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REACTIONS YIELDING VOLATILE OXIDES AT HIGH TEMPERATURES;
FREE ENERGIES OF GASEOUS Al_2O , ZrO , ThO , TaO , ZrO_2 ,
 ThO_2 , TaO_2 , UO_2 AND WO_3

by

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January, 1958

Operated by The University of Chicago
under
Contract W-31-109-eng-38

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REACTIONS YIELDING VOLATILE OXIDES AT HIGH TEMPERATURES;
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I. INTRODUCTION

Although the oxides such as Al_2O_3 , MgO , UO_2 , ThO_2 , BeO , and ZrO_2 are used as refractory materials, very little reliable thermodynamic data predicting the stabilities of the gases in equilibrium with the solids at temperatures above 1700°C exist. In most cases the vapor pressures are not accurately known and in some cases the gaseous molecules are uncertain. Hence one experiences difficulties in attempting to predict the interaction of these oxides with the refractory metals such as tungsten and tantalum. The problems are made even more difficult because of a lack of reliable information concerning the gaseous oxides of tungsten and tantalum. As a means towards establishing the thermodynamic stabilities of these refractory oxides, the authors propose to survey the existing results and to describe some rather crucial experiments relating to the interaction of these oxides with tungsten and tantalum. Although not establishing accurate free energies, these experiments, nevertheless, have shown conclusively the unreliability of some supposedly accurate thermodynamic properties because of a failure to examine the investigations in this manner. In addition, they indicate more reliable limits of free energies in certain cases.

No attempt is made in the subsequent discussion to effect an exhaustive survey of this subject. Such has already been performed.¹ Instead it is the intent of the writers to examine critically the published results so that well-established observations and data can be separated from the tenuous ones.

¹ L. Brewer, Chem. Rev. 52, 1 (1953).

II. SURVEY OF THERMODYNAMIC DATA

A. Refractory Oxides

1. Solids

The heats of formation of all the oxides listed have been determined. In some cases the entropies have been calculated; in other cases they have been estimated. In either case the free energies listed by Coughlin² are probably reliable and hence will be used herein. The solid suboxides such as AlO and Al₂O³ will not be considered herein since the interest is in the over-all reaction to yield gases.

2. Gaseous Aluminum Oxides

Two gaseous oxide molecules of aluminum have been identified. The molecule Al₂O has been observed by an analysis of sublimates from a mixture of silicon with aluminum oxide⁴ and by mass spectrometric measurements of vapor from a mixture of aluminum with aluminum oxide.⁵ The heat of formation obtained by Porter, Schissel and Inghram is probably reliable, but the free energy obtained by Brewer and Searcy⁶ may be incorrect, since it was obtained from a volatility measurement carried out in an open crucible containing a mixture of aluminum with aluminum oxide which did not yield the equilibrium vapor pressure of aluminum. The bands in the spectrum from an aluminum arc in air have been attributed to the molecule AlO. The free energy reported by Brewer and Searcy⁶ is in error because of the interaction between the oxide and the tungsten crucible.⁷

3. Gaseous Magnesium Oxide

The gaseous oxides of magnesium appear to be unstable at low oxygen pressures.⁸

² J. P. Coughlin, "Contributions to the Data on Theoretical Metallurgy: XII. Heats and Free Energies of Formation of Inorganic Oxides," Bureau of Mines Bulletin 542 (U.S. Government Printing Office, Washington, D.C., 1954)

³ M. Hoch and H. L. Johnston, J. Am. Chem. Soc. 76, 2560 (1954).

⁴ Grube, Schneider, Esch, and Flad, Z. anorg. Chem. 260, 120 (1949).

⁵ Porter, Schissel, and Inghram, J. Chem. Phys. 23, 339 (1955).

⁶ L. Brewer and A. W. Searcy, J. Am. Chem. Soc. 73, 5308 (1951).

⁷ R. J. Ackermann and R. J. Thorn, J. Am. Chem. Soc. 78, 4169 (1956).

⁸ Porter, Chupka, and Inghram, J. Chem. Phys. 23, 1347 (1955).

4. Gaseous Uranium Oxides

There appear to be at least two gaseous oxides of uranium. The molecule ion UO_2^+ is observed in a mass spectrometer. The vapor pressure measurements by Ackermann, Gilles, and Thorn⁹ are consistent with gaseous UO_2 and yield accurate values for the free energy of this molecule. The molecule UO_3 has been postulated to account for the volatility observed by Biltz and Müller¹⁰ of the solid compositions between $\text{UO}_{2.25}$ and $\text{UO}_{2.62}$ in vacuum. Starting with $\text{UO}_2(\text{s})$ the present writers have observed a significant volatility of uranium oxide by maintaining the solid at about 950°C and an oxygen pressure of 4×10^{-4} mm Hg. This molecule may have contributed to the increased volatility of the uranium dioxide at the higher temperatures.⁹ The free energy of this gas has not been measured.

5. Gaseous Thorium Oxides

The band spectrum from an arc of thoria in graphite has been interpreted¹¹ as that for ThO with a vibrational constant of 740 cm^{-1} . The data, however, are insufficient to enable one to calculate the free energy. In at least two investigations the existence of $\text{ThO}_2(\text{g})$ has been inferred.^{12,13} In both of these investigations the free energy of sublimation was supposedly obtained. However, the data of Shapiro may be in error because of inaccurate temperature measurements, and those of Hoch and Johnston may be in error as a result of the reduction of $\text{ThO}_2(\text{s})$ by tantalum. Hence, only an approximate value can be given for the free energy of the assumed $\text{ThO}_2(\text{g})$.¹⁴

6. Gaseous Beryllium Oxides

Sufficient band spectra data of BeO have been analyzed to establish its existence. Although the rotational and vibrational constants have been evaluated, the dissociation energy is not accurately known. Erway and Seifert¹⁵ have attempted to measure the vapor pressure of $\text{BeO}(\text{s})$, but according to Brewer¹ have measured the dissociation into gaseous elements.

⁹ Ackermann, Gilles, and Thorn, J. Chem. Phys. 25, 1089 (1956).

¹⁰ W. Biltz and H. Müller, Z. anorg. Chem. 163, 257 (1927).

