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Thermodynamics of the Ta-O System: The Dissociation Energies of TaO and TaO_2^{\dagger}

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Mass spectrometric analysis of the vapor in thermodynamic equilibrium with mixtures of Ta(s) and $Ta_2O_5(s)$ has shown TaO and TaO₂ to be the predominant gaseous molecules present. The experimental data yield 8.4 ± 0.5 ev and 15.0 ± 0.5 ev for the energies of atomization of these molecules at 0° K.

INTRODUCTION

HERE is very little information available on the thermodynamics of the Ta-O system. Brewer¹ has indicated that the vapor pressure of Ta_2O_5 is less than 10⁻³ atmos at 2000°K, Kiess and Stowell² have reported some emission bands which they have attributed to the TaO molecule, and Premaswarup^{3,4} has given preliminary rotational and vibrational analyses of some TaO bands. Thus no definitive information exists concerning (1) the volatility of the oxides of tantalum, (2) the nature of the gaseous species involved, or (3) the dissociation energies of these species. This study was undertaken to provide some of the answers to these questions.

Our interest in the Ta-O system was aroused in part by earlier mass spectrometric studies of the species vaporizing when ZrO₂ was heated in a tantalum Knudsen cell.⁵ Such studies showed that the vapor in the cell was predominantly a mixture of ZrO(g), TaO(g), and $TaO_2(g)$ rather than just $ZrO_2(g)$ as it had been assumed previously.6 Hence a revision of the thermodynamic data on ZrO2 was necessary. Since tantalum has been used extensively for Knudsen cell studies of oxide systems it is important to understand the Ta-Osystem itself.

EXPERIMENTAL ARRANGEMENT

The 60°-sector 12-in. radius of curvature single focusing mass spectrometer used for these experiments, as well as the associated Knudsen cell assembly, have been described earlier.7 The Knudsen cell used was of such size that the ratio of effusion hole area to inner geometric surface area, generally denoted by σ , was slightly less than 0.001. The first experiments were carried out with Ta₂O₅ powder inside a tantalum Knudsen cell. Later experiments employed an intimate mixture of Ta and Ta₂O₅ powders within the cell. The gaseous species observed under these conditions were TaO and TaO₂ indicating either that (1) Ta_2O_5 was being reduced by the tantalum cell or that (2) the vaporization of Ta₂O₅ involved liberation of oxygen. Due to large backgrounds at the O and O_2 positions, mass 16 and 32, it was difficult to rule out the latter hypothesis. However, severe attack of the tantalum cell by Ta_2O_5 shows that process (1) took place and was probably dominant. Although the data are conflicting, several investigators^{8,9} report x-ray evidence for a number of phases between Ta and Ta₂O₅. To further verify the interpretation of our experiments, Ta₂O₅ powder was vaporized from a tungsten crucible. Because the reaction of Ta₂O₅ with the cell leads to uncertainties in interpretation, a final cross check experiment was carried out using intimate mixtures of ZrO₂ and Ta powders in a tantalum cell.

EXPERIMENTAL RESULTS

In all of the above experiments two gaseous ions containing tantalum were observed, TaO⁺ and TaO₂⁺, corresponding to the gaseous molecules TaO and TaO₂. A search was made for polymeric tantalum oxide ions up to mass 950 with special care on Ta₂O₅ and Ta₄O₁₀. No such species were observed, the upper limit to their concentration in our experiments being one part in five hundred of the partial pressure of TaO₂. If molecules heavier than mass 950 were present in significant quantities they would have been observed indirectly as lower molecular weight fragments produced by the ionizing electron beam. No such fragment ions were observed. The absence of higher polymers may have been due to the reducing environments employed. Even in the less reducing tungsten cell, as was indicated by the larger TaO₂/TaO ratio, ion beams corresponding to WO3 and WO2 (and possibly WO) were observed in quantities comparable to the TaO2. It is, of course, still

[†] Supported by a joint program of the National Science Foundation and the Office of Ordnance Research.

¹ L. Brewer, Chem. Revs. 52, 8 (1953).

² C. C. Kiess and E. Z. Stowell, Bur. Standards J. Research 12, 459 (1934).

