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Thermochemical properties of the gaseous molecules VO, VO$_2$, and V$_2$O$_4$

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The gaseous molecules VO, VO$_2$, and V$_2$O$_4$ were characterized thermochemically from the study of various all-gas equilibria carried out by means of the high temperature-mass spectrometry. The bond dissociation energies here determined for VO and VO$_2$ are compared and discussed with previous results, while the molecule V$_2$O$_4$ was clearly identified for the first time. The thermochemical results obtained are: $D^\circ_0(VO) = 625.5 \pm 8.5$ kJ mol^{-1}, $\Delta H^\circ_{f,298}(VO,g) = 133.2 \pm 8.5$ kJ mol^{-1}; $D^\circ_0(VO_2) = 1\,177 \pm 18$ kJ mol^{-1}, $\Delta H^\circ_{f,298}(VO_2,g) = -174 \pm 14$ kJ mol^{-1}; $D^\circ_{0,at}(V_2O_4) = 2880 \pm 23$ kJ mol^{-1}, $\Delta H^\circ_{f,298}(V_2O_4,g) = -878 \pm 23$ kJ mol^{-1}.

INTRODUCTION

Despite substantial agreement in the reported values of heats of formation and bond dissociation energies of the gaseous lower oxides of vanadium VO and VO$_2$, as it emerges from reference compilations[1,2] they are only sparesely characterized, in particular VO$_2$(g).

For VO(g), the analysis made in JANAF[1] is essentially based on the results of Berkowitz *et al.*[3] for the sublimation reaction: VO(c) = VO(g) and on the results of Coppens *et al.*[4] who determined the third-law heat of the metathetical reaction: VO(g) + Ge(g) = GeO(g) + V(g) as only these experiments involve multiple data points while other studies involve only one or two data points[5] and/or the value of $D^\circ_0(VO)$ is dependent on $D^\circ_0(VO_2)$.[3,6] In their recent effort to assess the thermochemical data of gaseous monoxides, Pedley and Marshall[7] prefer as more reliable the results based on the metathetical reactions of Coppens *et al.*[4] and of Farber *et al.*[5] and discard the value of $D^\circ_0(VO)$ resulting from the data of Berkowitz *et al.*[3] Apparently, the procedure adopted in deriving the enthalpy of formation and, hence, the bond dissociation energy by Pedley and Marshall[7] is that to use the third-law analysis and results, and to use the second-law analysis only in a confirmatory way, while JANAF[1] compilators, whenever possible, submit the original experimental data to second-law analysis often selecting averages of second- and third-law results.

A more recent chemiluminescence study of VO(g) by Jones and Gole[8] set a lower limit to the dissociation energy of VO(g): $D^\circ_0(VO) \geq 6.034$ eV (139.15 kcal mol^{-1} or 582.2 kJ mol^{-1}). All summed up, the selected values for the dissociation energy of VO(g) round to 6.34–6.54 eV. This is the situation with VO(g). For VO$_2$(g) the enthalpy of formation, $\Delta H^\circ_{f,298}$, and, correspondingly, the dissociation energy, $D^\circ_0(VO_2)$, adopted in JANAF[1] are entirely based on the second- and third-law analysis of the results of Frantseva and Semenov[6] for the vaporization of VO$_2$(s, 1) [or V$_2$O$_4$(s, 1)] to VO$_2$(g). Other studies which were discarded in the JANAF analysis refer to all-gas reactions involving V(g), VO(g), VO$_2$(g) and Al(g), AlO(g), V(g), VO$_2$(g) and only one or two data points studied by Berkowitz *et al.*[3] and by Farber *et al.*[5] The correspondent $D^\circ_0(VO_2)$ is dependent on $D^\circ_0(VO)$ and $D^\circ_0(AlO)$, respectively. It should be men-

tioned that in all cases cited the entropy and free energy functions for VO$_2$(g) were calculated on the basis of entirely estimated (vibrational frequencies, bond angle, and bond distance) molecular parameters.[1]

Recently,[9] experimental data were reported for the vibrational frequencies of VO$_2$ trapped in inert gas matrices, the use of which may allow more realistic estimates for the thermodynamic functions.

In connection with our study for the identification and stability determination of ternary oxide gaseous molecules of the system europium–vanadium–oxygen and our continuing interest in other metal vanadate systems we deemed it useful to redetermine the thermochemical properties of the constituent lower vanadium oxides VO(g) and, especially, VO$_2$(g). In the conditions of the experiments we were able to perform extensive second-law measurements, i.e., measurements of the equilibrium constants over wide temperature ranges of all-gas isomolecular reactions involving VO(g), VO$_2$(g), and EuO(g). The resulting data for VO(g) and VO$_2$(g) constitute a contribution to the knowledge of the thermochemistry of these molecules.