¹¹ S. G. Krishnamurty, Proc. Phys. Soc. (London) 64A, 852 (1951).

¹² E. Shapiro, J. Am. Chem. Soc. 74, 5233 (1952).

¹³ M. Hoch and H. L. Johnston, J. Am. Chem. Soc. 76, 4833 (1954).

¹⁴ Ackermann, Gilles, and Thorn, J. Am. Chem. Soc. 78, 1767 (1956).

¹⁵ N. D. Erway and R. L. Seifert, J. Electrochem. Soc. 98, 83 (1951).

7. Gaseous Zirconium Oxides

The molecule ZrO has been identified by its spectrum and the rotational and vibrational constants have been calculated. The dissociation energy has been estimated to be 7.8 eV from the spectrum. The observation of ZrO_2^+ in a mass spectrometer¹⁶ indicates the existence of $\text{ZrO}_2(\text{g})$. Hoch, Nakata, and Johnston¹⁷ have measured the vapor pressure of $\text{ZrO}_2(\text{s})$, but these measurements are probably in error because of reaction of the oxide with the tantalum effusion cell.

B. Refractory Metals

1. Solids

There are two fairly well-established solid phases in the tungsten-oxygen system. These are the yellow WO_3 and the brown WO_2 .¹⁸ There also appears to be a blue phase of intermediate composition, but it has not been well characterized. Six phases have been reported to occur in the tantalum-oxygen system.¹⁹ Of these the only one well characterized is Ta_2O_5 , which is the product obtained by measurements of the heat of combustion of tantalum metal. The free energies of the tungsten and tantalum oxides given by Coughlin² will be accepted for all calculations given herein.

2. Gaseous Tungsten Oxides

Two gaseous oxides of tungsten have been reported. Langmuir²⁰ has shown indirectly that $\text{WO}_3(\text{g})$ exists at high temperatures by observing the change in oxygen pressure and the change in weight of a tungsten filament heated in a closed system. Strictly viewed, his results can be explained by the reactions

and

in which T_1 is the temperature of the filament and T_2 is the temperature of the wall of the vessel. Hence, Langmuir actually demonstrated the existence

¹⁶S. V. Stardodubtsev and Y. I. Timokhina, *Zhur. Tekh. Fiz.* 19, 606 (1949).

¹⁷Hoch, Nakata, and Johnston, *J. Am. Chem. Soc.* 76, 2651 (1954).

¹⁸K. C. Li and Chung Yu Wang, *Tungsten*, Reinhold Publ. Corp., New York, (1947).

¹⁹N. Schönberg, *Acta Chem. Scand.* 8, 240 (1954).

²⁰I. Langmuir, *J. Am. Chem. Soc.* 35, 105 (1913).

of $\text{WO}_3(\text{s})$ and inferred $\text{WO}_x(\text{g})$ to be $\text{WO}_3(\text{g})$. The evidence demonstrating the existence of $\text{WO}(\text{g})$ is meager. Emission band systems in the spectrum of a high voltage arc between tungsten electrodes have been attributed to the monoxide.²¹ An insufficient number of bands has been observed to characterize the molecule completely, although an approximate value of the vibrational frequency has been obtained. Ueno²² has reported measurements of the vapor pressure of $\text{WO}_3(\text{s})$.

3. Gaseous Tantalum Oxides

Two gaseous oxides of tantalum have been observed. Fernando and Krishnamurty²³ have observed the spectrum from tantalum electrodes in oxygen and have interpreted the bands as being caused by TaO . Ackermann and Thorn⁷ have deduced that $\text{TaO}(\text{g})$ is one product in the reaction between aluminum oxide and tantalum. The dissociation energies of TaO and TaO_2 have been reported by Inghram, Berkowitz and Chupka.²⁴

²¹A. Catterer and S. G. Krishnamurty, *Nature* 169, 543 (1952).

²²K. Ueno, *J. Chem. Soc. Japan* 62, 990 (1941).

²³I. Fernando and S. G. Krishnamurty, *Current Sci. (India)* 18, 371 (1949).

²⁴Inghram, Berkowitz, and Chupka, *Bull. Am. Phys. Soc. Series II*, 1, 341 (1956); see also *J. Chem. Phys.* 27, 569 (1957).

III. DETERMINATION OF STOICHIOMETRY OF INTERACTION

If one represents the oxide by MO_a and the effusion cell material by C, then, assuming no other solid phases to be present, one can write for the interaction:

In principle one should be able to determine the standard free energy for reaction (3) by measuring the effusion rates, provided the stoichiometry, $(a-b)/c$, is known and the equilibrium is not disturbed by the effusion process. The minimum condition for the attainment of the latter requirement is that the effusion rate must be less than the rate of reaction of $\text{MO}_a(s)$ with $\text{C}(s)$.

If w_r is the ratio of weights of $\text{MO}_a(s)$ and $\text{C}(s)$ reacted and m_r is the molecular weight ratio, then

$$\frac{a-b}{c} = \frac{m_r}{w_r} = s \quad (4)$$

One cannot uniquely determine the stoichiometry s by a measure of w_r alone, since both b and c are unknown. However, one can compare values of m_r/w_r with $(a-b)/c$ for assumed values and in certain cases infer the identity of the gaseous products.

Experimentally certain precautions must be exercised in the determination of w_r . Measurements of the weights of the oxide and the cell material transported must be truly independent. One of the most direct and accurate methods for these measurements is as follows. First, the vaporization rate of a well-outgassed effusion cell heated inductively is measured in an evacuated space surrounded by a condenser, so that no effusate returns to the cell. Then a weighed amount of the oxide is placed in the cell of known weight, and all of the oxide is vaporized out in the same evacuated condenser. By observing the time necessary for the rate of loss of weight to attain that of the cell alone, one can correct for a small amount of the cell material which vaporizes in the absence of the oxide. These data then enable one to calculate independently the weight of the oxide and the weight of cell material which have reacted and vaporized.

The results which have been obtained using this method are given in Table I.

