TABLE III

HEAT OF EVAPORATION OF TANTALUM USING FISKE'S DATA FOR RATE OF EVAPORATION

Temp., °K.	$m(T)$, g. cm.$^{-1}$ sec.$^{-1}$ × 10^8	$-R \ln p$, cal. mole^{-1} deg.$^{-1}$	$-\Delta\left(\frac{F^0 - H_0^0}{T}\right)$, cal. mole^{-1} deg.$^{-1}$	ΔH_0^0, kcal. mole^{-1}
2633	28.8	34.80	33.26	179.2
2649	28.0	34.85	33.26	180.4
2700	43.8	33.94	33.26	181.4
2737	65.9	33.12	33.25	181.7
2804	160	31.33	33.25	181.1
2807	120	31.90	33.25	182.9
2850	230	30.59	33.24	181.9
			Av.	181.2
			Mean deviation	0.9

TABLE IV

HEAT OF EVAPORATION OF TANTALUM USING D. B. LANGMUIR AND L. MALTER'S DATA FOR RATE OF EVAPORATION

Temp., °K.	$m(T)$, g. cm.$^{-1}$ sec.$^{-1}$ × 10^8	$-R \ln p$, cal. mole^{-1} deg.$^{-1}$	$-\Delta\left(\frac{F^0 - H_0^0}{T}\right)$, cal. mole^{-1} deg.$^{-1}$	ΔH_0^0, kcal. mole^{-1}
2000	0.000163	59.08	33.28	184.7
2200	.00978	50.85	33.28	185.1
2400	.304	43.94	33.27	185.3
2600	5.54	38.09	33.27	185.5
2800	66.1	33.09	33.25	185.7
3000	579	28.71	33.22	185.8
3200	3820	24.90	33.19	185.9
			Av.	185.4
			Mean deviation	0.3

the rates of evaporation published by Langmuir and Malter[2] and by Fiske,[3] and these results are summarized in Tables III and IV. As is seen, the data of Langmuir and Malter are in exact accord with our own while Fiske's vapor pressures are somewhat high.

By use of equation 6, in conjunction with equations 7 and 8 and the average value of 185.5 kcal. for ΔH_0^0, we obtain the vapor pressure equation

$$R \ln p = -(185.5 \times 10^3)/T + 3.7 \times 10^{-4}T - 8.4 \times 10^{-8}T^2 + 32.87 \quad (9)$$

where p is pressure in atmospheres and R is the gas constant in cal./mole/deg.

Summary

The vapor pressure of tantalum was determined over the temperature 2624 to 2948°K. by measuring the rate at which a metal surface evaporates in vacuum. Values of ΔH_0^0 were calculated from the individual vapor pressures and showed no appreciable trend, the average value being 185.5 ± 0.3 kcal. By combining this value with free energy functions for solid and gaseous tantalum, the following vapor pressure equation was obtained

$$R \ln p = -(185.5 \times 10^3)/T + 3.7 \times 10^{-4}T - 8.4 \times 10^{-8}T^2 + 32.87$$

Our experimental results agree accurately with the earlier work of Langmuir and Malter, but disagree with those of Fiske.

COLUMBUS 10, OHIO RECEIVED JULY 5, 1950

[CONTRIBUTION FROM THE CRYOGENIC LABORATORY AND THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

The Vapor Pressure of Inorganic Substances. V. Zirconium between 1949 and 2054°K.[1]

BY GORDON B. SKINNER, JAMES W. EDWARDS AND HERRICK L. JOHNSTON

Introduction

The vapor pressure of zirconium has been measured at this Laboratory by the vacuum evaporation method of Langmuir[2] as modified by Marshall, Dornte and Norton.[3] The method consists of measuring the rate at which a metal evaporates into a vacuum from a ring supported on a wire tripod and heated inductively by high frequency current.

Zirconium is difficult to volatilize apparently due to tightly adhering film that covers its surface even under relatively high vacuum conditions. We have overcome this obstacle by working at pressures of less than 2 × 10^{-7} mm.

Sample Purity.—A sample of zirconium was vacuum cast from crystalline zirconium which was prepared by the iodide method and furnished through the courtesy of the Philips Research Laboratory of Eindehoven, Holland. A spectrographic analysis[4] showed that the final sample contained 0.99 atom per cent. of hafnium, 0.05 atom per cent. wolfram, and 0.37 atom per cent. of all other impurities including silicon and aluminum. Wolfram is known to have a lower vapor pressure than that measured for zirconium. Vapor pressures are not known for hafnium, but general chemical considerations indicate that its vapor pressures should be at most one-tenth those of zirconium at any given temperature. The presence of these two metals should make the measured vapor pressures of the zirconium sample approximately 1% low, but since this value lies within the experimental error of our data and since it would be partially compensated by the presence of low percentages of the more volatile impurities, such as aluminum, we have applied no correction.

