Discussion

The dimensions of the $Se(SCN)_2$ molecule are Se–S = 2.21 Å., S–C = 1.69 Å., C–N = 1.13 Å., ∠S–Se–S = 101°, ∠Se–S–C = 104°, dihedral angle for S–Se–S–C = 79°. The sums of the covalent radii[3] are Se–S = 2.21 Å., S = 1.81 Å., S–C = 1.60 Å., $C \equiv N$ = 1.27 Å. and $C \equiv N$ = 1.15 Å. There is clearly no evidence for double-bond character in the Se–S bond. The S–C bond, however, is shorter than the normal single-bond distances found, for example, in dimethyl sulfide (1.82 Å.),[6] dimethyl sulfide (1.77 Å.)[7] and dimethyl trisulfide (1.78 Å.)[8] and corresponds to about 30% double-bond character. However, only small reliance can be placed on this result since the errors in the C coördinates could be as large as 0.15 Å. The C–N distance given above is certainly too small, although one expects this distance to be less than the value of 1.22 Å. found in HNCS.[9] The mean distances found in the compound $[Hg(SCN)_4][Cu(en)_2]$[10] are C–N = 1.34 Å. and S–C = 1.57 Å., which are in marked disagreement with our results. Since the SCN groups in the mercury compound appeared non-linear—a very unlikely result—we conclude that the interatomic distances are likely to be greatly in error.

The bond angles about Se and S are very close to those found in most sulfides, disulfides, trisulfides and comparable selenium compounds, although the S–S–S angle in 2,2′-diiododiethyl trisulfide[11] appears to have the abnormally large value of 113°. The dihedral angle between the S–Se–S and Se–S–C planes, 79°, seems small. Pauling[12] predicts that this type of angle should be 90° or larger in sulfur compounds and has used this concept to explain the stability of S_8. It is expected that selenium will show the same behavior, and Burbank[13] found the average dihedral angle in α-selenium to be 102°. On the other hand, Donohue[11] found the S–S–S–C dihedral angle in 2,2′-diiododiethyl trisulfide to be 82°, although he did not place much reliance in this result. We do not believe that the errors in this determination are sufficient to cause a deviation of 11° or more in this angle. It is easily shown that $\partial\varphi/\partial x'_C = -15$ deg./Å., $\partial\varphi/\partial y'_C = 21$ deg./A. and $\partial\varphi/\partial z'_C = 21$ deg./Å., where φ is the dihedral angle and x'_C, y'_C, and z'_C are the coördinates of carbon in Å. The corresponding derivatives for nitrogen are even smaller. Hence, changes in the coördinates of both C and N of the order of 0.4 Å. would be required to obtain a dihedral angle of 90°.

The packing of the molecules is such that the closest intermolecular distances are N · · · Se and N · · · S. The shortest of these are 3.03 Å., 3.32 Å., 3.58 Å. and 3.90 Å. for N · · · S, and 2.98 Å. and 3.58 Å. for N · · · Se.

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

Vapor Pressures of Inorganic Substances. XII. Zirconium Dioxide[1]

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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 $\Delta H^\circ_{298} = 153.6 \pm 1$ kcal. The vapor pressure can be represented by the equation $\log p(\text{atm.}) = -(34{,}383/T) - 7.98 \times 10^{-4}\,T + 11.98$. The heat of dissociation of $ZrO_2(g)$ into gaseous atoms was found to be $D_0 = 365 \pm 5$ kcal.

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 Searcy[2] who estimated a vapor pressure of 1.5×10^{-7} atm. at 2073°K. from measurements of Zintl, Morawietz and Gastinger.[3] Mott[4] reported the boiling point at 4570°K. Starodubtsev[5] 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 in. diameter and 3/4 in. high, with an orifice diameter of 1/16 in. The area of the orifice was corrected for thermal expansion by using the thermal expansion coefficient of tantalum determined previously in this Laboratory.[6] 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° before the runs were made.

The samples were heated in our metal cell,[7] and the temperature was measured with a disappearing-filament optical pyrometer, calibrated against a standard tungsten-ribbon

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amp. 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[8,9] was used. To correct for the thickness of the effusion hole (0.01 in.), all measured weight losses were multiplied by the factor 1/0.89 = 1.1236.[10,11]

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 from 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 Fig. 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.

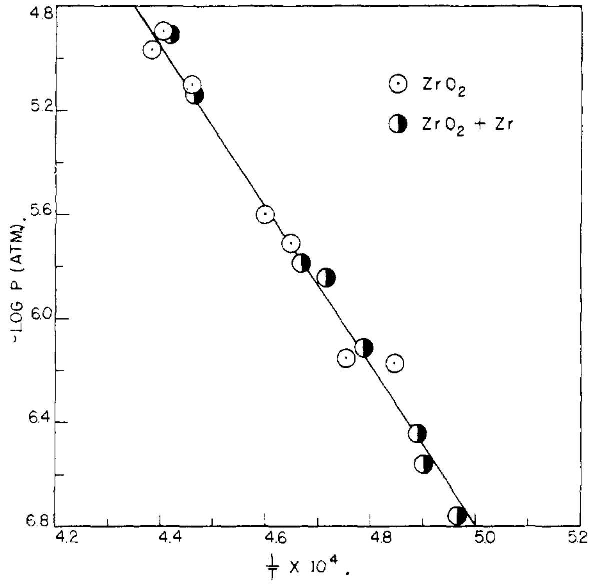

Fig 1.—Vapor pressure of ZrO_2 and ZrO_2 + Zr.

Table I

Vapor Pressure of ZrO_2

Run	Temp., °K.	Eff. time, sec.	Area, cm.²	Wt. loss, g.	Evapn. rate, g./cm.²/sec., × 10⁵	p, atm., × 10⁶	−log p
1	2064	47,903	0.0210	0.0073	0.7257	0.670	6.174
3	2104	44,971	.0210	.0081	0.8577	0.799	6.156
2	2151	34,206	.0210	.0148	2.0603	1.946	5.711
5	2175	32,658	.0210	.0181	2.6392	2.500	5.602
4	2244	24,071	.0211	.0418	8.2300	7.922	5.101
7	2271	17,435	.0211	.0481	13.075	12.660	4.898
6	2282	16,304	.0211	.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.	Evapn. rate, g./cm.²/sec., × 10⁵	p, atm., × 10⁶	−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

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.[9] 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 data are plotted in Fig. 1.

To obtain ΔH° and the equation for the vapor pressure, our data were treated by a sigma plot $[\Delta F^\circ/T + \Delta\alpha \ln T = \Sigma = \Delta H^\circ/T + 1]$. The necessary specific heat data were obtained from Kelley,[12] who gives $C_p = 17.80 - 4.00 \times 10^5 \times T^{-2}$ for solid ZrO_2 and we estimated the specific heat of gaseous ZrO_2 to be 10 cal. mole⁻¹ degree⁻¹. From the sigma plot we obtain $\Delta H_0^\circ = 157.3 \pm$ kcal. and

$$\Delta H = 157{,}300 - 7.80T - 4 \times 10^5 T^{-1}$$

After expanding the term $-7.80 \ln T + 2 \times 10^5 T^{-2}$ as a linear function of the temperature we obtain

$$\log p(\text{atm.}) = -\frac{34{,}383}{T} - (7.98 \times 10^{-4})T + 11.98$$

By using the value determined in the Laboratory[9] for the heat of evaporation of Zr, and the heat of formation of solid ZrO_2 given by Humphrey[13] a value of 368 ± 5 kcal./mole was obtained for the heat of dissociation of gaseous ZrO_2 into gaseous atoms of Zr and O.

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