A. Aluminum Oxide

It has been shown already that aluminum oxide reacts with tungsten.⁷ A more complete description of the results, however, is informative. A list of the most probable products per mole of Al_2O_3 and the calculated weight

TABLE I
Gaseous Products from Oxides in Tungsten and Tantalum

Oxide	Tungsten			Tantalum		
	T(°K)	Wt. ratio of oxide to metal transported	Gaseous Products	T(°K)	Wt. ratio of oxide to metal transported	Gaseous Products
Al ₂ O ₃	2544	1.23 ± 0.01	Al ₂ O + Al + (O) + WO _x	2523	0.19 ± 0.01	Al + TaO + smaller amounts of Al ₂ O and TaO ₂
	2582	1.16 ± 0.01				
	2635	1.13 ± 0.01				
MgO	2045	0.66 ± 0.01	Mg + WO ₃	--	--	--
UO ₂	1600 to 2500	≥ 50	UO ₂	2100 to 2500	≥ 50	UO ₂
ThO ₂	2765	≥ 50	ThO ₂ + (ThO + O)	2753	3.06	ThO + TaO + TaO ₂
BeO	2462	0.92	Be + WO _x + (O) Perhaps some BeO	--	--	--
ZrO ₂	2600	≥ 50	ZrO ₂ + ZrO + O	2560	0.89 ± 0.02	ZrO + TaO + TaO ₂

ratios is as follows:

1. $2\text{Al}(\text{g}) + 3\text{WO}(\text{g})$; 0.185
2. $\text{Al}_2\text{O}(\text{g}) + 2\text{WO}(\text{g})$; 0.277
3. $2\text{Al}(\text{g}) + \text{WO}_2(\text{g})$; 0.369
4. $2\text{Al}(\text{g}) + \text{WO}_3(\text{g})$; 0.554
5. $\text{AlO}(\text{g}) + 1/2 \text{WO}(\text{g})$; 0.554
6. $\text{Al}_2\text{O}(\text{g}) + \text{WO}_2(\text{g})$; 0.554
7. $\text{Al}_2\text{O}(\text{g}) + 2/3 \text{WO}_3(\text{g})$; 0.832
8. $2\text{AlO}(\text{g}) + 1/2 \text{WO}_2(\text{g})$; 1.108
9. $\text{AlO}(\text{g}) + 1/6 \text{WO}_3(\text{g})$; 1.663.

Examining the values given in Table I, one observes that this ratio decreases with increasing temperature. It was also observed that milligram quantities of tungsten were transported within the effusion cell from one region to another at a higher temperature. Possible explanations for these observations are that tungsten is transported out of the cell by a gaseous oxide which is sufficiently unstable to cause transportation of tungsten within the cell by dissociation, or that tungsten is transported out by two oxides one of which disproportionates at the higher temperature to cause transportation within the cell. In both of these cases the gaseous aluminum oxide may or may not be significantly dissociated. If the first combination with the aluminum oxide insignificantly dissociated represents the condition, then the experimental weight ratio must be equal to or greater than that calculated for the undissociated tungsten oxide. Hence if only one gaseous tungsten oxide is involved, the combination $\text{AlO}(\text{g}) + \text{WO}_3(\text{g})$ is not a possible one.

A comparison of the experimental weight ratio with the various theoretical values reveals that, if two gaseous tungsten oxides are involved, then one of them must be WO_3 and the gaseous aluminum oxide must be AlO . Assuming the molecules WO_3 and WO_c to be present, one deduces that, since the weight ratio decreases with increasing temperature, the ratio of $\text{WO}_c : \text{WO}_3$ must increase with increasing temperature. This conclusion predicts that the transport of tungsten within the cell by the reaction

would occur from one region to another at a lower temperature. Since this is contrary to the observed direction of transport, the combination of $\text{AlO}(\text{g})$, $\text{WO}_3(\text{g})$ and $\text{WO}_c(\text{g})$ ($c \leq 2$) cannot explain the experimental results. Therefore the vaporization of Al_2O_3 (ℓ) in a tungsten cell cannot involve two gaseous tungsten oxides and a stable gaseous aluminum oxide.

If only one oxide of tungsten is involved, then one might expect it to become less stable at higher temperatures, with the result that the weight ratio should increase with increasing temperature. Hence one surmises that the observed trend in w_r indicates that the aluminum oxide gaseous molecule is somewhat dissociated. The products must then be Al(g) , O(g) , an aluminum oxide gas, and one or more gaseous tungsten oxides. Recently Inghram, Chupka, and Berkowitz²⁵ have reported that they observe both $\text{Al}_2\text{O(g)}$ and Al(g) to effuse from a tungsten cell containing aluminum oxide.

B. Magnesium Oxide

In the case of magnesium oxide in tungsten the calculated ratio for the reaction

is 0.658. Hence it seems reasonable to conclude that $\text{WO}_3\text{(g)}$ (or a polymer thereof) is present and that the $\text{WO}_x\text{(g)}$ observed by Langmuir was in fact WO_3 . Porter²⁶ must have failed to obtain the correct stoichiometry because of an unreliable method of determining the ratio of MgO to tungsten transported.

The total weight loss of a tungsten effusion cell containing magnesium oxide was measured over a temperature range from 1922 to 2019°K (see Table II). Within the experimental error, mixtures of magnesium oxide and tungsten powders in a tungsten cell yield volatilities which agree with those obtained from magnesium oxide alone in a tungsten cell. The principal source of error is attributable to the magnesium deposit which reflected heat back to the cell and thereby caused an increase in temperature during a given experiment. In a representative experiment the probable error in the temperature is 2.5°. The white residues from several experiments gave X-ray diffraction patterns attributable to periclase in all experiments. In addition, tungsten lines were identified in the residues from experiments 6, 7, and 8, and an unidentified phase was found in both types of experiments. The lines originating from this phase did not correspond to those for the known oxides of tungsten or to those for magnesium tungstate. It is believed that its presence is not sufficient to affect the calculations given herein.

²⁵ Inghram, Chupka, and Berkowitz, Proceedings of the 1956 International Conference of Astrophysics.

