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**THE OHIO STATE UNIVERSITY
RESEARCH FOUNDATION**

VAPOR PRESSURES OF INORGANIC SUBSTANCES,
ZIRCONIUM DIOXIDE

by

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Technical Report

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FOREWORD

This work was carried out at The Ohio State University Cryogenic Laboratory under contract with U.S. Navy, Office of Naval Research Contract Number N6ori-17, Task Order IV, ONR Project Number N 358 039, with The Ohio State University Research Foundation. This report covers information obtained during the study entitled: "High Temperature Thermodynamics of Inorganic Substances." It represents the 11th Technical Report of this series.

Director - H. L. Johnston

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ABSTRACT

The vapor pressure of ZrO_2 has been determined by the method of Knudsen, between 2014° and 2290° K. ZrO_2 vaporizes undissociated as ZrO_2 (g), the heat of vaporization being 140.3 ± 1.5 kcal/mole. From the vapor pressure data obtained, the boiling point was determined to be 3735° K, and the heat of dissociation of ZrO_2 (g) into gaseous atoms was found to be $D_0 = 375$ kcal/mole.

INTRODUCTION

No experimental determination of the vapor pressure of zirconium dioxide is reported in the literature, and the question concerning which gaseous species are present when ZrO_2 vaporizes is still not settled.

The only available information on the vapor pressure of ZrO_2 is that of Searcy¹ who estimated a vapor pressure of 1.5×10^{-7} atm at $2073^\circ K$ from measurements of Zintl, Morawietz, and Gastinger.² Mott³ reported the boiling point at $4570^\circ K$. Starodubtsev⁴ observed ZrO_2 in a mass spectrograph, which indicates the existence of the gaseous ZrO_2 molecule.

In the present investigation, the Knudsen effusion method was used to determine the pressure over pure ZrO_2 and over a mixture of ZrO_2 and Zr.

APPARATUS AND EXPERIMENTAL PROCEDURE

Two tantalum Knudsen cells were used, of dimensions 1" diameter and $3/4$ " high, with an orifice diameter of $1/16$ ". The area of the orifice was corrected for thermal expansion by using the thermal expansion coefficient of tantalum determined previously in this Laboratory.⁵ ZrO_2 was introduced into one of the cells, while a mixture of ZrO_2 and Zr was introduced into the other. Both cells were degassed for two hours at $2000^\circ C$ before the runs were made.

The samples were heated in our metal cell,¹¹ and the temperature was measured with a disappearing filament optical pyrometer, calibrated against a standard wolfram ribbon lamp. The standard lamp had been calibrated by the National Bureau of Standards, and in the range of the present investigation, was reported to have a maximum uncertainty of 5° .

For the small temperature fluctuation during each run, and for evaporation during the initial heating and cooling periods, the averaging method^{6,7} was used. To correct for the thickness of the effusion hole (0.01"), all measured weight losses were multiplied by the factor $\frac{1}{0.89} = 1.1236$.^{8,9}

The ZrO_2 was obtained from the Oak Ridge National Laboratories, and its hafnium content was less than 0.025%. The Zr was in powder form; it was obtained from Charles Hardy Inc., New York, and its Zr metal content was better than 99.5%.

EXPERIMENTAL RESULTS AND DISCUSSION OF THE DATA

The experimental data for pure ZrO_2 are presented in Table I, and those for the stoichiometric $ZrO_2 + Zr$ mixture are given in Table II. The data from the two tables are plotted in Figure 1. The pressure was calculated from the rate of effusion data, using the equation $p = m \sqrt{2 \pi RT/M}$, where p is the pressure in atmospheres, R is the molar gas constant, T is the absolute temperature, m is the rate of effusion in $g./cm.^2/sec.$, and M is the molecular weight of the vapor. The molecular species was taken as ZrO_2 , according to the following discussion.

The rates of evaporation were found to be the same for both cases, indicating that ZrO_2 vaporizes as ZrO_2 . If dissociation into ZrO and O occurred, then the pressure above the $ZrO_2 + Zr$ mixture would be much larger than that above the pure ZrO_2 . Vaporization into Zr metal and oxygen is excluded because the measured rates of evaporation are 100 times larger than those for zirconium. The dissociation into gaseous oxygen and solid Zr is excluded by the following facts: 1) Twice as much material was vaporized from each cell as the amount of oxygen contained in the ZrO_2 and in the $ZrO_2 + Zr$ mixture, and 2) x-ray patterns taken after the runs showed only ZrO_2 lines in material from the ZrO_2 cell, and expanded Zr lines (saturated with oxygen) in the material from the $ZrO_2 + Zr$ cell.

The slope of the $\log p$ versus $1/T$ plot, shown in Fig. 1, yields a value of 140.3 ± 1.5 kcal/mole for the mean heat of evaporation of ZrO_2 over the temperature range 2014 - 2290° K. A least squares fitting of the data to the Clausius-Clapeyron equation yields the expression

$$\log p = - \frac{3.065 \times 10^4}{T} + 8.528$$

By using the value determined in this Laboratory,⁷ for the heat of evaporation of Zr, and the heat of formation of solid

TABLE I

VAPOR PRESSURE OF ZrO_2

Run	Temp ($^{\circ}K$)	Eff. Time (sec.)	Area (cm^2)	Wt. Loss (g)	Evaporation Rate ($g./cm^2/sec.$) $\times 10^5$	P (atm.) $\times 10^6$	$-\log P$
1	2064	47,903	0.0210	0.0073	0.7257	0.670	6.174
3	2104	44,971	0.0210	0.0081	0.8577	0.799	6.156
2	2151	34,206	0.0210	0.0148	2.0603	1.946	5.711
5	2175	32,658	0.0210	0.0181	2.6392	2.500	5.602
4	2244	24,071	0.0211	0.0418	8.2300	7.922	5.101
7	2271	17,435	0.0211	0.0481	13.075	12.660	4.898
6	2282	16,304	0.0211	0.0381	11.075	10.750	4.969