 ⁵⁹ (1954).
 ⁸ D. Premaswarup, Nature 175, 1003 (1955).
 ⁴ D. Premaswarup, Indian J. Phys. 29, 109–121 (1955).
 ⁵ Chupka, Berkowitz, and Inghram, J. Chem. Phys. (to be

published) ⁶ Hoch, Nakata, and Johnston, J. Am. Chem. Soc. 76, 2651

^{(1954).}

⁷ See, for example, W. A. Chupka and M. G. Inghram, J. Phys. Chem. 59, 100 (1955).

⁸ N. Schönberg, Acta Chem. Scand. 8, 240-245 (1954).

⁹ R. J. Wasilewski, J. Am. Chem. Soc. 75, 1001 (1953).

TABLE I. Heats of sublimation by the absolute pressure method.^a

Temp. °K	Partial pres- sure, atmos	ΔF_{T^0}	$\Delta S T^0$	$\Delta H \tau^{0}$	$\Delta H_{298^{0}}$	Remarks
A. TaO						
2148	1.35×10-6	57.7	(37.4)	(138.1)	(147.3)	Ta ₂ O ₅
2275	1 42×10-5	50.5	33.7	127.3	143.8	in Ta
2019	2.74×10-7	60.6	37.8	136.9	143.8	crucible
2176	1.66×10 ⁻⁶	57.6	34.0	131.6	148.1)	Ta and Ta ₂ O ₅
2194	1.82×10^{-6}	57.6	33.9	132.1	148.6	in Ta
2170	2.16×10 ⁻⁶	56.3	34.0	130.1	146.6 J	crucible
2210	4.6 ×10 ⁻⁷	64.1	33.9	139.1	155.6)	Activity
2309	2.4 ×10 ⁻⁶	59.4	33.6	137.1	153.6	diminishing
				Av	=145.8 k	cal/mole
B. TaO ₂						
2148	1.55×10-6	57.1	(37.5)	(137.7)	(152.7)	Ta ₂ O ₅
2019	6.84×10 ⁻⁷	57.0	(30.7) 38.0	(122.7) 133.7	(152.1) 146.7	in Ta crucible
2176	2.60×10 ⁻⁶	55.6	30.6	122.2	151.2)	Te end Te A
2206	2.18×10^{-6}	57.1	30.5	124.4	153.4	Ta and Ta ₂ O ₂
2020	2.72×10 ⁻⁷	60.7	38.0	137.5	150.5	ill Id
2170	3.5 ×10 ^{−6}	54.2	30.6	120.6	149.6)	crucipie
2207	7.6 ×10 ⁻⁷	61.8	30.5	129.2	158.2 \	Activity
2314	4.6 ×10 ⁻⁶	56.5	30.1	126.3	155.5	diminishing
				Av	=152.2 k	cal/mole

Parentheses indicate uncertainty of calculations due to lack of more precise information regarding the melting point and heat of fusion of TarOs. Results obtained with diminishing activity have not been averaged in obtaining the final values.

possible that under neutral or oxidizing conditions higher oxides of tantalum may exist in the gaseous phase.

The procedure for treating the data obtained has been described previously.⁷ For the present study the sensitivity of the machine was determined by vaporizing a known mass of silver from the cell and determining the integrated ion current resulting therefrom. This calibration experiment gave a constant of proportionality relating ion current to pressure. Using this constant and making small corrections for relative ionization cross sections and secondary electron production efficiencies at the electron multiplier, a given ion current of TaO+ could be identified with a partial pressure of TaO within the Knudsen cell. In a similar way TaO_2^+ could be identified with the partial pressure of TaO_2 within the cell. The subsequent analysis assumes the following reactions to take place in the tantalum cell:

$$\frac{1}{5} \operatorname{Ta}(s) + \frac{2}{5} \operatorname{Ta}_{2} \mathcal{O}_{5}(s) \to \operatorname{Ta}\mathcal{O}_{2}(g) \tag{1}$$

$$\frac{3}{5}\mathrm{Ta}(s) + \frac{1}{5}\mathrm{Ta}_{2}\mathrm{O}_{5}(s) \rightarrow \mathrm{TaO}(g).$$
(2)

The fact that lower oxides of tantalum probably were present, instead of the simple Ta-Ta₂O₅ mixture assumed in reactions (1) and (2), complicates the situation. However, since there are no thermodynamic data available for these oxides, and since it is likely that the heats of formation of these oxides from Ta and Ta₂O₅ are not large, this is the most feasible way to treat the data. The experiment mentioned above in which the

cell contained a mixture of Ta and ZrO₂ was carried out in order to check the validity of this treatment.