In addition, in the conditions of the present experiments, we were able to identify for the first time the molecule V$_2$O$_4$(g) which could not be studied in the previously reported[3,5,6] vaporization experiments of an-vanadium oxides, and to determine its stability.

The results obtained for VO(g), VO$_2$(g), and V$_2$O$_4$(g) are reported and discussed in this paper.

EXPERIMENTAL

The Knudsen effusion technique combined with the mass spectrometric analysis of the equilibrium composition of the vapor were used in the investigation. The mass spectrometer and the experimental procedure have been described elsewhere.[10,11] Briefly, it consists of a magnetic deflection 30.5 cm radius, 60° sector single focusing mass spectrometer coupled with a conventional Knudsen cell molecular source. As the experiment was designed also with the purpose to study the ternary gaseous compounds of the system europium–vanadium–oxygen, the Knudsen cell made of molybdenum, with an orifice diameter of 1 mm was charged with an intimate

TABLE I. Equilibrium data and heats of reactions (1) to (3), in $kJ\,mol^{-1}$.

T/K	$-\ln K_{(1)}$	$\Delta H^{\circ}_{0(1)}$	$\ln K_{(2)}$	$\Delta H^{\circ}_{0(2)}$	$-\ln K_{(3)}$	$\Delta H^{\circ}_{0(3)}$
2080	6.51	157.3	5.55	−74.2	0.96₅	83
2087	6.45₅	156.9	5.51	−74.8	0.94₅	83
2186	•••	•••	5.33₅	−74.7	•••	•••
2168	6.15	157.9	5.30₅	−73.5	0.84	84.4
2063	•••	•••	5.58₅	−74.1	•••	•••
2081	6.46₅	156.6	5.54	−74.0	0.93	82.7
2178	6.08	157.4	5.31	−74.0	0.77	83.5
2282	•••	•••	•••	•••	0.59	83.8
1971	7.03	157.1	5.79₅	−73.6	1.23	83.4
1969	•••	•••	•••	•••	1.27₅	84.1
2084	•••	•••	•••	•••	1.10₅	84.4
2143	•••	•••	•••	•••	0.85₅	83.7
1913	7.39	157.9	5.97	−73.9	1.42	84.1
1915	•••	•••	5.91₅	−73.1	•••	•••
2059	6.61₅	157.4	5.55	−73.3	1.07	84.2
2065	•••	•••	5.51₅	−72.9	•••	•••
2127	•••	•••	5.38₅	−73.2	•••	•••
2129	•••	•••	5.35	−72.7	•••	•••
2184	•••	•••	•••	•••	0.76₅	83.6
2044	6.67₅	157.2	5.57	−73.0	1.10	84.2
1933	•••	•••	5.89₅	−73.6	•••	•••
1926	•••	•••	5.97	−74.5	•••	•••
2004	•••	•••	5.72	−73.8	•••	•••
2031	•••	•••	5.70	−74.6	•••	•••
2010	6.90	158.2	5.73	−74.2	1.17	84.0
2069	6.595	157.9	5.54₅	−73.6	1.05	84.3

Avg. third-law ΔH°_0 157.5 ± 0.5   −73.7 ± 0.6   83.8 ± 0.5
Avg. temperature T_{av}/K 2057   1046   2076
Second-law ΔH°_T 169.5 ± 4.2   −87.0 ± 3.1   82.0 ± 2.9
Second-law ΔH°_0 158.8 ± 4.2   −73.8 ± 3.1   85.5 ± 2.9
Selected ΔH°_0 158.5 ± 6.0   −74 ± 6   84.5 ± 6
Derived D°_0(VO): 625.5 ± 8.5 D°_0(VO2): 1177 ± 18   1177 ± 12

mixture of Eu_2O_3, V_2O_5, and V reagents stated 99.0% to 99.9% pure (from Koch&Light Ltd., England). The cell was heated by electron bombardment from a tungsten filament or by radiation from a tungsten spiral resistance element. The temperatures were measured by optical pyrometry using a black-body cavity in the bottom of the cell. The vapors effusing from the cell were ionized with 70 eV electrons.

RESULTS AND DISCUSSION

Gaseous species effusing from the cell were identified from mass, threshold appearance potential (A.P.), isotopic distribution of the ions, and shutter profile. The A.P.'s values, given in brackets, were measured with a linear extrapolation method by reference with V^+ atomic ion (6.74) to calibrate the energy scale. Their values, in eV, are: Eu^+(5.7), VO^+(8.4), VO_2^+(10.5), EuO^+(6.5), all with an uncertainty of ± 0.3 eV, $V_2O_4^+$ ×(10.5 ± 0.5). Additional ion species observed were the ternary species of the system Eu−V−O of which it will be referred separately.