Experimental Apparatus and Procedure

The sample was machined to the form of an annular ring of about 1-in. o.d. by $^3/_8$-in. i.d. $^1/_2$-in. high, and was supported on three wolfram rods in the Pyrex apparatus shown in Fig. 1.

With the exception of the liquid air trap O, the system was baked out before each run. The charcoal trap was baked out for about 36 hours at 450° and the remainder flamed for 1 hour at about 400°. The apparatus was then

---

[1] This work was supported in part by the Office of Naval Research under contract with the Ohio State University Cryogenic Laboratory.

[2] I. Langmuir, *Phys. Rev.*, **2**, 329 (1913).

[3] Marshall, Dornte and Norton, THIS JOURNAL, **59**, 1161 (1937).

[4] Analyses were made by Mr. John Center, Chief Analyst of the Battelle Memorial Institute, Columbus, Ohio.

sealed off at position M, and liquid air placed around the charcoal trap L. The pressure, as measured by the hot cathode ionization gage (Distillation Products, Inc., VG1A type), soon fell to about 2×10^{-7} mm., and generally remained between 2×10^{-7} and 2×10^{-8} mm. during a run, except for a few minutes at the beginning during which slight amounts of residual gases were evolved. The sample was heated by radio frequency (r.f.) induction using the work coil E surrounding the sample tube B. After a run, the sample tube was opened at the position F to remove the sample. In order to prevent the formation of a continuous metal film around the sample tube, which would heat in the r.f. field, three long molybdenum rods P were placed vertically between the sample and the glass wall. These rods also served to give mechanical stability to the lower metal framework supporting the sample.

Temperatures were measured with a disappearing filament optical pyrometer which had been carefully calibrated against a standard wolfram ribbon filament lamp. The standard lamp had been calibrated by the National Bureau of Standards and, in the range of this investigation, was reported to have a maximum uncertainty of 5°. For purposes of estimating our errors we have considered this uncertainty to be equivalent to a standard (r.m.s.) deviation of 1.5°. The standard deviation of pyrometer readings in calibration against the standard lamp was 1.0° and in measuring temperatures during the runs 0.5°, so that the total standard deviation is 1.9°. The temperature of a run was taken as the average temperature read in a black-body hole very near the outer curved surface. It was found that there was a temperature gradient of 40 to 50°K. across the flat surface of the sample, the outer edge being hotter. Several measurements of this temperature gradient were made during each run and the effect was accounted for as described below. A similar correction was made for the inner curved surface, whose temperature was assumed to lie between the temperature of the inside edge of the flat surface and the temperature read in a black-body hole very near the inner curved surface.

It was found convenient to account for small temperature fluctuations during each run and for evaporation during initial heating and cooling, by using an averaging process to calculate an effective time, t_{eff}, of each run.[5] In this calculation it was assumed that the rate of evaporation $m(T)$ at temperature T could be expressed by the equation

$$\log m(T) = A/T + C \qquad (1)$$

in which A and C are constants determined from the actual times-at-high-temperature and weight losses of the various runs. This equation was then used for calculating $m(T)$ and $m(T_{\text{av}})$ in the equation

$$t_{\text{eff}} = \int m(T)\text{d}t/m(T_{\text{av}}) \qquad (2)$$

where the integration is performed graphically. The value T_{av} is the arithmetic average temperature over the run.

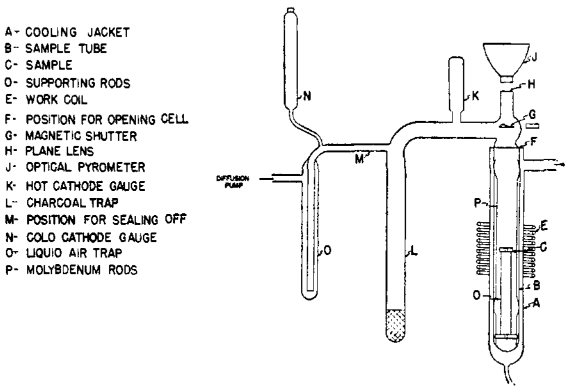

Fig. 1.—Pyrex vapor pressure cell.