²⁶ R. F. Porter, University of California Radiation Laboratory, Report UCRL-2416 (December 1953)

TABLE II
Volatility of Magnesium Oxide in a Tungsten Effusion Cell

Expt.	Weight Loss of cell and contents (mg)**	Time (sec)	T (°K)	Pressure of WO ₃ x 10 ⁶ (atm)	-log P _{WO₃}	10 ⁴ /T
1	10.4	1800	2005	8.458	5.0727	4.988
2	8.8	2100	1977	6.091	5.2153	5.058
3	8.6	4500	1922	2.739	5.5624	5.203
4	9.7	4740	1925	2.934	5.5325	5.195
5	6.2	1800	1956	4.980	5.3028	5.112
6*	7.3	900	2019	11.91	4.9241	4.953
7*	8.0	1841	1975	6.311	5.1999	5.063
8*	7.8	1200	1996	9.494	5.0255	5.010

*Mixture of MgO and tungsten powders

**Orifice area at average temperature = $2.88 \times 10^{-2} \text{ cm}^2$.

C. Thorium Oxide

The results given in Table I clearly demonstrate that the measurements by Hoch and Johnston¹³ do not yield directly the vapor pressure for thorium. The effusion data, however, are probably reliable, because the authors have found the volatility of ThO₂(s) in a tantalum effusion cell to agree within a factor of 3 with that reported by Hoch and Johnston. An examination of the gray residue at room temperature showed a single phase having a fluorite structure with a lattice parameter $a_0 = 5.5845 \pm 0.0005 \text{ kX}$. Recently Inghram, Chupka, and Berkowitz²⁵ have reported comparable ion currents in a mass spectrometer arising from ThO(g), TaO(g) and ThO₂(g) when ThO₂(s) is vaporized from a tantalum cell.

D. Beryllium Oxide

In the case of the beryllia-tungsten interaction, milligram quantities of tungsten are transported within the crucible from one region to another at a higher temperature. In this respect BeO in tungsten resembles Al₂O₃ in tungsten. If beryllia vaporizes to the gaseous atoms, as the entropy data of

Kelley²⁷ and the spectroscopic dissociation energy of BeO(g) predict,¹ then the gaseous products of the beryllia-tungsten experiments are Be(g), and one or more gaseous tungsten oxides. A further discussion will follow in a later section.

E. Zirconium Oxide

The results of preliminary effusion measurements of the volatility of ZrO₂(s) in tungsten cells are given in Table III. All weight losses were corrected for a small background weight loss of the tungsten and the pressures tabulated in column 4 are based on the molecular weight of ZrO₂. The zirconium oxide employed contained about 2% hafnium, but since the partial pressure of hafnium oxide is most probably small it is doubtful that its presence had any significant effect. An analysis by least squares yields the equation

$$\log p_z(\text{atm}) = \frac{-3.61 \times 10^4}{T} + 8.65 \quad (7)$$

X-ray analysis of the gray residue after appreciable vaporization had occurred indicated only the presence of the ZrO₂(s) phase, and spectrographic analysis thereof yielded less than 0.1% tungsten. However, combustion of a 0.14650-g sample of the gray residue at 900°C in air yielded a weight gain of 4.9mg and the reappearance of the original white color. If one assumes that the white material is ZrO₂, then one calculates a composition corresponding to ZrO_{1.97} for the gray residue. Compositions of the ZrO_{2-x} phase have been studied by Domagala and McPherson²⁸ and Kubaschewski and Dench.²⁹ At present the data are insufficient to enable one to state whether the ZrO_{1.97} phase represents a constant subliming composition. The data in Table III have been analyzed on the basis of the assumption that the solid is ZrO₂.

The average weight ratio obtained from two measurements of the interaction of ZrO₂ with tantalum at 2560°K is 0.89 ± 0.02 . A recent investigation²⁴ of this system indicates that the equilibrium vapor effusing from a tantalum cell containing ZrO₂(s) consists of ZrO(g), TaO(g) and TaO₂(g). Hence, the reaction that occurs can be represented by the equation

in which $\alpha = 0.52$.

²⁷K. K. Kelley, "Contributions to Data on Theoretical Metallurgy. XI. Entropies of Inorganic Substances" U. S. Bureau of Mines Bull. 477, U. S. Government Printing Office, Washington, D.C. (1950).

²⁸R. F. Domagala and D. J. McPherson, J. Metals 6, 238 (1954).

²⁹O. Kubaschewski and W. A. Dench, J. Inst. Metals 84, 440 (1955-6).

TABLE III
Volatility Data for $\text{ZrO}_2(\text{s})$

Temperature	Weight-Loss of ZrO_2 (mg)	Time (sec)	Pressure p_z *** (atm)
2526	1.7*	3600	1.90×10^{-6}
2434	1.2*	7200	6.56×10^{-7}
2745	13.0*	1800	3.02×10^{-5}
2632	11.3**	3600	9.43×10^{-6}

*Orifice area = $2.54 \times 10^{-2} \text{ cm}^2$.

**Orifice area = $3.46 \times 10^{-2} \text{ cm}^2$.

***Molecular weight assumed to be that for ZrO_2 .

Hoch, Nakata, and Johnston¹⁷ have measured the volatility of ZrO_2 by means of a tantalum effusion cell. They deduced that $\text{ZrO}_2(\text{g})$ was the principal gaseous species because the measured volatility was independent of the presence of zirconium metal inside the cell. This result erroneously infers that zirconium metal is less volatile than $\text{ZrO}_2(\text{s})$. The authors have measured the volatility of ZrO_2 using a thoroughly outgassed tantalum effusion cell and find at 2600°K a volatility which is about 0.1 that obtained by Hoch, Nakata, and Johnston. The high volatility obtained by these investigators possibly results from an effusion cell which was insufficiently outgassed.

IV. FREE ENERGIES DERIVED FROM INTERACTIONS

By considering the experiments described previously and by estimating some absolute entropies, one can derive the approximate free energies of some of the gaseous products involved. Although no great accuracy can be claimed for these derived quantities, they are at least qualitatively reliable in that they will enable one to predict whether a given reaction under specified conditions should be significant. In a number of cases the free energies have been expressed by equations which, because of the number of terms, may appear to be accurate. The reader is cautioned that these are accurate only within the bounds of certain assumptions.