In the ensuing thermochemical studies, the raw ion intensities were corrected, where necessary, for fragmentation and multiple ionization contributions, and were converted into pressure through silver calibration experiments.

All cross sections and multiplier gains were either obtained from the literature or estimated. The maximum cross sections for the atoms were taken from Mann,[12] those for the molecules were estimated with a previously used procedure.[13] Their values are: 7.93, 7.39, 10.45, 17.80, 14.60, 13.16₅, for V, VO, VO_2, V_2O_4, Eu, EuO, respectively. The multiplier gains were taken to be proportional to the inverse square root of the ion mass. Although they cannot be considered equilibrium pressures corresponding to a well known condensed phase, a set of partial pressures of the various species measured at $T = 2140$ K are as follows: $P(V) = 1.5 \times 10^{-6}$, $P(VO) = 3.5 \times 10^{-5}$, $P(VO_2) = 3.9 \times 10^{-6}$, $P(Eu) = 1.2 \times 10^{-5}$, $P(EuO) = 5.5 \times 10^{-7}$, $P(V_2O_4) = 6.1 \times 10^{-9}$, all in atm.

VO and VO_2

The following isomolecular equilibria were studied:

$$VO(g) + Eu(g) = EuO(g) + V(g) , \qquad (1)$$

$$VO_2(g) + V(g) = 2\,VO(g) , \qquad (2)$$

$$VO_2(g) + Eu(g) = EuO(g) + VO(g) , \qquad (3)$$
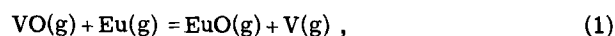
Equilibrium data, heats of reactions (1) to (3), and derived atomization energies of VO(g) and VO_2(g) are given in Table I. The errors quoted on the second- and third-law heats of reaction are standard deviations.

They appear rather low considering the errors inherent in the experimental method used. As the potential sources of error are many and differing in nature, very unlikely their effects could act in the same direction so that they can be reasonably supposed as randomly distributed. With this in mind, we assumed for the quoted errors in the selected ΔH_0° of reactions (1) to (3) an estimated standard deviation which should account for the distribution (assumed as normal) of the effects of all the possible uncertainties in data acquisition and evaluation. The selected values should, therefore, be reliable within three times the quoted uncertainties. The same significance was given to the errors associated with the ancillary data used in the derivation of the dissociation energies and, therefore, the propagation formula corresponding to the standard deviation was used in the evaluation of the errors associated to $D_0^\circ(VO)$ and $D_0^\circ(VO_2)$. The thermodynamic functions for the species needed in the evaluation of the heats of reactions were taken as described in the Appendix. The metathetical reaction (1) is particularly well suitable to check the dissociation energy of VO(g) and, therefore, it was firstly used to determine $D_0^\circ(VO)$ against EuO(g), the dissociation energy of which is now quite well known.[14] The selected heat of reaction (1), $\Delta H_0^\circ = (158.5 \pm 6)$ kJ mol⁻¹ was combined with $D_0^\circ(EuO) = (467 \pm 6)$ kJ mol⁻¹ [or (111.6 ± 1.5) kcal mol⁻¹][15] to obtain $D_0^\circ(VO) = (625.5 \pm 8.5)$ kJ mol⁻¹ [or (149.5 ± 2) kcal mol⁻¹], value which has been subsequently employed to derive $D_0^\circ(VO_2)$ from equilibria (2) and (3).

All these three interrelated equilibria were taken into account in order to minimize the different influence, particularly in the second-law values, of the experimental errors on the data points the number of which might not be as much large to represent a fully significant statistical set. Moreover, we note that actually some of the data points of the reactions reported were taken in different experiments at different temperatures.

The value here determined for $D_0^\circ(VO)$ agrees with and sets between the values quoted by JANAF[1] and by Pedley and Marshall[7] [(631 ± 21) or (150.9 ± 5) kcal mol⁻¹, and (621 ± 16.7) or (148.4 ± 4.0) kcal mol⁻¹, respectively]. However, it should be pointed out that the observed agreement between the last two values may well be somewhat apparent as they arise from different selections and treatments of data. In fact, the analysis of JANAF[1] for deriving the adopted $\Delta H_{f,298}^\circ$ of VO(g) and, hence, $D_0^\circ(VO)$ is based only on the second-law treatment of the two sets of measurements of the vaporization reaction VO(c) = VO(g) reported by Berkowitz et al.[3] and of the metathetical reaction VO(g) + Ge(g) = V(g) + GeO(g) reported by Coppens et al.[4] with use of proper ancillary data. The adopted $\Delta H_{f,298}^\circ(VO, g)$ is 127.6 or 30.5 kcal mol⁻¹, average of the results of the three sets of measurements. A third-law analysis of the one data set point reported by Farber et al.[5] for the metathetical reaction AlO(g) + V(g) = Al(g) + VO(g), which was discarded in the above analysis, results in a $\Delta H_{f,298}^\circ$ for VO(g) higher by 10.9 kJ mol⁻¹ (2.6 kcal mol⁻¹) when a more recent value (68.6 or 16.4 kcal mol⁻¹ is used for $\Delta H_{f,298}^\circ$ of AlO(g).[18] In the analysis of Pedley

