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Mass spectrometric study of the thermochemistry of gaseous EuTiO_3 and TiO_2

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The gaseous molecule EuTiO_3 has been investigated in a high temperature mass spectrometric study of vapors over the europium–titanium–oxygen system. From the enthalpy of reaction: $\text{EuTiO}_3(\text{g}) = \text{EuO}(\text{g}) + \text{TiO}_2(\text{g})$ and proper ancillary data, the atomization energy of this molecule has been determined. In addition, from the study of the gaseous exchange reaction: $\text{TiO}_2(\text{g}) + \text{Eu}(\text{g}) = \text{TiO}(\text{g}) + \text{EuO}(\text{g})$ the dissociation energy of $\text{TiO}_2(\text{g})$ has been derived and compared with previous results. The dissociation energies proposed are: $D_{0,\text{at}}^\circ(\text{EuTiO}_3) = 2278 \pm 28 \text{ kJ mol}^{-1}$ and $D_{0,\text{at}}^\circ(\text{TiO}_2) = 1260 \pm 12 \text{ kJ mol}^{-1}$.

I. INTRODUCTION

As part of a continuing investigation of the chemical reactivity of europia with refractory metals and alloys at high temperatures under vaporization conditions, as well as on the nature, stability, and relative importance of the possible gaseous mixed oxides products,^{1–4} mass spectrometric measurements were made on the system europium–titanium–oxygen. We present here the results of the study of a gaseous reaction from which the thermodynamic properties of $\text{EuTiO}_3(\text{g})$, the first europium mixed oxide molecule of the IVB group metals to be identified, are derived.

Under the conditions of the experiments it was also possible to study a new gaseous exchange reaction involving europium and titanium oxides the result of which further contribute to the knowledge of the dissociation energy of $\text{TiO}_2(\text{g})$.^{5,6,13}

II. EXPERIMENTAL

Details of the apparatus employed, a combination of a 30.5 cm radius of curvature, magnetic deflection, 60° single focusing mass spectrometer coupled with a Knudsen cell molecular source, as well as the general features of the method and procedure have been described elsewhere.^{8,9}

Intimate mixtures of Eu_2O_3 and TiO_2 reagents (with a stated purity of 99.9% and 99.5%, respectively, from Koch–Light Laboratories) in the approximate molar ratios $\text{Eu}_2\text{O}_3:\text{TiO}_2$ ranging from 0.85 to 1.27 were used as initial samples in the various vaporization experiments. In all cases a molybdenum crucible with an effusion orifice 1 mm in diameter was used as a Knudsen cell and the cell itself was heated by electron bombardment from a tungsten strip or by radiation from a tungsten spiral resistance element. The cell temperatures were measured with a disappearing optical pyrometer by sighting into a blackbody cavity in the bottom of the cell and proper corrections were made from prism and window transmission. The vapors effusing from the cell were ionized using electron energies of 70 eV, or less in the appearance potential studies.

III. RESULTS AND DISCUSSION

A. Identification of ions

The ions produced were identified in the usual manner, i.e., according to their mass-to-charge ratios, isotopic abundance distributions, shutter profiles, and appearance potentials (AP). The AP value for EuTiO_3^+ , obtained by the linear extrapolation method, was found to be $6.5 \pm 0.5 \text{ eV}$ on an electron energy scale where the AP values, given in brackets, for $\text{Eu}^+(6)$, $\text{EuO}^+(6.5)$, $\text{TiO}^+(6.5)$, and $\text{TiO}_2^+(9)$ agree with reported values^{1,2,4,6} within the $\pm 0.5 \text{ eV}$ uncertainty.

Shutterable peaks at isotopic masses corresponding to the EuTiO_2^+ ion were also observed, but due to a rather large contribution from spurious effects (e.g., surface ionization) to the intensity, the possible presence of small amounts of parent ions could not be positively ascertained. Therefore, the portion of the shutterable ion intensity in excess of the surface ionization contribution was assigned to the EuTiO_2^+ fragment (which, moreover, was fairly temperature independent) coming from the dissociative ionization of $\text{EuTiO}_3(\text{g})$ and the measured EuTiO_3^+ intensity was corrected in accord. Corrections were also applied to take into account the multiple ionization processes of $\text{Eu}(\text{g})$ and the contribution to the EuO^+ intensity coming from the dissociative ionization of $\text{EuMoO}_4(\text{g})$ small amounts of which were observed in the initial part of the experiments with fresh Mo crucibles.

