

VAPORIZATION OF ZIRCONIUM OXIDE

By

M. M. NAKATA  
R. L. McKISSON  
B. D. POLLOCK

**ATOMICS INTERNATIONAL**

A DIVISION OF NORTH AMERICAN AVIATION, INC.  
P.O. BOX 309 CANOGA PARK, CALIFORNIA

CONTRACT: AT(11-1)-GEN-8  
ISSUED: APR 15 1961

## DISTRIBUTION

This report has been distributed according to the category "Chemistry-General" as given in "Standard Distribution Lists for Unclassified Scientific and Technical Reports" TID-4500 (15th Ed.), August 1, 1959. A total of 600 copies was printed.

## ACKNOWLEDGMENT

The authors wish to thank Mrs. Laura Fink for assisting in the evaporation rate measurements.

## CONTENTS

	Page
Abstract . . . . .	iv
I. Introduction . . . . .	1
II. Apparatus and Experimental Procedure . . . . .	2
III. Experimental Results and Discussion . . . . .	4
IV. Conclusions . . . . .	8
References . . . . .	9
Appendix . . . . .	10

## TABLES

I. Evaporation Rates of $ZrO_2$ . . . . .	4
II. Dissociation Energies of $ZrO$ and $ZrO_2$ <u>vs</u> Composition. . . . .	7

## FIGURES

1. Tungsten Knudsen Cell Assembly . . . . .	2
2. Mass Spectrum of the Vapor Over $ZrO_2$ . . . . .	5

## ABSTRACT

The vaporization rate of zirconium oxide in the temperature range 2410 to 2830 °K was measured using the Knudsen effusion technique, and the composition of the vapor was estimated from a mass spectrometric observation. These data were used, with pertinent thermodynamic quantities obtained from the literature, to calculate the dissociation energies  $D^\circ(\text{ZrO}) = 7.8 \pm 0.2$  ev, and  $D^\circ(\text{ZrO}_2) = 14.9 \pm 0.2$  ev.

## I. INTRODUCTION

The vaporization of  $ZrO_2$  has been reported by Ackermann and Thorn<sup>1</sup>. They calculated the partial pressures of  $ZrO_2(g)$ ,  $ZrO(g)$ , and  $O(g)$  over solid  $ZrO_2$ , using free energies of formation of  $ZrO_2(s)$ ,  $ZrO(g)$ , and  $O(g)$ ; and reported  $ZrO_2(g)$  to be the predominant species. More recently, however, the same authors<sup>2</sup> have reported that congruent evaporation and a minimum in the volatility occur when the dioxide phase has the composition  $O/Zr = 1.96$ . At this composition, the  $ZrO(g)$  is the predominant species. The dissociation energy of  $ZrO_2$  was given as  $D^\circ = 15.3 \pm 0.3$  ev, the value of which is dependent on the acceptance of  $7.8$  ev<sup>3,4</sup> for the dissociation energy of  $ZrO$ .

Chupka, Berkowitz and Inghram<sup>4</sup> made a mass spectrometric analysis of the vapors effusing from a Knudsen cell containing either  $ZrO_2$  or a mixture of  $Zr$  and  $ZrO_2$ , and determined the vapor pressures and heats of sublimation of the gaseous species. Their results yielded  $7.8 \pm 0.2$  ev and  $14.5 \pm 0.2$  ev for the dissociation energies of  $ZrO$  and  $ZrO_2$ , respectively. The dissociation energy of  $ZrO_2$  given by Chupka, et al, is less than that given by Ackermann and Thorn by 14 kcal, even after correcting for the different values used for the heat of sublimation of zirconium in deriving the value for  $D^\circ (ZrO_2)$ .

In the present work, the evaporation rate of  $ZrO_2$  from a tungsten cell was measured using the Knudsen effusion technique over the temperature range 2410 to 2830°K. Vapor species were identified at 2575°K using a time-of-flight mass spectrometer. The dissociation energies of  $ZrO$  and  $ZrO_2$ , and the partial pressures of the gaseous species were calculated from these data.