and Marshall,[7] the selected value of $\Delta H_{f,298}^\circ$ for VO(g) is based only on third-law analysis of the metathetical reactions of Farber et al.[5] and of Coppens et al.[4]; the value adopted is 138 kJ mol⁻¹ (33 kcal mol⁻¹). The data of Berkowitz et al.,[3] which were not included in the analysis because considered unreliable, would give $\Delta H_{f,298}^\circ(VO, g) = 100.1$ kJ mol⁻¹ (23.9 kcal mol⁻¹) and $D_0^\circ(VO) = 658.6$ kJ mol⁻¹ (157.4 kcal mol⁻¹) with a third-law treatment of the data, and $D_0^\circ(VO) = 630.1$ kJ mol⁻¹ (150.6 kcal mol⁻¹) with a second-law treatment of the data. The average would be 644.3 kJ mol⁻¹ (154.0 kcal mol⁻¹). As concerns the metathetical reaction with GeO(g) studied by Coppens et al.,[4] with the same ancillary data [free energy functions, $D_0^\circ(GeO)$] used by Pedley and Marshall[7] one obtains a third-law heat of 28.5 kJ mol⁻¹ (6.8 kcal mol⁻¹) and $D_0^\circ(VO) = 625.5$ kJ mol⁻¹ (149.5 kcal mol⁻¹), which is that accounted for by Pedley and Marshall,[7] and a second-law heat of reaction of 49 kJ mol⁻¹ (11.7 kcal mol⁻¹) and $D_0^\circ(VO) = 605$ kJ mol⁻¹ (144.6 kcal mol⁻¹). The average would be 615 kJ mol⁻¹ (147.0 kcal mol⁻¹). In contrast we obtained a splendid agreement between second- and third-law results for metathetical reaction (1).

Our selected value for $D_0^\circ(VO_2)$, average of the values obtained from the two independent isomolecular reactions (2) and (3), is 1177 ± 11 kJ mol⁻¹ (281.3 ± 2.6 kcal mol⁻¹) which corresponds to $\Delta H_{f,298}^\circ(VO_2, g) = -174 \pm 14$ kJ mol⁻¹ (-41.6 ± 3.3 kcal mol⁻¹). This value is appreciably less negative (by 59 kJ mol⁻¹) than that adopted in JANAF[1] entirely based on the results of Frantseva and Semenov[6] for the vaporization of $V_2O_4(s, l)$ to $VO_2(g)$, but it is in accord with the value (-177 ± 21 kJ mol⁻¹) calculated by JANAF[1] from the results of Killingbeck[16] for the evaporation of $V_2O_3(s)$.

It is however interesting to compare our results with other determinations[3,5] of heat of formation and dissociation energy for $VO_2(g)$ based on all-gas reactions cited in JANAF[1] and apparently discarded in the analysis as they involve only one or two data set points and are dependent on $D_0^\circ(VO)$ and/or $D_0^\circ(AlO)$. Of particular interest for this comparison are the data of Berkowitz et al.[3] which refer to two values of the equilibrium constant for the same reaction (2), $VO_2(g) + V(g) = 2 VO(g)$, measured at 15 and 80 eV at one temperature (1945 K).

From the basic ion intensity data, in the hypothesis that the fragmentation effects are quite negligible at 15 eV and do not drastically change between 70 and 80 eV, by using our assumptions for fragmentation corrections at 70 eV, for cross sections, multiplier efficiencies, free energy functions for V(g), VO(g), VO₂(g), and the value here determined for $D_0^\circ(VO)$, we recalculated for $D_0^\circ(VO_2)$ the values 1181 and 1183.6 kJ mol⁻¹ from the data measured at low and high electron energies, respectively, and hence the values -178.2 and -180.7 kJ mol⁻¹ for $\Delta H_{f,298}^\circ(VO_2, g)$ which compare well with the value we obtained from sixteen data set points measured in a wide temperature interval. This may be taken as an indication that our fragmentation corrections should be used with a certain confidence at least as long as the VO_2^+ intensity is appreciably lower than the VO⁺ and V⁺ intensities.