With regards to the dissociative ionization of $\text{TiO}_2(\text{g})$ to TiO^+ and Ti^+ both these processes were reported to be important at 70 eV with $\text{TiO}_{\text{frag}}^+/\text{TiO}_2^+$ and $\text{Ti}_{\text{frag}}^+/\text{TiO}_2^+$ ratios larger than unity from a study of the ionization efficiency curves.¹⁰ However, these findings disagree with the upper limits for the aforementioned ratios obtained by taking the total intensities of TiO^+ and Ti^+ ions measured under suitable conditions as entirely due to fragment ions. Indeed, the upper limit for the ratio $\text{TiO}_{\text{frag}}^+/\text{TiO}_2^+$ measured at 70 eV was set at $\leq (2.5 \pm 1.3)\%$, and the “true” value was inferred to be probably very nearly zero by Gilles and co-workers.¹¹ In the course of the present investigation we could establish an upper limit of 0.07 for the extent of fragmentation of

$\text{TiO}_2(\text{g})$ to Ti^+ at 70 eV, in agreement with the limit of 0.1 measured at 100 eV in a previous study.¹²

For the dissociative ionization of $\text{TiO}(\text{g})$ to Ti^+ , the results of Banon *et al.*¹⁰ agree with the upper limit of 0.04 for $\text{Ti}_{\text{frag}}^+/\text{TiO}^+$ we measured in the present investigation. Therefore we chose not to apply corrections in the measured TiO^+ and TiO_2^+ intensities for use in the subsequent thermodynamic calculations and to discuss *a posteriori* the effects of a few percent of fragmentation contribution on the obtained results. To sum up, the relations for obtaining the intensities of the parent ions, I_p , utilized in the computations from the raw intensities, I , measured at 70 eV were the following

$$I_p(\text{Eu}^+) = 1.35I(\text{Eu}^+);$$

$$I_p(\text{EuO}^+) = I(\text{EuO}^+) - I(\text{EuMoO}_4^+);$$

$$I_p(\text{TiO}^+) = I(\text{TiO}^+); \quad I_p(\text{TiO}_2^+) = I(\text{TiO}_2^+);$$

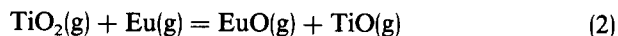
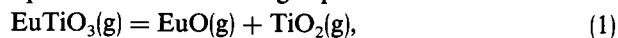
$$I_p(\text{EuTiO}_3^+) = 1.2I(\text{EuTiO}_3^+).$$

The corrected ion intensities were converted into pressures through silver calibration runs repeatedly performed in the course of the investigation. The electron multiplier yields were taken as proportional to the inverse square root of the ion mass. The maximum atomic cross sections were taken from the Mann's compilation,¹³ for the molecules they were estimated in the same manner as reported in previous investigations.^{1,2,4} Their values are: 6.80, 10.83, 14.60, 13.16, 24 for TiO , TiO_2 , Eu , EuO , and EuTiO_3 , respectively.

The calculated partial pressures are reported in Table I. It is worth noting that these pressures do not have the significance of equilibrium partial pressures over a well specified condensed phase; however, the values reported for the relevant species are indicative of the detectability conditions for $\text{EuTiO}_3(\text{g})$.

B. Reaction enthalpies and dissociation energies for $\text{EuTiO}_3(\text{g})$ and $\text{TiO}_2(\text{g})$

The partial pressures given in Table I were used to derive equilibrium data for the gas-phase reactions:



which have been studied rather extensively (16 and 14 data points, respectively) in the temperature interval 2229–2489 K.