## II. APPARATUS AND EXPERIMENTAL PROCEDURE

A total-weight-loss Knudsen effusion method was used. The effusion rate measurements were made in a vacuum induction furnace heated by a 6-kw Ajax high frequency converter. The vacuum in the system was maintained in the range of  $10^{-5}$  to  $10^{-6}$  mm Hg during the runs, except during the brief warmup period. The temperatures were measured with a Leeds and Northrup optical pyrometer by sighting into the effusion hole. The pyrometer was calibrated against a secondary standard tungsten ribbon lamp; and the maximum estimated uncertainty in the temperature measurements is  $\pm 15^\circ$ .

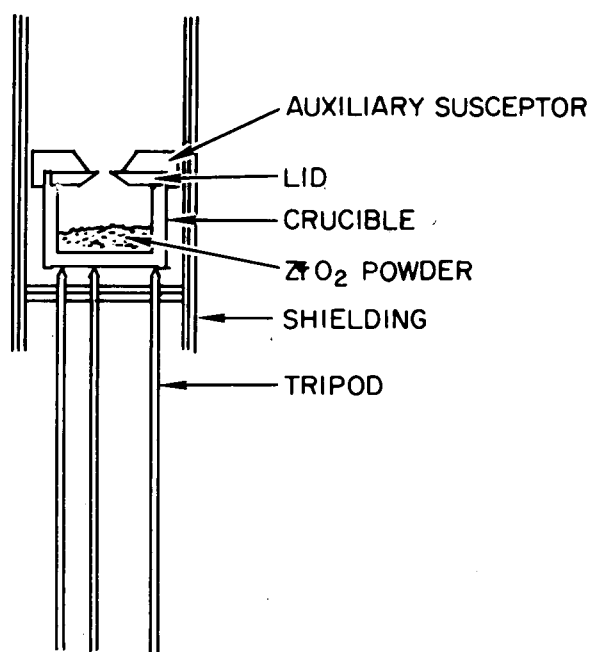


Figure 1. Tungsten Knudsen Cell Assembly

The tungsten Knudsen cell was made in two parts, as shown in Figure 1. The crucible measured 5/8-in. O.D, 1/2-in. ID, and 1/2-in. high. The lid, with an approximately 1 mm-diameter orifice, was a 1/16-in. thick disc which fitted into a recess cut in the crucible. The orifice was ground to a knife-edge, and was placed with the flat surface facing out. An auxiliary tungsten susceptor was used above the cell assembly to reduce heat loss from the lid, and to minimize the temperature differential between the lid and the crucible. Both the Knudsen cell and the auxiliary susceptor were heated in hydrogen for 1-1/2 hr at 1775°K, and then degassed in vacuum at

2900°K for 8 hr, previous to the vaporization runs. The cell was supported on a tungsten tripod and shielded with 1-mil tungsten foil.

Before making the effusion rate runs, the cell containing the  $ZrO_2$  powder was heated in vacuum at 2850°K for 4 hr. The gray residue obtained was assumed to be the congruently vaporizing zirconium oxide composition.

The orifice diameter was measured before and after each run with a micrometer comparator mounted in a stereomicroscope; and the average reading was used, after applying a small correction for the thermal expansion of tungsten<sup>5</sup>.

It is estimated that the orifice diameters are accurate to 0.01 mm. All weight losses were multiplied by the factor 1/0.98 to correct for the thickness of the orifice wall.<sup>6</sup>

The averaging method of Skinner, et al,<sup>7</sup> was used to correct for the temperature fluctuation during each run, and for the initial heating and cooling periods.

The Knudsen cell was weighed before and after each run on an analytical balance to 0.1 mg. A small weight loss of the empty tungsten cell was subtracted from the weight-loss measurements.