TABLE II. Summary of dissociation energies of VO(g) and VO_2(g) derived from different studies (see text).

Source	Reaction	$D^{\circ}_0(VO)$, kJ mol⁻¹				$D^{\circ}_0(VO_2)$, kJ mol⁻¹			
		2nd Law	3rd Law	Avg.	Selected	2nd Law	3rd Law	Avg.	Selected
(3) Berkowitz (1957)	VO(c) = VO(g)	630.1	658.6	644.3					
	$VO_2(g) + V(g) = 2VO(g)$						1181^d / 1183.6^d		
(4) Coppens (1967)	VO(g) + Ge(g) = GeO(g) + V(g)	605.0	625.5	615					
(6) Frantseva (1969)	$0.5\ V_2O_4(c) = VO_2(g)$					1238.4	1238.3	1238.3	
	$0.5\ V_2O_4(l) = VO_2(g)$					1230.2	1235.0	1232.6	
(16) Killingbeck (1964)	$V_2O_3(c) = VO(g) + VO_2(g)$		620.2^a						1180.0^f
(5) Farber (1972)	AlO(g) + V(g) = VO(g) + Al(g)								
	$VO_2(g) + 2Al(g) = V(g) + 2AlO(g)$						1181^a		
	$VO_2(g) + V(g) = 2VO(g)$						1200.8^e		
(1) JANAF (1975)					631^b				1236.4^a
(7) Pedley (1982)					621^e				
This work	VO(g) + Eu = EuO(g) + V(g)	626.8	624.5	625.6	625.5				
	$VO_2(g) + V(g) = 2VO(g)$					1171.1	1177.3	1177.2	
	$VO_2(g) + Eu(g) = EuO(g) + VO(g)$					1178.0	1176.3	1177.2	1177

a Recalculated using ancillary data for Al(g) and AlO(g) given in Refs. 17 and 18.
b Based on the 2nd law treatment of the data from Refs. 3 and 4.
c Based on the 3rd law analysis of the data from Refs. 4 and 5.
d Recalculated from the two data set points from Ref. 3 (see the text).
e Recalculated from the original data of Ref. 5 using $D^{\circ}_0(VO) = 625.5$ kJ mol⁻¹.
f As calculated by JANAF (Ref. 1) from the data of Ref. 16.
g Based entirely on the vaporization data of Ref. 6.

Similarly, from intensities measured at 2270 K by Farber et al.[5] we recalculated the heats $\Delta H^{\circ}_{0,r}$ of reactions: $VO_2(g) + 2Al(g) = V(g) + 2AlO(g)$; $VO(g) + Al(g) = V(g) + AlO(g)$, and of reaction (2), by employing proper free energy functions for $Al(g)$[17] and $AlO(g)$,[18] and found the values: 179, 118, and −51.5 kJ mol⁻¹, respectively. By combination with $D^{\circ}_0(AlO) = 502.1 \pm 8.4$ kJ mol⁻¹ quoted in JANAF 1978 Supplement[18] and the other proper ancillary data we obtained for the dissociation energy and the standard heat of formation (in parenthesis) of $VO_2(g)$ the values: 1181 kJ mol⁻¹ (−180.3 kJ mol⁻¹) from reaction involving AlO(g), and 1188.7 kJ mol⁻¹ (−185.8 kJ mol⁻¹), or 1200.8 kJ mol⁻¹ (−196.6 kJ mol⁻¹) from reaction (2) according to whether the value (internal) of 620 kJ mol⁻¹ determined against AlO(g) or our selected value of 625.5 kJ mol⁻¹ is used for $D^{\circ}_0(VO)$.

To facilitate the comparison a summary of the various derived values for $D^{\circ}_0(VO)$ and $D^{\circ}_0(VO_2)$ is reported in Table II. All these results arising from different all-gas reactions and different authors are in substantial mutual agreement and concur to indicate a heat of formation appreciably less negative and a dissociation energy lower than that reported in JANAF[1] for $VO_2(g)$. We note that a certain inconsistency emerges between the VO(g) and $VO_2(g)$ pressure data of Frantseva and Semenov[6] and the heat of formation of $VO_2(g)$ derived therefrom.[1] When these same data are utilized for the study of reaction (2) it is found that, at $T = 2180$ K, $P(V) \approx 0.15P(VO_2)$ and $P(V) \approx 0.17P(VO)$, which should lead, in the usual conditions of the mass spectrometry, to a measurable intensity of primary V^+ at least at the highest temperatures of the experiment, while Frantseva and Semenov[6] attributed the measured V^+ intensity entirely to a fragment ion coming from the dissociation of VO(g) and $VO_2(g)$.