The necessary thermodynamic functions for use in the second-law and third-law evaluation of the reaction enthalpies were taken from literature for $\text{Eu}(\text{g})$,¹ $\text{EuO}(\text{g})$,¹ $\text{TiO}(\text{g})$,⁵ and $\text{TiO}_2(\text{g})$,⁵; for $\text{EuTiO}_3(\text{g})$ they were calculated from estimated molecular parameters. For this molecule a ring structure of c_{2v} symmetry, the same hypothesized for $\text{EuVO}_3(\text{g})$,⁴ was adopted and the molecular constants were estimated according to the same criteria used in deriving those of $\text{EuVO}_3(\text{g})$.⁴ The bond lengths resulting were: $r(\text{Ti}-\text{O}) = 0.183$, $r(\text{Ti}=\text{O}) = 0.169$, and $r(\text{Eu}-\text{O}) = 0.220$ nm; The bond angle $\text{O}-\text{Ti}-\text{O}$ was taken as 120° . The force constants were estimated in a similar fashion as in $\text{EuVO}_3(\text{g})$ ⁴ and the vibrational frequencies were evaluated by the G - F matrix method. The resulting values of the nine normal frequencies were: 705, 961, 349, 202, 907, 331, 253, 304, and 70 cm^{-1} . The electronic contribution was taken as zero.

Calculated values of the Gibbs energy function, $-(G_T^\circ - H_0^\circ)/T$ were: 279.585, 434.525, 439.262, 443.800, 448.156, 452.344, and 456.375 $\text{J K}^{-1} \text{ mol}^{-1}$ at the temperatures of 298.15, 2000, 2100, 2200, 2300, 2400, and 2500 K, respectively. At the same temperatures the enthalpy increments $(H_T^\circ - H_0^\circ)$ were 18.318, 193.673, 204.393, 215.120, 225.854, 236.594, and 247.340 kJ mol^{-1} , respectively.

As shown in Tables II and III the second- and third-law enthalpies agree within the quoted errors which represent the standard deviations on slopes and experimental points.

TABLE I. Measured partial pressures of the gaseous species involved in the equilibria (1) and (2) in atm.^{a,b}

T/K	$P(\text{TiO}) \times 10^6$	$P(\text{TiO}_2) \times 10^6$	$P(\text{Eu}) \times 10^6$	$P(\text{EuO}) \times 10^6$	$P(\text{EuTiO}_3) \times 10^8$
2489	37.3	15.4	54.9 ₅	6.44	20.2
2390	...	3.42	...	3.99	7.99 ₅
2246	0.431	0.404 ₅	10.8	1.57	...
2401	8.86	4.45	34.7	4.00 ₅	9.51
2407	11.7	5.10	28.4	2.89 ₅	7.04
2393	16.9	6.30 ₅	13.4	1.12	3.98 ₅
2229	...	1.14 ₅	...	0.090 ₅	0.417
2387	21.4	7.26 ₅	11.2	0.822	3.51
2432	36.9 ₅	11.3 ₅	13.8 ₅	1.03 ₅	4.28
2302	0.296 ₅	0.274	32.2	5.30 ₅	2.32 ₅
2463	5.41 ₅	3.77	78.5	14.3 ₅	14.3 ₅
2381	10.8	4.81	15.7 ₅	1.54	4.87 ₅
2347	9.14	3.60	9.74	0.769 ₅	2.60 ₅
2268	...	1.64	4.24	0.238	0.928 ₅
2291	5.18 ₅	1.92	3.65 ₅	0.233	0.817
2350	11.1 ₅	4.11	5.71	0.424	1.63
2395	23.0	7.35	9.46	0.683	2.69

^a 1 atm = 101 325 Pa.

^b The number of digits merely reflects the necessity of minimizing the numerical inconsistencies.

TABLE II. Equilibrium data for the reaction: $\text{EuTiO}_3(\text{g}) = \text{EuO}(\text{g}) + \text{TiO}_2(\text{g})$, $-\Delta(G_T^\circ - H_0^\circ)/T$ in $\text{J K}^{-1} \text{mol}^{-1}$, heat of reaction in kJ mol^{-1} .