The mass spectrometric data were obtained using a Model 12-101 Bendix time-of-flight mass spectrometer. A zirconia sample supported on a resistance-heated tungsten ribbon was used as the spectrometer source. The apparent temperature was observed by sighting on the sample, using a Leeds and Northrup optical pyrometer. The mass spectrum was obtained with an electron energy of 50 v, and was displayed on a Tektronic Model 541 oscilloscope and recorded using a 35-mm Bolsey oscilloscope camera.

The operating procedure consisted of calibrating the spectrometer and adjusting the oscilloscope to display the mass range of interest, 85 to 135. Then, the temperature of the tungsten strip source was raised, keeping the system pressure below  $10^{-5}$  mm Hg. The mass spectrum was photographed, a check for shutter dependency was made, and the temperature observed to complete the measurement.

The zirconium oxide was reactor grade material obtained from The Carborundum Metals Corp.

### III. EXPERIMENTAL RESULTS AND DISCUSSION

The effusion data are given in Table I. For convenience in performing the calculations to be described later in this section, the Clausing correction was applied to the measured effusion rates. These corrected or "ideal" values are given in the sixth column of the table. The pressures in the last column were calculated by means of the Knudsen equation <sup>6</sup>,

$$P^* \text{ (atm)} = 0.02256 G (T/M)^{1/2}, \quad \dots (1)$$

where G is the effusion rate in gram/cm<sup>2</sup>/sec, T is the absolute temperature, and M is the molecular weight. The pressures, P\*, were calculated assuming the vapor to consist entirely of ZrO<sub>2</sub>(g), and are represented as a function of temperature by Equation 2, obtained by a least squares treatment of the P\* values,

$$\text{Log } P^* \text{ (atm)} = - 34,020/T + 7.828 . \quad \dots (2)$$

TABLE I  
EVAPORATION RATES OF ZrO<sub>2</sub>

Run	Temp (°K)	Time (sec)	Orifice Area x 10 <sup>3</sup> (cm <sup>2</sup> )	Wt Loss (gm)	Evap Rate x 10 <sup>5</sup> (gm/cm <sup>2</sup> /sec)	P* x 10 <sup>5</sup> (atm)
9	2830	6830	6.94	0.0427	90.1	9.74
6	2800	8100	8.40	0.0216	31.8	3.41
10	2730	10800	6.79	0.0157	21.4	2.27
2	2715	17580	7.54	0.0202	15.24	1.61
7	2625	17910	8.40	0.0115	7.64	0.796
1	2605	14060	7.54	0.0072	6.79	0.705
3	2535	27970	7.84	0.0056	2.55	0.261
8	2515	31400	8.59	0.0053	1.96	0.200
4	2475	31620	8.17	0.0024	0.93	0.094
5	2410	60380	8.17	0.0030	0.61	0.061



The mass spectrometric data are presented in the form of the photograph of Figure 2, which shows the characteristic patterns for the  $Zr^+$ ,  $ZrO^+$ , and  $ZrO_2^+$  isotopes; and also those for  $Hg^{++8}$ . The  $Zr^+$  peaks are attributed mainly to fragmentation produced by the 50-v electron beam. Comparison of measured effusion rates with those to be expected for simple dissociation to the elements,



indicates that molecular species and oxygen must greatly predominate in the vapor, and that  $Zr(g)$  could have been present to the extent of less than about 2%.