From the partial pressures of TaO and TaO₂ the standard free energies of reactions (1) and (2) can be computed by use of the relation

$$\Delta F_T^0 = -RT \ln P. \tag{3}$$

An estimate of the entropy change for reactions (1) and (2) then permits the calculation of the heats of sublimation of these species from the equation

$$\Delta F^0 = \Delta H - T \Delta S^0. \tag{4}$$

The estimate of entropy change is complicated by the scarcity of data on these molecules. The heat capacity of Ta(s) given by Kelley^{9,10} has been extrapolated beyond the 1900°K limit set by Kelley. Recent heat capacity studies for $Ta_2O_5(s)^{11}$ extend only to 1800°K. Brewer¹ gives $2150^{\circ} \pm 100^{\circ}$ K as the melting point of Ta₂O₅. Since most of our measurements were above this temperature, it was necessary to estimate an entropy and heat of fusion for Ta_2O_5 , as well as a heat capacity for $Ta_2O_5(1)$.¹² Fortunately, only a fraction of the error incurred by these estimates manifests itself in the calculated heats of sublimation.

The rotational analysis of Premaswarup³ indicates that the ground electronic state of TaO is ${}^{2}\Sigma$, having an internuclear distance of 1.827 A. Using these results and a vibrational energy contribution computed from the vibrational frequency given by Premaswarup,4 the gaseous entropy values listed in Table I were calculated. For computing the entropy of $TaO_2(g)$, the same Ta-Odistance was employed and the molecule was assumed to be linear.

The heats of reaction deduced from the foregoing information are summarized in Table I. The relative ionization cross sections of TaO: TaO2: Ag have been taken as 1, while secondary electron efficiencies taking into account both mass¹³ and molecular structure¹⁴ were taken to be 0.8:0.8:1. The partial pressures of TaO and TaO₂ were observed to diminish slowly with time. This was probably due to reaction of Ta₂O₅ with the tantalum cell. In addition the ratio TaO^+/TaO_2^+ increased with time, varying by a factor of 10 from the beginning to the very end of an experiment. This served to show that the major part of the TaO+ observed was produced by direct ionization of TaO rather than by dissociative ionization of TaO₂, since in the latter case the ratio TaO+/TaO2+ would remain constant. Further evidence for the existence of the gaseous TaO species in the concentrations reported is provided by appearance po-

¹⁰ K. K. Kelley, U. S. Bur. Mines, Bull. 476, p. 180 (1949).
¹¹ R. L. Orr, J. Am. Chem. Soc. 75, 2808 (1953).
¹² The estimates suggested by K. K. Kelley (private communication) were employed here, viz. 16.8 cal/deg mole as the entropy of function of the prior of the prior of the prior of the prior. of fusion, 56 cal/deg mole as C_p for Ta₂O₅(1).

 ¹³ Inghram, Hayden, and Hess, Mass Spectroscopy in Phys.
 Research, N.B.S. Circular 522, 257 (1953).
 ¹⁴ Stanton, Chupka, and Inghram, Revs. Sci. Instr. 27, 109

^{(1956).}

tential measurements which were made when the TaO^+/TaO_2^+ ratio was that indicated by Table I. The measurements yielded 6 ± 0.5 ev and 9 ± 0.5 ev for TaO⁺ and TaO₂⁺, respectively. Attempts to obtain an accurate temperature dependence of vapor pressure for TaO and TaO_2 were not successful because of the change of activity with time. Instead, the third experiment mentioned above, was carried out. In this experiment a mixture of ZrO₂ and Ta powders was placed in a tantalum Knudsen cell, and the reaction

$$\operatorname{ZrO}_2(s) + \operatorname{Ta}(s) \longrightarrow \operatorname{ZrO}(g) + \operatorname{TaO}(g)$$
 (5)