T/K	$-\ln Kp$	$-\Delta(G_T^\circ - H_0^\circ)/T$	ΔH_0°
2489	7.62	158.85	553.0
2390	8.67 _s	159.23	552.9
2401	8.58	159.19	553.5
2407	8.47	159.16	553.6
2393	8.64	159.22	552.8
2229	10.60	159.89	552.8
2387	8.68	159.24	552.4
2432	8.20	159.07	552.7
2302	9.68	159.59	552.7
2463	7.88	158.95	553.0
2381	8.79	159.27	553.3
2347	9.15	159.40	552.7
2268	10.08	159.72 _s	552.4
2291	9.81	159.63	552.6
2350	9.14 _s	159.39	553.3
2395	8.58 _s	159.21	552.3
Avg ΔH_0° : 552.8 ± 0.4			
T_{avg} : 2257			
2nd law ΔH_T° : 527.5 ± 3.1			
2nd law ΔH_0° : 549.8 ± 3.1			
Proposed ΔH_0° : 551 ± 25			

This agreement and the lack of appreciable temperature trends in the individual third-law enthalpies could, however, be in part accidental because the effects of the various sources of errors could have been compensatory.

Among the sources of uncertainties, the effects of fragmentation should not have been of particular importance in the present case as compared with the assumptions made in the intensity-to-pressure conversion and in the structures used for thermodynamic function calculations. This is particularly true in the case of the pressure-dependent reaction (1) which requires instrumental calibration and involves the novel species $\text{EuTiO}_3(\text{g})$ for which the molecular structure and related parameters had to be completely estimated. Moreover, in this case, due to the much lower concentrations compared to those of $\text{EuO}(\text{g})$ and $\text{TiO}_2(\text{g})$, possible errors in the fragmentation estimated for the molecular species involved should have affected the calculated equilibrium constants only by a constant factor which may be included in the uncertainties associated to the cross sections estimates.

In the case of reaction (2) similar considerations hold for the effects of possible errors in the fragmentation contributions of $\text{TiO}(\text{g})$ and $\text{TiO}_2(\text{g})$ to Ti^+ , while the introduction of, say, a 5% fragmentation of $\text{TiO}_2(\text{g})$ to TiO^+ would raise the third-law values by 1.5 kJ mol^{-1} and the second law by 5.2 kJ mol^{-1} , respectively. It is however to be noted that different estimates of the molecular cross sections (e.g., by assuming the additivity of the atomic cross sections) would result in a third-law enthalpy variation of 2.9 kJ mol^{-1} for reaction (1) and 10.5 kJ mol^{-1} for reaction (2); additional uncertainties are introduced with the thermodynamic functions estimates for $\text{TiO}_2(\text{g})$ and $\text{EuO}(\text{g})$.¹⁴

In connection with the use of the second-law procedure, even if the data sets reported can not be considered as fully statistical ensembles, gross failures due to the statistical

treatment are unlikely. Indeed, the variations caused by different ion intensities and temperature readings within the accuracy of the measurements were found comparable with the reported standard deviations. These variations are similar for the two reactions but, while for the reaction (1) they are much less important as compared to the uncertainty introduced in the third law because of the Gibbs functions estimates for $\text{EuTiO}_3(\text{g})$, in the case of reaction (2) they are of comparable importance provided that the adopted ground state degeneracy for $\text{EuO}(\text{g})$ is not wrong. Assuming that errors in temperature measurements may affect the second-law results more, and assuming that, due to their number and nature, the various sources of uncertainty most probably do not act all in the same direction, we selected for the enthalpies of reactions (1) and (2) the average values of the respective second-law and third-law results with associated estimated standard deviations which should account for all the uncertainties in data acquisition and evaluation. The resulting selected values are $\Delta H_0^\circ(1) = 551 \pm 25 \text{ kJ mol}^{-1}$ and $\Delta H_0^\circ(2) = 118 \pm 12 \text{ kJ mol}^{-1}$.