In a similar way an "effective area" was used to account for temperature gradients in the sample. Since the average temperature of the outer curved surface was actually T_{av}, no correction was required for it. For the flat surfaces, equation (1) was used to calculate $m(T)$ at intervals across the surface, and the effective area of each flat surface calculated by the equation

$$A_{1\text{eff}} = 2\pi \int_{r_1}^{r_2} m(T)r\text{d}r \Big/ m(T_{\text{av}}) \qquad (3)$$

in which r_1 is the radius of the center hole and r_2 the outer radius. The effective area of the inner curved surface of a sample of this type has been calculated in a previous paper[6] to be

$$A_2 = \pi h\left(\sqrt{r_1^2 \pm h^2} - h\right) \qquad (4)$$

where h is the height of the sample. A further correction was applied here to account for the fact that the average temperature of the inner curved surface was lower than T_{av}. Thus the effective area of this surface was

$$A_{2\text{eff}} = A_2(m(T_2)/m(T_{\text{av}})) \qquad (5)$$

where T_2 is the average temperature of the inner curved surface, determined as described above. The sample was measured with a micrometer caliper. Its size did not change noticeably during the course of the experiments. However, a correction was applied for thermal expansion of the sample. Since the only measurements of the thermal expansion of zirconium at high temperatures, those of Zwikker,[7] extend only to 1500°K., there is some uncertainty due to the extrapolation, but this is not very serious since the correction is small in any case. These various areas were added together to give the total effective area of the sample. A maximum uncertainty of about 4% in the effective area was possible because of the uncertainty in measuring the temperature gradients. For the purpose of propagation of errors we assume this uncertainty to be twice the standard deviation.

The amount of metal evaporated during a run was measured in two ways. First, the sample was weighed to within ±0.00010 g. before and after each run. Second, the evaporated metal film was dissolved off the glass with concentrated sulfuric acid, precipitated as the hydroxide, and ignited to ZrO_2. In the second case, correction factors were calculated for metal that condensed on the supporting rods, the molybdenum rods going up the sides, and other places, which could not be included in the analysis. The total correction was 7.6%. It was estimated that there would be a maximum uncertainty of 4% in the measured weight loss, partly due to the weighing and partly to slight uncertainties in the correction factors. This error is again considered to be twice the standard deviation.

Data and Thermodynamic Treatment

The experimental results are summarized in Table I. Of the two sets of values listed for each temperature, the first refers to the weight loss obtained by collecting and analyzing the evaporated film, and the second from the directly measured

---

[5] This is essentially the method used by H. L. Johnston and A. L. Marshall, THIS JOURNAL, **62**, 1382 (1940).

[6] R. B. Holden, R. Speiser and H. L. Johnston, *ibid.*, **70**, 3897 (1948).

[7] C. Zwikker, *Physica*, **6**, 361 (1926).

TABLE I

RATES OF EVAPORATION AND VAPOR PRESSURES OF ZIRCONIUM

Run	Temp., °K.	Eff. time, sec.	Eff. area, sq. cm.	Wt. loss, g.	Rate, g./sq. cm./sec. $\times 10^8$	P, atm. $\times 10^9$	$-\log P$
8	1949	199,390	15.210	0.02474	0.816	0.851	9.0701
				.02473	0.815	0.850	9.0706
7	1980	111,590	15.365	.02397	1.398	1.469	8.8330
				.02431	1.418	1.490	8.8268
6	2007	53,470	15.773	.01792	2.124	2.248	8.6482
				.01745	2.069	2.189	8.6598
9	2029	95,900	15.267	.04913	3.356	3.568	8.4476
				.04946	3.378	3.594	8.4444
4	2049	30,740	15.545	.02098	4.390	4.693	8.3286
				.02136	4.469	4.779	8.3207
5	2054	30,040	15.548	.02298	4.920	5.267	8.2784
				.02273	4.866	5.209	8.2832

weight loss of the sample. The two values agree closely, the greatest difference being 2.5%. The vapor pressure was calculated using the equation

$$P = \frac{m}{\alpha}\sqrt{\frac{2\pi RT}{M}} \qquad (6)$$

where R is the gas constant, M the molecular (= atomic) weight of zirconium and α is the condensation coefficient. In the present calculation it was assumed that α has the value of unity. It was not possible to test this assumption directly since the vapor pressure of zirconium is too low to use the Knudsen method as was done for beryllium.[6]

