partial pressures is given by the expression

$$p_+/p = (Q_+/Q) \exp [(\phi - I)/RT] \quad ,$$

in which the Q 's are the partition functions, I is the ionization potential of uranium, and ϕ is the work function of the surface from which the ions are evaporating. At 1406°K $Q = 19.63$ and $Q_+ = 26.90$. The ionization potential of uranium has been estimated by Hubbard and Meggers⁽¹¹⁾ to be 4 ev. The question now arises as to the more nearly correct value of ϕ to be employed. Since there are essentially no collisions in the gas phase at pressures of the order of 10^{-5} mm Hg, each uranium atom or ion must suffer its last contact with the condensed uranium and/or uranium oxide surface before leaving the oven. If there is no oxide present (Exposure Series 3a), then the value of ϕ may be as low as 3.27 ev.⁽¹²⁾ This corresponds to a value of $p_+/p = 3.4 \times 10^{-3}$ and indicates that in this case there is no appreciable error because of positive ions. In the presence of oxide, however, ϕ may be as large as 5.94 ev,⁽¹³⁾ in which event $p_+/p = 6.3 \times 10^6$ and there may or may not be an error because of positive ions. From these estimates one concludes that the value for the vapor pressure and heat of vaporization obtained in Exposure Series 3a are probably not in error because of positive ions, but that the interpretation of Exposure Series 3b, 3c, 3d, and 3e may be only partially complete.

V. DISCUSSION OF ERRORS

In the derivation of Eq. (1) the square of collimator radius was assumed to be small compared with the square of the orifice-to-collimator distance (see Section II, A, 1). Under this assumption the factor $(1 + r^2/d^2)$ was taken as unity and Eq. (1) took the form shown. If Eqs. (1) and (7) are combined and rearranged, p may be expressed

$$p = \left[(R/M)^{1/2} \right] \left[(d^2/r^2 \rho^2) \overline{W}_M \right] \left[\left(T^{1/2}/t \right) \frac{C_i - C_m(B\ell/C_m\ell)}{C_m - C_m(B\ell/C_m\ell)} \right] 2/\pi^{1/2} \quad (1')$$

In the first bracket are those quantities which introduce inherent errors or uncertainties arising from incomplete knowledge of some quantity not measured directly. In the second bracket are those quantities which introduce systematic errors or uncertainties which affect a computed value of p in a non-random manner. In the third bracket are those quantities which introduce statistical errors or uncertainties which affect a computed value of p in a random manner.

A. Inherent Errors

The inherent error in R is certainly negligible. The quantity M refers to the species effusing from the orifice, and the actual value to be assigned to M is determined by the isotopic content of the oven charge and by the degree of association in the gas phase. The average molecular weight of the oven charge was known to better than 0.05 mass units. Since it is improbable that any degree of association would be sufficiently constant over a 500° range of temperature to permit the high degree of linearity observed in the $\log p, 1/T$ plots, the vapor may be safely considered monatomic.

B. Systematic Errors

The assumption that $(1 + r^2/d^2) = 1$ introduces a systematic error of -0.1% into the geometry. The errors in the measurements of ρ , r , and d may be obtained from the values given in Tables II through VI. The errors given are the average errors in a single reading. The probable error in the average of a group of observations is related to the average error in a single observation by the factor $0.845/n^{1/2}$. The probable errors in ρ , r and d are estimated to be $\pm 0.04\%$, $\pm 0.07\%$, $\pm 0.01\%$, respectively.

The geometry factor was corrected at each temperature for the changes in d and ρ due to the expansion of the tantalum and tungsten in the effusion vessel. The errors in d and ρ due to uncertainties in the coefficients of expansion of tantalum and tungsten can easily be shown to be negligible. The change of r upon cooling to liquid nitrogen temperatures has been shown to be -0.066%.⁽⁹⁾

A probable error of $\pm 0.3\%$ has been calculated for $\overline{W}_M$ (see Table I).

C. Statistical Errors

There are five experimental observations involved in every assignment of a value to $\underline{T}$: (1) the calibration by the Bureau of Standards of the standard band lamps, (2) the standardization of the pyrometer against these lamps, (3) the determination of the transmissivity of the window and prism used in the observation of the oven, (4) the degree of blackness of the black body hole in the oven, and (5) the measurement of the oven temperature. The probable error assigned to the combination of (1) and (2) is $\pm 1.6^\circ$. The transmissivity of the window and prism was found to be

$$1/T_a - 1/T = (0.123 \pm 0.002) \times 10^{-4}$$

(measured before and between series of exposures) which introduces a maximum error in $\underline{T}$ of 0.8° . The degree of blackness of the black body hole was calculated to be 99.996%.⁽¹⁴⁾ The maximum probable error in the average of any of the exposure temperatures was found to be $\pm 0.6^\circ$. From these the maximum probable error in any value of $\underline{T}$ reported is estimated to be $\pm 0.15\%$.