If the only species present are those given in equation (3), then to maintain stoichiometry one writes that

$$\frac{\int_0^t Z_c dt}{\int_0^t Z_m dt} = \frac{a - b}{c} = s, \quad (9)$$

in which the Z 's are the mole effusion rates of metal oxide and cell oxide. Using the effusion equation one writes that

$$\frac{\int_0^t Z_c dt}{\int_0^t Z_m dt} = \sqrt{\frac{M_m}{M_c}} \frac{\int_0^t p_c(0,t) dt}{\int_0^t p_m(0,t) dt}, \quad (10)$$

in which the M 's are the molecular weights and the p 's are the pressures at the orifice at time t . For the total weight loss one writes that

$$W(t) = \frac{a}{\sqrt{2\pi RT}} \left\{ \sqrt{M_m} \int_0^t p_m(0,t) dt + \sqrt{M_c} \int_0^t p_c(0,t) dt \right\}, \quad (11)$$

in which a is the orifice area, R is the gas constant, and T is the absolute temperature. Combining equations (9), (10), and (11) one finds that

$$\int_0^t p_m(0,t) dt = \frac{\sqrt{2\pi M_m RT}}{a(sM_c + M_m)} W(t), \quad (12)$$

and a similar equation for the cell. Since $\frac{d}{dt} \int p \, dt = p$, one obtains the result that

$$p_m(0,t) = \frac{\sqrt{2\pi M_m RT}}{a(sM_c + M_m)} \frac{dW(t)}{dt} \quad (13)$$

Provided that the cell containing the oxide loses weight at a constant rate, then one can calculate $p_m(0)$ and $p_c(0)$ from the total weight loss. If equilibrium exists at the orifice, one writes that

$$p_m(0) p_c^s(0) = K \quad , \quad (14)$$

and one can evaluate the standard free energy for the reaction.

A. Estimation of Some Free Energies

1. Gaseous Al_2O

As stated previously the heat of formation of gaseous Al_2O can be obtained from the measurements by Porter, Schissel, and Inghram⁵ with the system

Using data furnished us by R. F. Porter, we obtain a value of 86.9 kcal/mole for the heat of reaction (15) at approximately 1650°K. The entropy change for this reaction can be estimated by at least two methods. First, one can estimate the ratio of ionization cross-sections of $\text{Al}_2\text{O}(g)$ to $\text{Al}(g)$ and using the observed ion intensities calculate ΔS° from the vapor pressure of aluminum. Secondly, one can estimate the molecular structure of $\text{Al}_2\text{O}(g)$ and calculate ΔS° from the absolute entropies of the reactants and products. With a ratio of ionization cross sections of Al_2O to Al of 2.5 and the vapor pressure of aluminum given by Baur and Brunner³⁰ the first method yields 35.21 eu. Assuming that Al_2O has a ring structure with Al-O distances of 1.6 Å and Al-Al distances of 2.8 Å, with vibrational frequencies the same as those for ethylene oxide³¹ corrected for the mass ratio of aluminum to CH_2 , and with a non-degenerate ground state, one obtains a value of 37.82 eu. If the first value is arbitrarily accepted, and one retains the same vibrational constants, 570, 610, and 896 cm^{-1} , but corrects the interatomic distances, one obtains 1.03 Å for the Al-O distances and 1.81 Å for the Al-Al

³⁰E. Baur and R. Brunner, *Helv. Chem. Acta* **17**, 958 (1934).

³¹G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules*, D. Van Nostrand, New York, (1945).

distance. Since these distances are not unreasonable, we shall accept the first value and write for reaction (15) that

$$\Delta F_{15}^{\circ} \cong 86900 - 35.21T \text{ cal/mole}, \quad (16)$$

which yields for the free energy of formation of $\text{Al}_2\text{O}(\text{g})$ the equation,

$$\Delta F_f^{\circ} (\text{Al}_2\text{O}) \cong -47200 - 9.27T \text{ cal/mole}. \quad (17)$$

The assumed structure of Al_2O yields for the temperature dependent part of the free energy,³² $F^{\circ} - H_0^{\circ}$,

$$f^{\circ} (\text{Al}_2\text{O}) = -R'T(7 \log T + 649/T - 7.51) \quad , \quad (18)$$

in which $R' = 2.303 R$. The corresponding equations for atomic oxygen and aluminum at temperatures above 2000°K derived from data in Moore³³ are

$$f^{\circ} (\text{O}) = -R'T(5/2 \log T - 48.69/T + 31193/T^2 + 1.169) \quad (19)$$

and

$$f^{\circ} (\text{Al}) = -R'T(5/2 \log T - 46.67/T + 1254/T^2 + 1.333). \quad (20)$$

Using equations (17), (18), (19), and (20), together with an expression for the free energy of dissociation of molecular oxygen,³⁴

$$\Delta F_D^{\circ} (\text{O}_2) = 121,945 - 32.22T \text{ cal/mole} \quad , \quad (21)$$

one finds for the standard free energy of dissociation of Al_2O the equation

$$\Delta F_D^{\circ} (\text{Al}_2\text{O}) \cong 252,100 - 2.288 T \log T - 51.92T \text{ cal/mole}. \quad (22)$$

The terms involving $1/T$ and $1/T^2$ have been omitted since they are negligible.

2. Gaseous Tungsten Oxide

Assuming that effusion rate of material from the magnesium oxide-tungsten interaction measures the pressures of magnesium and WO_3 gases, and substituting the proper values into equation (13), one obtains the values of $\log p\text{WO}_3$ listed in Table II and plotted in Figure 1.

³² In all calculations used herein the high temperature forms for the free energy function are used. See J. E. Mayer and M. G. Mayer, Statistical Mechanics, John Wiley and Sons, Inc., New York (1940).

³³ C. E. Moore, Atomic Energy Levels, U. S. National Bureau of Standards Circular 467 (1949 and 1952).

³⁴ U. S. National Bureau of Standards, Selected Values of Chemical Thermodynamic Properties, Series III.