For the ancillary data required for deriving the atomization energy of $\text{EuTiO}_3(\text{g})$ from reaction (1), the values adopted were $D_0^\circ(\text{EuO}) = 467 \pm 6 \text{ kJ mol}^{-1}$, as discussed and used in previous works,^{1,2,4,15} and $D_0^\circ(\text{TiO}_2) = 1260 \pm 12 \text{ kJ mol}^{-1}$. This last value has been obtained by combining $D_0^\circ(\text{TiO}) = 668 \pm 8.4 \text{ kJ mol}^{-1}$ given recently by Pedley and Marshall,¹⁶ who quote practically the same value as in the compilation of Gurvich *et al.*, with the value $592 \pm 8 \text{ kJ mol}^{-1}$ for the difference $D_0^\circ(\text{TiO}_2) - D_0^\circ(\text{TiO})$. This value has been selected by averaging the results obtained for the other two gaseous exchange reactions leading to this difference, namely: $\text{TiO}_2(\text{g}) + \text{Ti}(\text{g}) = 2\text{TiO}(\text{g})$ and $\text{TiO}(\text{g}) + \text{WO}_3(\text{g}) = \text{TiO}_2(\text{g}) + \text{WO}_2(\text{g})$, in addition to the novel reaction (2) we have studied here.

The reaction $\text{TiO}_2(\text{g}) + \text{Ti}(\text{g}) = 2\text{TiO}(\text{g})$ has been studied by various authors and the results of these studies prior to

TABLE III. Equilibrium data for the reaction: $\text{TiO}_2(\text{g}) + \text{Eu}(\text{g}) = \text{EuO}(\text{g}) + \text{TiO}(\text{g})$, $-\Delta(G_T^\circ - H_0^\circ)/T$ in $\text{J mol}^{-1} \text{K}^{-1}$, heat of reaction in kJ mol^{-1} .

T/K	$-\ln Kp$	$-\Delta(G_T^\circ - H_0^\circ)/T$	ΔH_0°
2489	1.26	36.72	117.5
2246	1.86 _s	36.87	117.7
2401	1.47	36.78	117.7
2407	1.45 _s	36.77 _s	117.6
2393	1.49 _s	36.78	117.7
2387	1.53	36.79	118.2
2432	1.41	36.76	118.0
2302	1.72 _s	36.83 _s	117.8
2463	1.33 _s	36.74	117.9
2381	1.51 _s	36.79	117.6
2347	1.60 _s	36.81	117.7
2291	1.76	36.84	117.9
2350	1.60	36.81	117.8
2395	1.49	36.78	117.7
Avg ΔH_0° : 117.7 ± 0.2			
T_{avg} : 2376			
2nd law ΔH_T° : 115.2 ± 1.7			
2nd law ΔH_0° : 118.6 ± 1.7			
Proposed ΔH_0° : 118 ± 12			

1975 were reviewed and reevaluated using new thermodynamic functions for $\text{TiO}_2(\text{g})$ in the JANAF Tables 1975 Supplement.⁵ The average of the values of the reaction enthalpy resulting from the JANAF analysis⁵ is in accord with the result of a later study by Hildenbrand.⁶

The analysis of all the results reported for the same reaction by Pedley and Marshall¹⁶ leads to an average reaction enthalpy of $-65 \pm 9.4 \text{ kJ mol}^{-1}$. This value, when combined with $D_0^\circ(\text{TiO}) = 668 \pm 8.4 \text{ kJ mol}^{-1}$ yields $D_0^\circ(\text{TiO}_2) - D_0^\circ(\text{TiO}) = 603 \pm 14 \text{ kJ mol}^{-1}$ which is somewhat higher but not inconsistent with the value we obtained in the present experiments from reaction (2), namely, $585 \pm 13 \text{ kJ mol}^{-1}$.