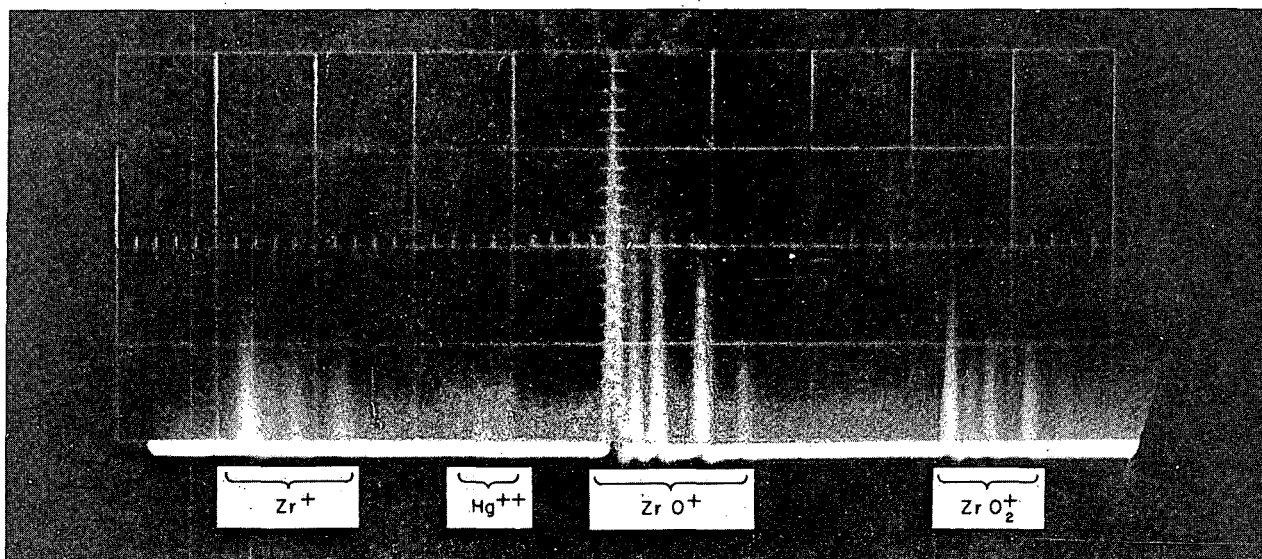


Figure 2. Mass Spectrum of the Vapor Over  $ZrO_2$

An estimate of vapor composition was made, based on the known abundances of the Zr isotopes, as follows: visual inspection showed that the intensity of the  $Zr^{91}O$  peak (relative abundance 11.2%) is slightly greater than that of the  $Zr^{90}O_2$  peak (relative abundance 51.5%), so that the apparent  $ZrO$ -to- $ZrO_2$  ratio is about 5 to 1. Because of uncertainties resulting from fragmentation, no further analysis will be given, although it is believed that the effect of fragmentation in this case would tend to compensate for differences in ionization probabilities. As will be shown later, dissociation energies of  $ZrO$  and  $ZrO_2$  are not sensitive to moderate uncertainties in vapor composition. In summary, therefore, the mass spectrometric examination and thermodynamic considerations lead to the conclusions that the predominant vaporization processes are



and



and that about 5/6 or 83% of the vapor is ZrO and O; and about 1/6, or 17% is ZrO<sub>2</sub> at 2600°K.

The dissociation energies of ZrO and ZrO<sub>2</sub> may be obtained from the vaporization data, the estimated vapor composition, and thermodynamic data available in the literature, as described below for ZrO.

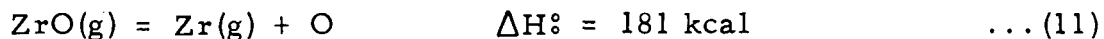
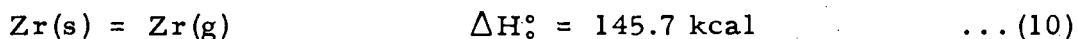
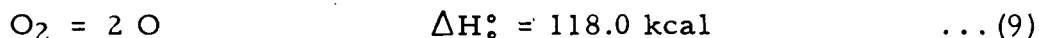
First,  $\Delta F_T^\circ$  for reaction 5 is calculated by use of Equation 6,

$$\Delta F_T^\circ = -RT \ln K_p = -4.576 T \text{ Log } P_{\text{ZrO}} P_{\text{O}}. \quad \dots (6)$$