V_2O_4

Farber, Uy, and Srivastava[5] in their vaporization of $V_2O_5(s)$ from an alumina cell report to have observed ions of mass corresponding to $V_2O_4(g)$ which could not be definitely identified because quickly disappeared relative to $V_4O_{10}(g)$ and $V_4O_8(g)$. Berkowitz, Chupka, and Inghram[3] report to have observed in the vaporization of $V_2O_5(s)$ from a platinum cell ions corresponding to $V_2O_4(g)$ but they could not measure the appearance potential nor perform temperature variation experiment because of sudden drop of the ion intensity. With respect to the above experiments, the conditions of our experiments were more favorable to the observation and measurement of $V_2O_4(g)$.

The dissociation energy of the molecule $V_2O_4(g)$ has been derived from the study of the two following independent equilibria:

$$V_2O_4(g) = 2\ VO_2(g) \tag{4}$$

$$V_2O_4(g) + 2\ Eu(g) = 2\ EuO(g) + 2\ VO(g) . \tag{5}$$
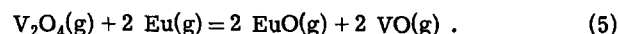
The equilibrium data and the heats of reaction are reported in Table III. The conditions for the measurements of the $V_2O_4(g)$ molecule were attained in the highest range of temperatures in the final part of the vaporization experiments. Therefore, only a limited

TABLE III. Equilibrium data, heats of reactions (4) and (5) and derived atomization energy of V$_2$O$_4$ (g), in kJ mol^{-1}.

T/K	$-\ln K_{(4)}$	$\Delta H^\circ_{0(4)}$	$-\ln K_{(5)}$	$\Delta H^\circ_{0(5)}$
2282	4.28	527.5	5.46$_5$	695.2
2246	4.71$_5$	527.5	···	···
2251	···	···	5.93	694.9
2143	6.01	527.4	7.72	694.9
Avg. third-law ΔH°_0		527.5 ± 0.1		695.0 ± 0.4
Avg. temperature T_{av}		2222		2224
Second-law ΔH°_T		504 ± 21		661 ± 53
Second-law ΔH°_0		527.5 ± 21		693 ± 53
Selected		527.5 ± 15		694 ± 30
Derived $\Delta H^\circ_{0,at}$ (V$_2$O$_4$):		2881.5 ± 27		2879 ± 37

TABLE IV. Thermodynamic functions of VO$_2$(g) and V$_2$O$_4$(g), $-(G^\circ_T - H^\circ_0)/T$ in J K^{-1} mol^{-1}, $(H^\circ_T - H^\circ_0)$ in kJ mol^{-1}.

	VO$_2$(g)		V$_2$O$_4$(g)[a]	
T/K	$-(G^\circ_T - H^\circ_0)/T$	$(H^\circ_T - H^\circ_0)$	$-(G^\circ_T - H^\circ_0)/T$	$(H^\circ_T - H^\circ_0)$
298.15	226.670	10.623	256.819	16.860
1500	295.141	74.213	390.765	160.384
1600	298.349	79.900	397.712	173.361
1700	301.389	85.602	404.320	186.375
1800	304.278	91.317	410.619	199.420
1900	307.030	97.042	416.638	212.492
2000	309.658	102.777	422.400	225.588
2100	312.172	108.519	427.924	238.702
2200	314.582	114.269	433.231	251.833
2300	316.897	120.024	438.336	264.979
2400	319.123	125.785	443.253	278.138
2500	321.266	131.551	447.997	291.308

[a]Referred to the bridge-bonded structure described in the Appendix.

number of data could be collected and their analysis required a procedure somewhat different from the usual. At each temperature point the value quoted for $\ln K$ represents an average of the values obtained by combining in all the possible ways all the ion intensity readings compatible with the statistical noise of the recording device. The straight line plot $\ln K$ vs $1/T$ obtained by a least square fit of the experimental points lies between those of maximum and minimum slope which may be drawn when the experimental uncertainties are accounted for and, therefore, its slope should give a ΔH°_T value reliable within a maximum error equal to the semi-difference of the values corresponding to the maximum and minimum slopes. Values for ΔH°_T so obtained for reactions (4) and (5) are reported in Table III with the associated errors. Reduction of these values to 0 K introduces additional uncertainties connected with the estimation of the thermodynamic functions of V$_2$O$_4$(g) (see Appendix and Tables IV and V).