The isomolecular exchange reaction $\text{TiO}(\text{g}) + \text{WO}_3(\text{g}) = \text{TiO}_2(\text{g}) + \text{WO}_2(\text{g})$ has been studied, though not in great detail, by Hampson and Gilles;¹⁷ the analyses of their data as made by JANAF Tables⁵ compilers and by Pedley and Marshall¹⁶ lead to the values of 11.1 ± 2.1 and $13.7 \pm 0.4 \text{ kJ mol}^{-1}$, respectively, for the 0 K enthalpy of reaction, where the errors associated are standard deviations. For the difference $D_0^\circ(\text{WO}_3) - D_0^\circ(\text{WO}_2)$ employed in deriving $D_0^\circ(\text{TiO}_2) - D_0^\circ(\text{TiO})$, the value of $614 \pm 10 \text{ kJ mol}^{-1}$ utilized by Pedley and Marshall¹⁶ following JANAF Tables⁵ is somewhat higher than both the values of $594 \pm 23 \text{ kJ mol}^{-1}$, as deduced from the data adopted by Gurvich *et al.*,⁷ and of $602.5 \pm 4.6 \text{ kJ mol}^{-1}$ we selected and used in previous studies.^{1,15} As the different values are substantially due to different evaluations of the same data, and the value we adopted is practically coincident with the average of the three values, its selection still appears a reasonable choice. Thus, combining $D_0^\circ(\text{WO}_3) - D_0^\circ(\text{WO}_2) = 602.5 \pm 4.6 \text{ kJ mol}^{-1}$ with the 0 K enthalpy of reaction $\text{TiO}(\text{g}) + \text{WO}_3(\text{g}) = \text{TiO}_2(\text{g}) + \text{WO}_2(\text{g})$ and quoting for this reaction an estimated standard deviation of the same order as that attached to the enthalpy of reaction (2), we obtain for $D_0^\circ(\text{TiO}_2) - D_0^\circ(\text{TiO})$ the value $589 \pm 14 \text{ kJ mol}^{-1}$, in very nice agreement with the value $585 \pm 13 \text{ kJ mol}^{-1}$ derived from the study of reaction (2).

Incidentally, the value $592 \pm 8 \text{ kJ mol}^{-1}$ quoted here is in close accord with the result of $594 \pm 21 \text{ kJ mol}^{-1}$ derived previously by Balducci *et al.*¹² from a study of the gaseous reaction $\text{TiO}_2(\text{g}) = \text{TiO}(\text{g}) + \text{O}(\text{g})$ using different thermodynamic functions for $\text{TiO}_2(\text{g})$ and different choices for cross sections and multiplier yields. This indicates that, whichever might have been the errors made in that study, they acted in a compensatory way to give essentially correct and self-consistent second-law and third-law enthalpy values.

However, such a fortunate compensation of errors from different sources did not occur in the case of the exchange reaction $\text{TiO}_2(\text{g}) + \text{Ti}(\text{g}) = 2\text{TiO}(\text{g})$ studied by the same investigators¹² since the reaction enthalpy (-8.4 ± 8.4

kJ mol^{-1}) they proposed on the basis of their apparently self-consistent results appears definitely out of the range of the values compatible with the presently quoted values of $D_0^\circ(\text{TiO})$ and $D_0^\circ(\text{TiO}_2)$. We believe therefore that it was the use of the above incorrect value for the enthalpy of the exchange reaction that was responsible for the rather low values of the dissociation energies of $\text{TiO}(\text{g})$ and $\text{TiO}_2(\text{g})$ (602.5 ± 21 and $1197 \pm 42 \text{ kJ mol}^{-1}$, respectively) derived at that time by Balducci *et al.*¹² rather than presumed bias in the mass spectrometric values for the partial pressures of oxygen employed in the dissociation reaction $\text{TiO}_2(\text{g}) = \text{TiO}(\text{g}) + \text{O}(\text{g})$.^{5,6}

The value proposed here for $D_0^\circ(\text{TiO}_2)$, $1260 \pm \text{kJ mol}^{-1}$, has been used to derive the atomization energy and the standard heat of formation of $\text{EuTiO}_3(\text{g})$: $\Delta H_{0,\text{at}}^\circ(\text{EuTiO}_3) = 2278 \pm 28 \text{ kJ mol}^{-1}$ and $\Delta H_{f,298}^\circ(\text{EuTiO}_3, \text{g}) = -887 \pm 28 \text{ kJ mol}^{-1}$.

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