The partial pressures are computed from the evaporation rates corresponding to  $P_{\text{ZrO}_2}^*$  given by Equation 2. It should be noted that although Ackermann and Thorn showed that zirconium dioxide vaporizes congruently at elevated temperatures in vacuum at the composition ZrO<sub>1.96</sub>, no significant error will be made if the assumption of stoichiometry is made. Thus the effusion rates of ZrO and O, in gram-mol/cm<sup>2</sup>/sec, will be equal; and would be in the proportion 107.2/16 by weight. The heat of reaction 5 at 0°K is then calculated using free energy functions:

$$\Delta H^\circ = \Delta F_T^\circ - \Delta \left( \frac{F_T^\circ - H^\circ}{T} \right) T. \quad \dots (7)$$

The heat of reaction thus obtained is combined in the usual manner with those for other reactions to give  $\Delta H^\circ$  for the dissociation of ZrO(g):



\*The negative sign refers to the reverse of reaction 5.

where  $\Delta H^\circ = D^\circ(\text{ZrO})$ . The calculations for  $D^\circ(\text{ZrO}_2)$  are similar. Based on the estimated vapor composition, the calculations outlined above lead to  $D^\circ(\text{ZrO}) = 181 (\pm 4)$  kcal, or  $7.8 (\pm 0.2)$  ev, and to  $D^\circ(\text{ZrO}_2) = 343 (\pm 5)$  kcal, or  $14.9 (\pm 0.2)$  ev. The values are based on the effusion rate at  $2600^\circ\text{K}$ , because this temperature is near the midpoint of the experimental temperature range and is also near that at which the vapor composition was determined.

The sources of thermodynamic data used in the calculations were: Stull and Sinke<sup>9</sup> for heats of formation and free energy functions of the elements; Brewer and Chandrasekharaiah<sup>10, 11</sup> for the free energy functions of  $\text{ZrO}(\text{g})$  and  $\text{ZrO}_2(\text{g})$ ; Kelley<sup>12, 13</sup> for heat capacities and entropies; Coughlin<sup>14</sup> for heat of formation and of transition of  $\text{ZrO}_2(\text{s})$ . The quantity  $(H_{298}^\circ - H^\circ)$  for  $\text{ZrO}_2(\text{s})$  was estimated to be 2000 cal from the low-temperature heat capacity data in Reference 13. The table of the free energy functions for the temperature range of the experiments is given in the Appendix.

To illustrate the effect of error in vapor composition, the dissociation energies were calculated for a number of other vapor compositions; and these are given in Table II. As may be seen by inspection of the  $D^\circ$  values vs composition, a twofold error in the fraction of  $\text{ZrO}_2$  in the vapor, i. e., 9% or 34% vs 17%  $\text{ZrO}_2$ , would affect  $D^\circ(\text{ZrO}_2)$  to the extent of only 3.5 kcal, and the corresponding effect on  $D^\circ(\text{ZrO})$  would be less.

TABLE II  
DISSOCIATION ENERGIES OF  $\text{ZrO}$  AND  $\text{ZrO}_2$  vs COMPOSITION

% $\text{ZrO} + \text{O}$ in vapor	% $\text{ZrO}_2$ in vapor	$D^\circ(\text{ZrO})$ (kcal)	$D^\circ(\text{ZrO}_2)$ (kcal)
100	0	182.7	-
95	5	182.1	336.3
90	10	181.6	339.8
83	17	180.8	342.6
80	20	180.4	343.4
70	30	179.0	345.5
60	40	177.4	347.0
0	100		351.8

#### IV. CONCLUSIONS

The results of this work appear to be in excellent agreement with those of Chupka, Berkowitz, and Inghram; and in fair agreement with those of Ackermann and Thorn. Somewhat different values of the thermodynamic quantities were used in calculating the dissociation energy of  $ZrO_2$  in each of the two previous reports and in this work. To properly compare the results, therefore, the values given in the two previous reports were adjusted, using the values of the thermodynamic quantities used in this report. The result is that our value is greater than that of Chupka, et al, by 6.4 kcal, or 0.3 ev; and less than that of Ackermann and Thorn by 9.2 kcal, or 0.4 ev. The partial pressures used by Ackermann and Thorn in obtaining their value, 15.3 ev, are probably subject to somewhat greater experimental error than those obtained in this work, in that their method involved correcting initial loss rates of stoichiometric  $ZrO_2$  for loss of ZrO-and-O. It is therefore suggested that the weighted average, 342( $\pm$ 4) kcal or 14.8 ( $\pm$ 0.2) ev, be taken as the best value for  $D^\circ(ZrO_2)$ . There appears to be little question concerning  $D^\circ(ZrO) = 7.8$  ev.