The equation derived by least squares' from these values is

$$\log p_{\text{WO}_3} \text{ (atm)} = -\frac{24760}{T} + 7.409 \quad (23)$$

Although the vapor pressure of magnesium is not accurately known one can obtain an approximate value by combining the data of Hartmann and Schneider³⁵ with absolute entropies. The result is

$$\log \text{vpMg} \text{ (atm)} = \frac{-6969}{T} + 5.013 \quad (24)$$

Combining equations (23) and (24) with the free energy of magnesium oxide one finds that, at 2020°K, $\Delta F^\circ(\text{WO}_3\text{g}) = -44,287$ cal/mole.

The absolute entropy of gaseous WO_3 can be estimated as follows. It is assumed that the molecule has a planar XY_3 structure with a W-O distance of 2 Å and with a force constant of $k_1 = 10^6$ dynes/cm. The other force constants can be evaluated by averaging the ratios of force constants for the molecules given by Herzberg.³¹ The vibrational constants so calculated are 1030, 392, 1096, and 395 cm^{-1} , the last

³⁵H. Hartmann and R. Schneider, Z. anorg. Chem. 180, 275 (1929).

two being two-fold degenerate. Using the high-temperature form of the free energy function one obtains the equations

$$f^\circ(\text{WO}_3) = -R'T(10 \log T + \frac{1376}{T} - \frac{147.2 \times 10^3}{T^2} - 15.35) \quad , \quad (25)$$

and

$$S^\circ(\text{WO}_3) = 45.76 \log T + \frac{6736 \times 10^3}{T^2} - 50.39 \quad . \quad (26)$$

The free energy functions and absolute entropies of molecular oxygen and metallic tungsten can be expressed by equations which are quite accurate. To do this for O_2 one uses a moment of inertia of $19.38 \times 10^{-40} \text{ g cm}^2$, a vibrational constant of 1568 cm^{-1} , and a ground state electronic degeneracy of 3. The equations are

$$f^\circ(\text{O}_2) = -R'T(4.5 \log T - 2.829 + \frac{490}{T} - \frac{921 \times 10^2}{T^2} + \frac{39 \times 10^8}{T^4}) \quad , \quad (27)$$

and

$$S^\circ(\text{O}_2) = 20.59 \log T + \frac{421 \times 10^3}{T^2} - \frac{54 \times 10^9}{T^4} - 4.015 \quad . \quad (28)$$

For tungsten one uses a Debye temperature of 310°K and finds that

$$f^\circ(\text{W}) = 30.63T - 13.22T \log T - 0.38 \times 10^{-3}T^2 - 60 \text{ cal/mole} \quad , \quad (29)$$

and

$$S^\circ(\text{W}) = 13.22 \log T + 0.76 \times 10^{-3}T - 24.89 \quad . \quad (30)$$

Using equations (25), (27) and (29) one writes that

$$\begin{aligned} \Delta F_f^\circ(\text{WO}_3) &\stackrel{\sim}{=} -75,649 - 1.650T \log T + 20.20T \\ &\quad + 38 \times 10^{-5} T^2 \text{ cal/mole.} \end{aligned} \quad (31)$$

From equations (26), (28), and (30) and the entropy of formation of solid WO_3 , one obtains a value of 40 eu for the entropy of vaporization of solid WO_3 to gaseous WO_3 at 1400°K . The value obtained by Ueno is 58.38 eu. It is very doubtful that the estimated value is in error by more than about 5 eu. There are at least two possible explanations for the high value obtained by Ueno. Gaseous polymers probably constitute a large fraction of the vapor since the vaporization behavior of $\text{WO}_3(\text{s})$ should be similar to that of $\text{MoO}_3(\text{s})$.²⁵ The solid composition in Ueno's experiment was no doubt oxygen-deficient WO_3 because the authors have found that $\text{WO}_3(\text{s})$ preferentially loses oxygen when heated in vacuo at about 900°C . This loss of oxygen is always associated with a color change of the solid from yellow to blue.

3. Gaseous ZrO

The molecular constants of ZrO determined by Lowater³⁶ for the $^3\pi$ state are $\omega_e = 936.6 \text{ cm}^{-1}$, $B_e = 0.619 \text{ cm}^{-1}$, $T_e = 0.297$, and 605 cm^{-1} . According to the analysis by Tanaka and Horie³⁷ the coupling of the angular momenta is not quite Hund's case a. Comparing ZrO with TiO one surmises that an intermediate case between a and b occurs. However, since the electronic contribution to the free energy function is only about 5 per cent of the total, a calculation based on type a will not be significantly in error. Hence one finds for the temperature dependent part of the free energy,

$$f^\circ(\text{ZrO}) = -R'T(9/2 \log T - 0.849 + 105/T) \quad (32)$$

For the dissociation energy of ZrO we accept the value of 7.8 ev given by Herzberg.³⁸ The value for the heat of sublimation of zirconium, ΔH_0° s, given by Skinner, Edwards, and Johnston³⁹ must be corrected for a more accurate free energy function for zirconium solid. Using the heat capacity data obtained by Coughlin and King⁴⁰ and by Skinner and Johnston⁴¹ one finds that

$$f^\circ(\beta\text{-Zr}) = 38.70T - 16.74T \log T + 150 \text{ cal/mole}, \quad (33)$$

and that ΔH_0° s for zirconium in 145.0 kcal/mole instead of 142.1 kcal/mole. Using this information one finds that

$$\Delta F_f^\circ(\text{ZrO}) \cong 25,320 + 7.588T \log T - 45.58T \text{ cal/mole}. \quad (34)$$

4. Gaseous TaO

Fernando and Krishnamurty²³ report a value of 713 cm^{-1} for the vibrational wave number of TaO. Premaswarup⁴² has reported the

³⁶F. Lowater, Phil. Trans. Roy. Soc. (London) 234A, 355 (1935). See also G. Herzberg, Spectra of Diatomic Molecules, D. Van Nostrand Co., Inc. New York, Second ed.

³⁷T. Tanaka and T. Horie, Proc. Phys. Math. Soc. Japan 23, 464 (1941).

³⁸G. Herzberg, Spectra of Diatomic Molecules, D. Van Nostrand Co., Inc. New York, (1950).

³⁹Skinner, Edwards, and Johnston, J. Am. Chem. Soc. 73, 174 (1951).