Preliminary calculation of ΔH°_0 of reaction (4), using thermal functions based on the structural assumptions described in the Appendix, yielded values of 527.5 and 532 kJ mol^{-1} according to whether the bridge-bonded structure or the O$_2$V–VO$_2$ structure, both of D_{2h} symmetry, is chosen for V$_2$O$_4$(g). The correspondingly calculated average third-law values were 527.5 and 459.1 kJ mol^{-1}. Although for each structure different choices of the molecular parameters, and in primis of the lowest frequencies, may result in appreciable differences in the third-law heats, the range of the possible
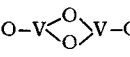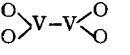
values obtained by employing the bridge-bonded structure appear better centered with respect to the possible range of the second-law values. Therefore, the thermodynamic functions calculated for the bridge-bonded structure of V$_2$O$_4$(g) were used to obtain the second-law and third-law results reported in Table III. The errors quoted on the average third-law heats are only standard deviations, those on the second-law heats at 0 K are maximum errors which reflect the experimental uncertainties in ΔH°_T, and those on the selected values, which are averages of the second- and third-law results, are standard deviations estimated with the criteria and the significances already given for reactions (1) to (3).

By combining the selected heats of reactions (4) and (5) with the atomization energies of VO$_2$(g), VO(g), and EuO(g), the values 2881.7 ± 27 and 2879 ± 37 kJ mol^{-1}, respectively, are obtained for the atomization energy of V$_2$O$_4$(g). The selected value is: $D^\circ_{0,at}$(V$_2$O$_4$) = 2880 ± 23 kJ mol^{-1}, corresponding to $\Delta H^\circ_{f,298}$(V$_2$O$_4$, g) = − 878 ± 23 kJ mol^{-1}.

To get more information about the most probable structure of the V$_2$O$_4$(g) molecule, similar calculations were also performed using thermodynamic functions evaluated for the structure O$_2$V–VO$_2$. These calculations yielded $D^\circ_{0,at}$(V$_2$O$_4$) = 2849 kJ mol^{-1}.

This value, together with the preceding one, can be

TABLE V. Summary of molecular constants for VO$_2$(g) and V$_2$O$_4$(g) adopted for thermodynamic functions evaluation.

Molecule	σ	$I \times 10^{39}$/g cm^2	g_0	ω_i/cm^{-1}
VO$_2$	2		2	983, 538, 1034
V$_2$O$_4$				
O–V⟨O/O⟩V–O	4	9.8796 / 61.8706 / 71.7502	1	a_g: 1030, 830, 400 b_{1u}: 430, 150 b_{1g}: 830, 430 b_{2u}: 830, 400 b_{2g}: 280 b_{3u}: 1030, 830
O/O⟩V–V⟨O/O	4	21.1766 / 67.5116 / 88.6881	1	a_g: 983, 177, 538 a_u: 33 b_{1g}: 1034, 322 b_{1u}: 983, 538 b_{2g}: 448 b_{2u}: 286 b_{3u}: 1034, 254

compared with those which are derived through a bond additivity scheme. For the O_2V-VO_2 structure, by employing the atomization energy of $VO_2(g)$ here determined and the dissociation energy of the vanadium dimer[2] the atomization energy of 2593 kJ mol^{-1} is obtained. In the case of the bridge-bonded structure, in the attempt to be as coherent as possible with the assumed molecular parameters (see the Appendix), we used the value 625.5 kJ mol^{-1} (as in the monoxide) for the terminal V–O bond energy, while a range of values from 403 to 435 kJ mol^{-1} were assumed for the bridge bond energy taking into account the atomization energies of the $V_4O_8(g)$ and $V_4O_{10}(g)$ molecules, respectively, after reduction to 0 K of the values given by Farber et al.[5] Therefore, the atomization energy of $V_2O_4(g)$ obtained with the bond additivity model range from 2863 to 2991 kJ mol^{-1}. These values compare more favorably with the corresponding experimental results than the preceding one. This may be taken as an additional indication that the bridge-bonded structure is to be considered the more likely one.

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APPENDIX

$Eu(g)$, $EuO(g)$: Free energy functions were taken the same used in a previous investigation by Balducci, Gigli, and Guido (Ref. 14).

$V(g)$, $VO(g)$: Free energy functions were taken from JANAF Thermochemical Tables.[1]

$VO_2(g)$: A bent structure, with a valence bond angle of 110°, has been assumed in JANAF Thermochemical Tables[1] for this molecule. Recently, Serebrennikov and Malt'sev,[9] on the basis of the measured isotopic shifts of the antisymmetric stretching ω_3, derived for the valence bond angle the value 95° which was adopted here. The fundamental frequencies were taken from the same source, while for the bond length the value 0.163 nm was estimated from the interatomic distance of the vanadium monoxide[1,2] taking into account the lengthening of the bond which occurs in going from NbO^2 to NbO_2.[19] A ground state quantum weight of 2 was adopted as in JANAF Thermochemical Tables.[1]

$V_2O_4(g)$: Two different structures, both of D_{2h} symmetry, were considered for the calculation of the the thermodynamic functions of this newly identified molecule.