To predict the behavior of the oxide in various environments, it would be helpful to have information concerning the equilibrium constants as a function of temperature for the important equilibria. Thus, utilizing the fact that free-energy function differences change very slowly with temperature, one may write for Reaction 4

$$-\Delta F_T^\circ = 4.576 T \text{ Log } P_{ZrO_2} = -\Delta H^\circ - \Delta \left( \frac{F_T^\circ - H^\circ}{T} \right) T . \quad \dots (12)$$

Substituting and simplifying,

$$\text{Log } P_{ZrO_2} (\text{atm}) = -39,730/T + 9.18 . \quad \dots (13)$$

Similarly, for Reaction 5, one finds

$$\text{Log } P_{ZrO} P_O = -74,910/T + 17.68 . \quad \dots (14)$$

Reaction 4 would be predominant in air or in an oxygen-bearing atmosphere, and Reaction 5 would be predominant in vacuum.

## REFERENCES

1. R. J. Ackermann and R. J. Thorn, "Reactions Yielding Volatile Oxides at High Temperatures," ANL-5824 (1958)
2. Ibid, Paper presented at the ACS Sept 1960 meeting
3. G. Herzberg, Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules, D. Van Nostrand Co., Inc., New York (1950)
4. W. A. Chupka, J. Berkowitz, and M.G. Inghram, "Thermodynamics of the Zr - ZrO<sub>2</sub> System: The Dissociation Energies of ZrO and ZrO<sub>2</sub>," J. Chem. Phys. 26, No. 5 (1957), pp 1207-10
5. Metallwerkplansee, Tungsten
6. S. Dushman, Scientific Foundations of Vacuum Technique, John Wiley and Sons, Inc., New York (1949), pp 20, 96.
7. G. B. Skinner, J. Edwards and H. L. Johnston, "Vapor Pressures of Inorganic Substances. V. Zirconium between 1949 and 2054°K," J. Am. Chem. Soc. 73, (1951) p 174
8. G. T. Seaborg and I. Perlman, "Table of Isotopes," Rev. Mod. Phys. 20, No. 4 (1948), pp 585-667
9. D. R. Stull and G. C. Sinke, Thermodynamic Properties of the Elements, American Chemical Society, Washington, D. C. (1956)
10. L. Brewer and M. C. Chandrasekharaiah, "Free Energy Functions for Gaseous Monoxides," UCRL - 8713 Rev (1960)
11. M. C. Chandrasekharaiah and L. Brewer, "Free Energy Functions for Some MO<sub>2</sub> Oxides," UCRL - 8736 (1959)
12. K. K. Kelley, Contributions to the Data on Theoretical Metallurgy, Bur. Mines Bull. 476 (1949)
13. Ibid, Contributions to the Data on Theoretical Metallurgy, Bur. Mines Bull. 477 (1950)
14. J. P. Coughlin, Contributions to the Data on Theoretical Metallurgy, Bur. Mines Bull. 542 (1954)

APPENDIX

TABLE OF  $-\frac{F_T^\circ - H^\circ}{T}$  USED IN CALCULATIONS

Species	Temperature (°K)		
	2400	2600	2800
O	43.93	44.34	44.72
Zr(g)	50.43	50.95	51.44
ZrO(g)	68.6	69.4	70.0
ZrO <sub>2</sub> (g)	73.7	74.9	75.8
ZrO <sub>2</sub> (s)	31.5	32.8	34.0