The values of ΔH_0^0 for the evaporation process have been calculated according to the equation

$$\frac{\Delta H_0^0}{T} = -\left(\frac{F^0 - H_0^0}{T}\right)_{\text{gas}} + \left(\frac{F^0 - H_0^0}{T}\right)_{\text{solid}} - R\ln P \qquad (7)$$

for each value of the pressure given in Table I. The free energy functions of the gas were obtained from spectroscopic data.[8] Free energy functions of solid zirconium had to be approximated, using the low-temperature data of Squire[9] and the high-temperature data (to 1200°) of Jaeger and Veenstra.[10] Measurements of the thermal properties of solid zirconium are now being carried out in this Laboratory, so that this uncertainty will be removed in the near future. The calculations of ΔH_0^0 are shown in Table II.[11] Using the previously listed standard deviations of the temperature (1.9°), the weight loss of the sample (2%) and the effective area (2%), the standard deviation in ΔH_0^0 due to all factors except the free energy functions of solid zirconium is 174 cal./mole. This figure is considerably larger than the standard deviation of the values of ΔH_0^0 listed in Table II (126 cal./mole) because errors in temperature calibration would not cause random variations in the values of ΔH_0^0, but an approximately constant shift from the true value. Following the procedure recommended by Rossini and Deming[12] in which the uncertainty in a quantity is defined as twice the standard deviation, we obtain as the mean value of ΔH_0^0, 142,150 ± 350 cal./mole, not including errors in the free energy function of solid zirconium.

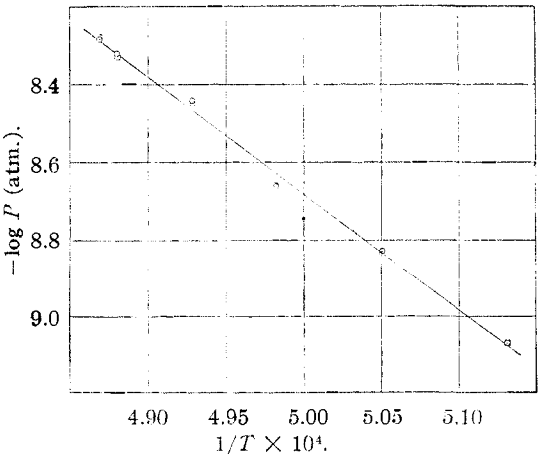

Fig. 2.—Vapor pressure of zirconium: □, values using weight of evaporated film; O, values using weight loss of sample.

TABLE II

THERMODYNAMIC CALCULATIONS FOR ZIRCONIUM

Temp., °K.	$-\left(\frac{F^0-H_0^0}{T}\right)_{\text{solid}}$	$-\left(\frac{F^0-H_0^0}{T}\right)_{\text{gas}}$	$-R\ln p$	ΔH_0^0, cal./mole
1949	17.69	49.100	41.502	142,105
			41.504	142,109
1980	17.82	49.200	40.417	142,158
			40.388	142,101
2007	17.94	49.285	39.571	142,328
			39.624	142,435
2029	18.03	49.356	38.653	141,987
			38.639	141,959
2049	18.12	49.418	38.109	142,215
			38.073	142,141
2054	18.14	49.434	37.879	142,081
			37.902	142,129

Mean ΔH_0^0 = 142,146 cal./mole

The equation for the vapor pressure has been determined by inserting the average value of ΔH_0^0 into equation (7) and expanding the term $\Delta(F^0 - H_0^0/T)$ as a linear function of the temperature

$$\log P\text{ (atm)} = -(31{,}066/T) + 7.3351 - 2.415 \times 10^{-4}T$$

This is the curve that has been shown with the experimental points in Fig. 2.

Summary

The vapor pressure of zirconium has been determined in the temperature range 1949 to 2054°K. by measuring the rate at which a zirconium surface evaporates into a vacuum. Values of ΔH_0^0 have been calculated from the individual vapor pressures and show no appreciable trend, the average value being 142,150 ± 350 cal./mole. By combining this value with free energy functions of gaseous zirconium and with extrapolated values for the solid, the following equation for vapor pressure is obtained.

$$\log P\text{(atm)} = -(31{,}066/T) + 7.3351 - 2.415 \times 10^{-4}T$$

COLUMBUS, OHIO

RECEIVED JULY 5, 1950

---

(8) C. E. Moore, "Term Designations for Excitation Potentials," Princeton University Press, Princeton, N. J., 1934.

(9) C. F. Squire, *Phys. Rev.*, **58**, 202 (1940).

(10) F. M. Jaeger and W. A. Veenstra, *Rec. trav. chim.*, **53**, 917 (1934).

(11) Values of the physical constants used for all calculations are from D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **34**, 143 (1945).

(12) F. D. Rossini and W. E. Deming, *J. Wash. Acad. Sci.*, **29**, 416 (1939).