Bridge-bonded structure: No experimental parameters, to our knowledge, have been reported for metal oxide molecules of this geometry. Estimations have been made for the $P_2O_4(g)$[20] and $Te_2O_4(g)$[21] molecules, but no details were given in this last case. For the present case of the $V_2O_4(g)$ molecule, the terminal V–O bond length, $r(V-O)_t = 0.159$ nm, was assumed to be equal to that of the diatomic molecule, while the

$r(V-O)_b = 0.178$ nm value was estimated from the lengthening of the bridge with respect to the terminal bond length which is observed in a number of metal–oxygen molecules and ions [e.g., $Cr_4O_{12}(g)$,[22] $Mo_3O_9(g)$,[23] $W_3O_9(g)$,[22] $P_4O_{10}(g)$,[24] $Nb_6O_{19}^{8-}$ and $Ta_6O_{19}^{8-}$ ions[25]]. The ratio $r(V-O)_b / r(V-O)_t = 1.12$ we used is also very similar to that used by Farber et al.[5] in the case of $V_4O_{10}(g)$. The O_b–$\hat{V}$–O_b angle was assumed to be 100° by taking into account the corresponding angles measured or estimated in the aforementioned molecules and ions, and in $Si_2O_2(g)$,[26] $Ge_2O_2(g)$,[27] $Sn_2O_2(g)$,[28] and $Te_2O_2(g)$.[21] A description of the fundamental modes for molecules of this type which can be given[29-31] is as follows: $3a_g$ (terminal V–O stretching, ring stretching, ring bending), $2b_{1g}$ (ring stretching, terminal V–O bending in plane), b_{2g} (V–O bending out-of-plane), $2b_{1u}$ (terminal V–O out-of-plane bending, ring puckering), $2b_{2u}$ (ring stretching, terminal V–O bending in-plane), $2b_{3u}$ (terminal V–O stretching, ring stretching). Terminal ($V=0$) and bridge (V–O–V) stretchings have been assigned by Beattie et al.[32] to the two prominent bands at 1020.9 and 828.4 cm^{-1} they observed in the matrix isolation IR spectra of V_4O_{10}. These bands were also found to be close in frequency to prominent IR absorptions in solid vanadium pentoxide[33] where both bridging and terminal oxygen are present. By taking into account these findings, the two terminal V–O stretchings were taken to be 1030 cm^{-1} in value while the four ring stretchings were all assumed to be equal to 830 cm^{-1}. From the frequencies observed in $V_2O_5(s)$[34] all the three V–O bending in-plane frequencies and the terminal V–O bending out-of-plane were taken to be respectively 400 and 280 cm^{-1}. The remaining ring puckering-terminal V–O out-of-plane bendings were estimated to be 150 and 430 cm^{-1}. Finally, no ground state electronic degeneracy was included in the calculations.

O_2V-VO_2 *structure*: The molecular parameters for this geometry were estimated from those of the N_2O_4 gaseous molecule[35] and of the $VO_2(g)$ molecule (see above). The V–O bond length used was 0.163 nm as it has been estimated for VO_2 while the V–V interatomic distance was assumed to be 0.240 nm taking into account the r_{X-X}/r_{X-O} ratio which is found in N_2O_4. Again, as in N_2O_4 the O–$\hat{V}$–O angle was taken as 120°. Six of the fundamental frequencies were taken from the VO_2 molecule. Indeed, six modes can be described to be symmetric and antisymmetric stretchings as well as symmetric bendings of the XO_2 group. Having estimated the X–O stretchings all the remaining six frequencies could be derived from the N_2O_4 fundamentals[36] through a procedure similar to that used by Farber et al.[5] in scaling the V_4O_{10} frequencies from those of the P_4O_{10} molecule. Therefore, by taking into account the ratio between the XO_2 group stretchings in N_2O_4 and V_2O_4 the relation has been derived: $(V_2O_4) = 0.666 (N_2O_4)$, which has been used to estimate the ω_2, ω_5, ω_6, ω_7, ω_{10}, and ω_{12} frequencies of this structure. As for the bridge-bonded structure, no ground quantum state weight was taken into account.

A summary of the molecular constants adopted is given in Table V and the numerical values of the thermodynamic functions are given in Table IV.

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