⁴⁰J. P. Coughlin and E. G. King, J. Am. Chem. Soc. 72, 2262 (1950).

⁴¹G. B. Skinner, and H. L. Johnston, J. Am. Chem. Soc. 73, 4549 (1951).

⁴²D. Premaswarup, Nature 175, 1003 (1955).

interatomic distance of the $^2\Sigma$ ground state to be $1.827\text{\AA}$. If one ignores the contribution of other electronic states the free energy function is

$$f^\circ(\text{TaO}) = 4.576T \log [1 - \exp(-1026/T)] - 16.016T \log T - 11.184T \text{ cal/mole} \quad (35)$$

This equation together with the heat of sublimation and free energy function for tantalum,⁴³ the free energy function of molecular oxygen, and the dissociation energy for TaO(g) , $8.5 \pm 0.5 \text{ ev}$,²⁴ yield for the standard free energy of formation the equation,

$$\Delta F_f^\circ(\text{TaO}) \cong 43,754 - 19.13T \text{ cal/mole.} \quad (36)$$

Equation (36) is a linear approximation of a more complex expression and its use should be restricted to the temperature range $1500^\circ\text{K} \leq T \leq 3000^\circ\text{K}$ over which range the error associated with its use is less than $\pm 5\%$. The principal uncertainty in Eq. (36) results from the relatively large probable error in the dissociation energy of TaO(g) .

5. Gaseous TaO_2

The standard free energy of formation of $\text{TaO}_2(\text{g})$ can be estimated according to the valence force model discussed by Herzberg.³¹ The molecule is arbitrarily assumed to have a non-linear XY_2 structure with a Ta-O distance equal to $1.8\text{\AA}$ and a stretching force constant equal to $10^6 \text{ dynes cm}^{-1}$. The bending force constant and the angle between the two oxygen atoms were obtained by averaging the ratios of force constants and valence angles given by Herzberg. This treatment yields for the three modes of vibration and wave number values, 483, 1065, and 1086 cm^{-1} . Neglecting electronic excitation one obtains the free energy function:

$$f^\circ(\text{TaO}_2) = 32.132T - 32.034T \log T + \frac{436,347}{T} - 3,766 \text{ cal/mole.} \quad (37)$$

This equation when combined with the heat of sublimation and free energy function for tantalum,⁴³ the free energy function for molecular oxygen, and the dissociation energy for $\text{TaO}_2(\text{g})$, $14.9 \pm 0.5 \text{ ev}$,²⁴ yields, for the standard free energy of formation,

$$\Delta F_f^\circ(\text{TaO}_2) \cong -6.650T + 0.505T \log T + 9.773 \times 10^{-4} T^2 + \frac{721,825}{T} - 40,845 \text{ cal/mole} \quad (38)$$

It is interesting to note that equation (38) shows that $\Delta F^\circ(\text{TaO}_2)$ is rather insensitive to temperature over a large range on either side of the minimum value at about 2500°K .

⁴³ Edwards, Blackburn, and Johnston, J. Am. Chem. Soc. 73, 172 (1951).

B. Discussion of Estimated Free Energies

It is important to ascertain whether the free energies for the gaseous oxides derived herein predict certain experimental observations.

If one assumes that the reaction of aluminum oxide with tungsten is represented by the reaction,

then one can calculate the expected volatility from the free energies previously derived. At 2582°K the weight ratio of oxide-to-tungsten transported yields the relation,

$$\beta = \frac{0.554}{w_r} (1 + \frac{\alpha}{2}) \quad . \quad (40)$$

The rate at which aluminum in grams per cm² per minute, w , effuses from a cell is given by the equation,

$$\log w \sqrt{T} = - \frac{29095}{T} + 9.759 \quad , \quad (41)$$

derived by a least square calculation of Brewer and Searcy's data. Using the appropriate relations derived from equation (13) for the pressures of Al₂O, Al and O, together with equation (40), one obtains the result that

$$\log \left\{ \frac{7.04 \times 10^{-6} (0.723 + \alpha) \alpha^2}{(2.593 + \alpha)^2} \right\} = - \frac{\Delta F_D^\circ(\text{Al}_2\text{O})}{R'T} - 2 \log w \sqrt{T}. \quad (42)$$

Substituting the values $\log w \sqrt{T} = -1.509$ and $\Delta F_D^\circ(\text{Al}_2\text{O})/R'T = 8.280$ at 2582°K and solving for α , one finds a value of 2.502. For the equilibrium involving WO₃(g) one finds that

$$\begin{aligned} 2 \log w \sqrt{T} = \log \left\{ \frac{1.63 \times 10^5 (1 + \alpha/2)(2.593 + \alpha)^2}{(0.566 + 0.783 \alpha)^3} \right\} \\ + \frac{1}{R'T} \left\{ \Delta F_f^\circ(\text{WO}_3) - 3/2 \Delta F_D^\circ(\text{O}_2) \right\} \quad . \end{aligned} \quad (43)$$

At 2582°K equation (31) yields $\Delta F_f^\circ(\text{WO}_3) = -35,495$ cal/mole and equation (21) yields $3/2 \Delta F_D^\circ(\text{O}_2) = 58,130$. Hence equation (43) yields a value of 8.4×10^{-2} g deg^{1/2} cm⁻² sec⁻¹ for $w \sqrt{T}$ compared with a value of 3.1×10^{-2} obtained from Brewer and Searcy's data. In view of the extrapolations involved one can only state that reaction (39) is a plausible explanation for

the volatility observed when aluminum oxide is heated in a tungsten container, but one cannot state that the products have been unequivocally established. Gaseous WO_2 may be present.

In the case of the Al_2O_3 -tantalum reaction the free energies for $\text{Al}_2\text{O}(\text{g})$, $\text{Al}(\text{g})$, $\text{Al}_2\text{O}_3(\text{s})$, $\text{TaO}(\text{g})$, $\text{TaO}_2(\text{g})$, and $\text{Ta}_2\text{O}_5(\text{s})$ can be used to predict the vaporization behavior experimentally observed, i.e., the principal gaseous products are $\text{Al}(\text{g})$ and $\text{TaO}(\text{g})$ with lesser amounts of $\text{Al}_2\text{O}(\text{g})$ and $\text{TaO}_2(\text{g})$. It is also interesting to note that these free energies predict pressures that agree within about a factor of two with the pressures obtained by Ruff and Kenschak⁴⁴ when they heated Al_2O_3 in tantalum containers over the temperature range 2633° to 2853°K.