was assumed to occur. The equilibrium constant of the reaction could be computed at a particular temperature by an extension of the methods previously outlined. For example, at 2288°K the measured vapor pressures of ZrO and TaO were 3.56×10⁻⁶ atmos and 1.79×10⁻⁶ atmos, respectively. Hence, $\Delta F^0 = -RT \ln K_{eq}$

$$= -4.567 \times 2288 \times \log(3.56 \times 1.79 \times 10^{-12})$$

$$\Delta F^{0} = 117.2 \text{ kcal/mole.}$$

The entropy change for this reaction was computed to be 80.9 eu. Thus the enthalpy change is 302.4 kcal/mole. The relationship,

$$d\ln K/dT = \Delta H/RT^2,$$
 (6)

describing the temperature variation of this equilibrium constant was also used to deduce the heat of this reaction. A plot of the experimental data is shown in Fig. 1. The slope obtained corresponds to $\Delta H_{2200} = 317 \pm 7$ kcal/mole.

By appropriate combination of thermodynamic data, the enthalpies of reaction corresponding to Eqs. (2) and (5) can be used to deduce a dissociation energy for TaO by two independent methods. With Eq. (2), the data required are as follows:

$$\frac{{}^{2}_{5}}{5}Ta(s) + \frac{1}{2}O_{2}(g) \rightarrow \frac{1}{5}Ta_{2}O_{5}(s); \Delta H_{0}^{15} = -98 \text{ kcal/mole}$$
(7)

 $\frac{3}{5}$ Ta(s) $+\frac{1}{5}$ Ta₂O₅(s) \rightarrow TaO(g); $\Delta H_0 = 146$ kcal/mole (8)

$$Ta(g) \rightarrow Ta(s); \Delta H_0^{16} = -186 \text{ kcal/mole}$$
 (9)

$$O(g) \rightarrow \frac{1}{2}O_2(g); \quad \Delta H_0^{17} = -59 \text{ kcal/mole.}$$
(10)

Addition of these equations yields

or

$$Ta(g)+O(g) \rightarrow TaO(g); \quad \Delta H_0 = -197 \text{ kcal/mole}$$

$$D_0 = 8.5_4 \pm 0.5$$
 ev.

A similar combination of data can be used to deduce the energy of atomization of TaO₂, and yields 15.0 ± 0.5



FIG. 1. Variation of $\log K_{eq}$ with 1/T for the reaction Ta(s) $+ZrO_2(s) \rightarrow TaO(g) + ZrO(g)$. Arbitrary units have been chosen for the ordinate.

ev. With reaction (5) we proceed as follows:

$$ZrO_2(s) + Ta(s) \rightarrow ZrO(g) + TaO(g);$$

 $\Delta H_0 = 335 \text{ kcal/mole}$ (11)

$$ZrO_2(g) \rightarrow ZrO_2(s); \quad \Delta H_0^5 = -187 \text{ kcal/mole}$$
(12)

$$Ta(g) \rightarrow Ta(s); \quad \Delta H_0^{17} = -186 \text{ kcal/mole}$$
(13)

$$O(g) + ZrO(g) \rightarrow ZrO_2(g);$$

$$\Delta H_0^5 = -154.5 \text{ kcal/mole.} \quad (14)$$

This summation yields $8.3_5 \pm 0.5$ ev for the dissociation energy of TaO.

DISCUSSION OF RESULTS

It is to be noted that the procedure based on Eq. (5)eliminates all estimates regarding the properties of Ta_2O_5 . In addition, the slope of the plot in Fig. 1, used to determine the enthalpy of this reaction, is independent of ionization efficiencies and secondary electron efficiencies. Hence, despite the numerous estimates described in Sec. III, there is good evidence for the accuracy of the results quoted.

The dissociation energy obtained for TaO shows that it is one of the most stable of the diatomic molecules. In Gaydon's¹⁸ compilation, only CO and N₂ definitely have higher dissociation energies.

¹⁵ G. L. Humphrey, J. Am. Chem. Soc. 76, 978 (1954).

 ¹⁶ L. Brewer, University of California Radiation Laboratory Rept. 2854 (November, 1955).
 ¹⁷ P. Brix and G. Herzberg, Can. J. Phys. 32, 110 (1954).

¹⁸ A. G. Gaydon, Dissociation Energies (Dover Publications, New York, 1950).