In estimating the error in $\underline{t}$ a probable error of 0.01 minutes in starting and 0.01 minutes in terminating an exposure is assumed. The probable error of 0.014 minutes represents probable errors in $\underline{t}$ of 3% to 0.016% for the shortest and longest exposure times, respectively.

In determining the counting uncertainties which vary from count to count, exposures 1-15 and 1-20 have been selected as examples. For each of these exposures the probable error has been calculated from the total number of counts and the background (these do not appear in the tables) according to Jarrett.⁽¹⁵⁾ The calculated probable errors for exposures 1-15 and 1-20 are, respectively, $\pm 0.8\%$ and $\pm 4.6\%$.

For convenience the errors are tabulated in Table IX.

The probable error in the measurements of $\underline{p}$ can now be calculated from the relationship

$$P_p = [(\partial p / \partial M)^2 P_M^2 + (\partial p / \partial \rho)^2 P_\rho^2 + \dots]^{1/2} \quad (27)$$

where $\underline{P}$ is the probable error in the quantity indicated by the subscript. The calculated errors for exposures 1-15 and 1-20 are, respectively, 1.9% and 4.8%. It should be remembered that these errors are for the experimental values of $\underline{p}$ and include all inherent, systematic, and statistical errors, but do not include possible basic errors or uncertainties arising from failure of the experiment to fulfill an ideal condition necessary for the validity of the equation.

Table IX
SUMMARY OF ERRORS

Error	Quantity	Probable error for 1-15	Probable error for 1-20
Inherent	R	negl.	negl.
	M	$\pm 0.02\%$	$\pm 0.02\%$
Systematic	$(1 + r^2/d^2)$	-0.10%	-0.10%
	ρ	$\pm 0.04\%$	$\pm 0.04\%$
	r	$\pm 0.10\%$	$\pm 0.10\%$
	d	$\pm 0.01\%$	$\pm 0.01\%$
	$\overline{W}_M$	$\pm 0.3\%$	$\pm 0.3\%$
Statistical	T	$\pm 0.15\%$	$\pm 0.15\%$
	t	$\pm 0.22\%$	$\pm 0.003\%$
	counting	$\pm 0.8\%$	$\pm 4.6\%$

The data for Exposure Series 1 was analyzed by the least squares method (Section III, A), and, for statistical reasons, exposures 1-4, 1-5, and 1-6 were rejected. A least squares treatment of the remaining exposures gave the equation

$$\log p \text{ (mm)} = -\frac{(26752 \pm 159)}{T} + (10.0529 \pm 0.0878) \quad (28)$$

and a probable error in $\underline{p}$ for exposures 1-15 and 1-20 of 2.1% and 2.2% respectively. It must be remembered, however, that these errors do not include either the inherent or systematic errors since these merely result in a mass displacement of all experimental points in the $\log p, 1/T$ frame without affecting their relative placement which alone determines the least squares probable error. From the expression for the propagation of errors [Eq. (27)] the contribution of the statistical errors alone may be calculated; these are 1.10% and 1.45% for exposures 1-15 and 1-20 respectively. About half of the least squares error is thus accounted for by the statistical uncertainties in the experimentally measured quantities. An additional error in $\underline{T}$ can be considered; an error in $\underline{p}$ appears because the least squares line is based upon residuals in $\log p$ and carries the assumption that there are no errors in $1/T$. Although much of the uncertainty in $\underline{T}$ is reflected in the scatter of the data, the uncertainty in $1/T$ must in some way contribute to the least squares error. (A not too meaningful calculation using Eq. (28) and an error in $\underline{T}$ of $\pm 3^\circ$ shows a reflected error in $\underline{p}$ of 3-6%.) It is concluded that the data are internally consistent, but that there are basic errors which can appear on occasion (for example, during exposures 1-4, 1-5, and 1-6).

VI. SUMMARY

In view of the fact that all the data in Table VII can be interpreted quantitatively in terms of an impervious oxide film and because the extrapolated values are internally consistent, the authors conclude that the vapor pressure of uranium metal is represented by the equation

$$\log P_u(\text{mm}) = - \frac{(23330 \pm 21)}{T} + (8.583 \pm 0.011) \quad . \quad (29)$$

From this we conclude a value of 106.7 ± 0.1 kcal/mole for the heat of vaporization, a value of 116.6 ± 0.1 kcal/mole for the heat of sublimation at 0°K, and 4.7 ± 0.2 kcal/mole for the heat of fusion. The error given for the last quantity is a statistical error only. Since there is considerable uncertainty in the partial pressures of oxygen, the error in the heat of fusion is undoubtedly larger than 0.2 kcal/mole.

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