Although to date no investigator has produced positive evidence for the existence of $\text{UO}(\text{g})$, Ackermann, Gilles and Thorn⁹ have estimated an upper limit of 7.5 ev for the dissociation energy as a result of volatility measurements of $\text{U}(\ell)$ - $\text{UO}_2(\text{s})$ mixtures. Based on the results of the uranium dioxide-tantalum interaction at 2500°K, i.e., $P_{\text{UO}} \leq 0.10 P_{\text{UO}_2}$, one can fix a lower limit of the standard free energy of formation of $\text{UO}(\text{g})$ at -42 kcal mole⁻¹. Using this value, some known thermodynamic data, and assumed values of $\omega_e = 500 \text{ cm}^{-1}$ and $r_e = 1.5 \text{ \AA}$ for $\text{UO}(\text{g})$, one is able to fix an upper limit to the dissociation energy. The value of D_0 thus obtained is 7.9 ev.

The standard free energy of formation of $\text{ThO}(\text{g})$ at 2500°K can be calculated from the effusion measurements of Hoch and Johnston¹³ if one interprets their weight losses as resulting primarily from $\text{ThO}(\text{g})$ and $\text{TaO}(\text{g})$. By combining these weight loss data with equation (36) and Coughlin's² ΔF_f° (ThO_2, s) extrapolated to 2500°K, one obtains ΔF_f° (ThO) equal to approximately -53 kcal mole⁻¹. Actually the system is probably complicated by the contribution of $\text{TaO}_2(\text{g})$ to the volatility, as is indicated by the authors' experimental weight ratio at 2753°K, which is larger than the theoretical value for the products, $\text{ThO}(\text{g})$ and $\text{TaO}(\text{g})$. Also, the contribution of $\text{ThO}_2(\text{g})$ to the weight loss is unknown, but is probably of lesser importance. Hence, the value of ΔF_f° (ThO) reported represents only a lower limit.

If one assumes that the beryllia-tungsten interaction is represented by the equation,

then the use of the free energy equation for $\text{WO}_3(\text{g})$ predicts a value of $4.2 \times 10^{-5} \text{ atm}$ for the partial pressure of beryllium at 2462°K, compared

⁴⁴O. Ruff and M. Kenschak, Z. Elektrochem. 32, 515 (1926).

with a value of 4.7×10^{-6} atm obtained by Erway and Seifert. According to Seifert⁴⁵ if the collector which these authors used attained a temperature of 760°C , then one would expect complete reflection of the beryllium vapor. The dissociation energy of BeO listed by Gaydon⁴⁶ predicts insignificant amounts of BeO(g). Hence the "best" interpretation appears to be that most of the beryllium vaporizes as gaseous atoms and that at least one other oxide of tungsten in addition to gaseous WO_3 is present, so that the figure 4.2×10^{-5} atm represents the upper limit and the figure 4.7×10^{-6} atm represents the lower limit for the partial pressure of the beryllium.

Consider the reaction between $\text{ZrO}_2(\text{s})$ and tungsten to yield $\text{ZrO}(\text{g})$ and $\text{WO}_3(\text{g})$. By means of equations (31) and (34), and the equation for $\Delta F_f^\circ(\text{ZrO}_2\text{s})$ given by Coughlin,² one calculates a weight ratio equal to or greater than 70 for ZrO_2 to tungsten transported at 2600°K . The experimental value, ≥ 50 indicates good agreement if the tungsten oxide is correctly interpreted as $\text{WO}_3(\text{g})$.

From equations (21), (34), and the equation for $\Delta F_f^\circ(\text{ZrO}_2\text{s})$ one can calculate the importance of the process

over the temperature range of the volatility measurements of ZrO_2 carried out in a tungsten effusion cell and reported in the previous section. The results of these calculations are reported in Figure 2. The upper line is a plot of equation (7) which shows the experimental points. The partial pressure of $\text{ZrO}_2(\text{g})$ was obtained by subtracting the volatility resulting from equation (45) from the total measured volatility. Hence, for the partial pressure of $\text{ZrO}_2(\text{g})$ above $\text{ZrO}_2(\text{s})$ one obtains the equation

$$\log p(\text{atm}) = \frac{-3.57 \times 10^4}{T} + 8.30 \quad , \quad (46)$$

from which one extracts $163 \text{ kcal/mole}^{-1}$ for the heat and 38.0 eu for the entropy of sublimation of ZrO_2 .

⁴⁵R. L. Seifert, Private communication

⁴⁶A. C. Gaydon, Dissociation Energies, Dover Publications, Inc., New York (1950).

FIGURE 2
PARTIAL PRESSURES OF PRINCIPLE EFFUSING SPECIES
FROM ZrO_2 IN TUNGSTEN CELL.

$$\log P_{\text{ZrO}_2} (\text{atm}) = -3.57 \times 10^4/T + 8.30$$

C. Suggested Trends in Stabilities of Gaseous Oxides

The data presented and discussed previously enable one to suggest certain trends in the stabilities of the gaseous oxides of the A subgroups of the fourth, fifth, and sixth groups of elements. The high-temperature properties of the oxides also suggest that thorium can be considered as a Group IV A element, uranium as a Group VI element, and probably protactinium as a Group V A element; hence they will be so considered here. In the case of the gaseous monoxides the most stable ones are those of Group IV A (i.e., TiO , ZrO , HfO , ThO); the next most stable ones are those of Group V A elements (i.e., VO , TaO , etc.); and the least stable are those of Group VI A. The last probably will be observed only under very special conditions. The situation with respect to the dioxides is less clearly defined. With regard to all known modes of decomposition UO_2 appears to be the most stable dioxide. The dioxides of Group IV A appear to be more stable than those of Group V A. However, this aspect needs further study. It appears that the gaseous trioxides of Group VI A are the most stable and apparently the trioxides of the other two groups are of no importance.