TABLE II

VAPOR PRESSURE OF $ZrO_2 + Zr$

Run	Temp (°K)	Eff. Time (sec.)	Area (cm. ²)	Wt. loss (g)	Evaporation Rate (g./cm. ² /sec.) $\times 10^5$	P (atm) $\times 10^6$	-log P
3	2014	28,851	0.02041	0.0011	0.1868	0.174	6.759
1	2040	57,022	.02042	.0035	.3006	.275	6.561
4	2046	70,123	.02042	.0056	.3911	.361	6.443
5	2089	43,823	.02043	.0074	.8265	.769	6.114
2	2121	38,680	.02044	.0121	1.5304	1.436	5.843
6	2142	50,873	.02045	.0184	1.7686	1.666	5.778
7	2240	21,963	.02049	.0339	7.5330	7.253	5.139
8	2290	17,811	.02051	.0463	12.6744	12.330	4.909

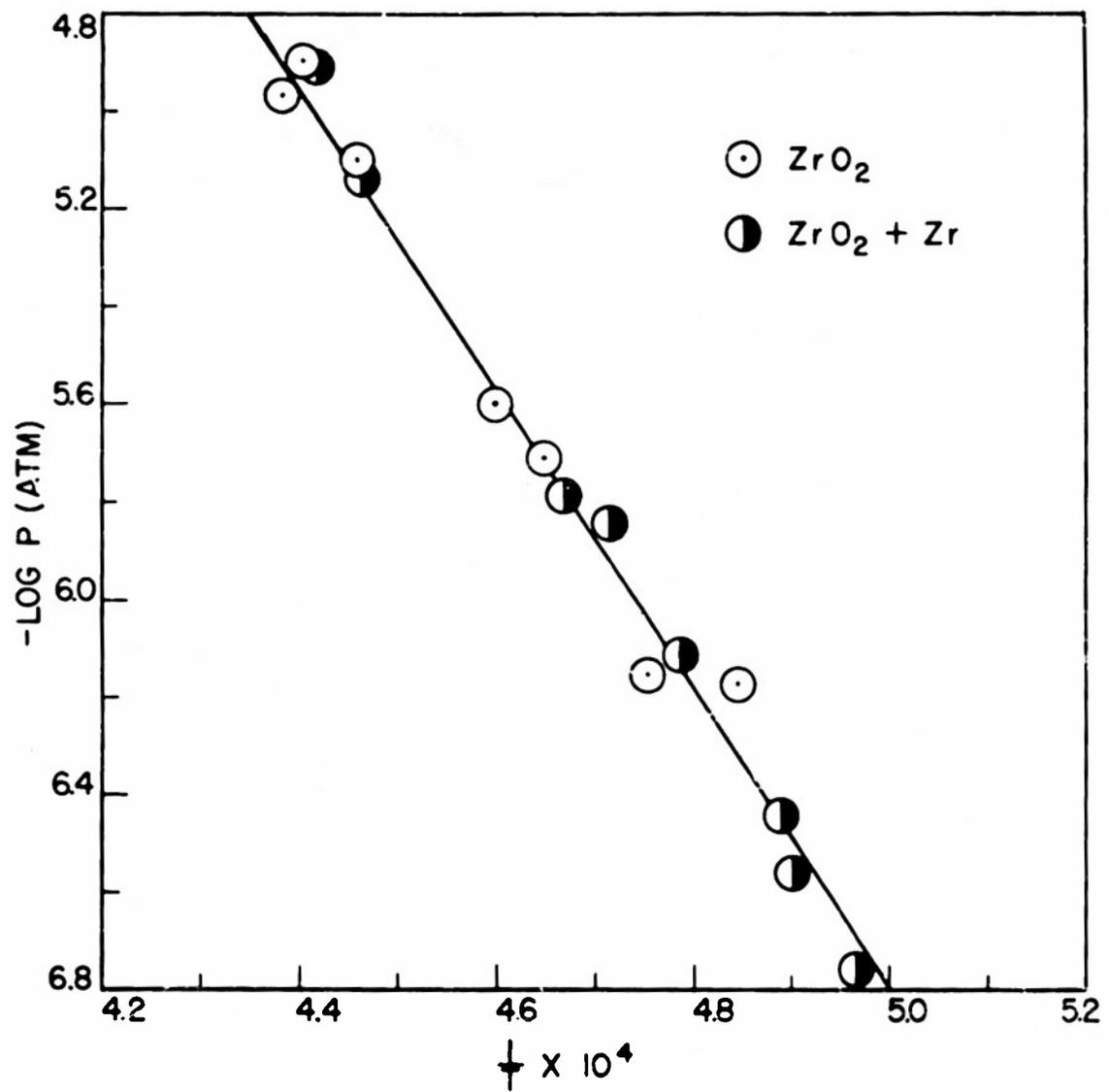


FIG. 1 - VAPOR PRESSURE OF ZrO_2 AND $ZrO_2 + Zr$

ZrO₂, given by the National Bureau of Standards,¹⁰ a value of 375 ± 5 kcal/mole was obtained for the heat of dissociation of gaseous ZrO₂ into gaseous atoms of Zr and O. From data given by the National Bureau of Standards¹⁰ for the temperature, heat, and entropy of fusion, the boiling point of ZrO₂ was calculated to be 3735°K.

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