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Gaseous Vanadium Molybdate and Tungstates: Thermodynamic Properties and Structures

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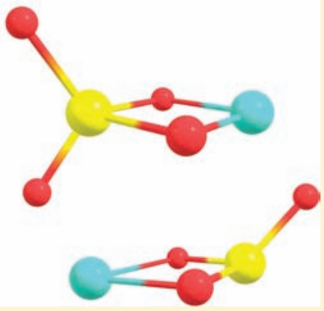
S *Supporting Information*

ABSTRACT: The stability of gaseous vanadium molybdate and vanadium tungstates was confirmed by high-temperature mass spectrometry. A number of gas-phase reactions involving vanadium-containing salts were studied. On the basis of equilibrium constants, the standard formation enthalpies of gaseous $VMoO_4$ (−676 ± 27 kJ/mol), VWO_3 (−331 ± 29 kJ/mol), and VWO_4 (−706 ± 23 kJ/mol) at 298 K were determined. A theoretical study of these salts revealed the structure with bidentate binding of the vanadium cation to the anion part to be the lowest-lying isomer, with a quartet spin state for $VMoO_4$ and VWO_4 molecules as well as a sextet spin state for the VWO_3 molecule. On the basis of critical analysis of the literature data concerning standard formation enthalpies of gaseous VO and VO_2, we adopted new values of $\Delta_f H°(298)$ = 135 ± 10 kJ/mol for VO(g) and −185 ± 15.0 kJ/mol for VO_2(g). Overall, the results obtained allowed us to estimate the standard formation enthalpy of $VMoO_3$ to be −318 kJ/mol with an accuracy near 40 kJ/mol.



1. INTRODUCTION

Vanadium compounds are well-known to be of great importance (see, for example, ref 1). Therefore, the data about their gas-phase behavior might be useful for predicting the stability of vanadium-containing materials at elevated temperature.

The existence of a number of gaseous salts formed by vanadium oxides (V_2O_3) had been known before our investigation. On the one hand, there are a number of investigations concerning different gaseous vanadates: the study of the thermodynamic properties of alkali metal vanadates has been described in refs 2−7, alkali-earth metal vanadates have been investigated in refs 8−10, and the thermodynamic properties of gaseous lead and europium vanadates have been determined in refs 11−13, respectively.

On the other hand, while reacting with relatively more acidic oxides, V_2O_3 plays the cation-forming role, and vanadium salts are formed. Described in ref 14 are vanadium phosphates VPO_2 and VPO_3. The equilibrium constants of gas-phase reactions (1) and (2) were obtained, while the standard formation enthalpies of VPO_2 and VPO_3 have been calculated to be −273 ± 17 and −615 ± 16 kJ/mol, respectively, at 298 K.

$$VO_2 + PO = VPO_3 \qquad (1)$$

$$VO_2 + 2PO = VPO_2 + PO_2 \qquad (2)$$

Bennet et al.[15] have determined the composition of the vapor over a $V_2O_5 + WO_3$ mixture in the temperature range 1255−1465 K and found a lot of gaseous associates (VW_2O_8, VW_3O_{11}, VW_4O_{14}, $V_2W_2O_{10}$, $V_2W_3O_{14}$, V_3WO_{10}, $V_3W_2O_{13}$, and $V_4W_2O_{16}$). The thermodynamic properties and structures of the associates mentioned have not been determined. Meanwhile, similar molybdenum-containing substances have not been investigated, to the best of our knowledge.

In view of the aforementioned, the main goal of the present investigation has been defined as determining the thermodynamic properties of gaseous V−Mo−O- and V−W−O-containing species.

2. EXPERIMENTAL AND COMPUTATIONAL METHODS

2.1. High-Temperature Mass Spectrometry. The experiments were carried out using the Knudsen effusion technique, combined with mass spectrometric analysis of the vapor composition, described in detail elsewhere,[16] on a MS 1301 mass spectrometer (Construction Bureau, Academy of Sciences, St. Petersburg, Russia). Ionization of vapor species was made by electron impact, with the energy of ionizing electrons being 25 eV. Molybdenum and tungsten effusion cells were heated by electron bombardment. The temperature was measured using an EOP-66 optical pyrometer in the temperature range 1600−2100 K, with the accuracy of the measurements being 5 K. Testing of the instrument was conducted by measuring the vapor pressure of calcium fluoride and subsequently comparing the values obtained with the reference data.[17] V_2O_3 used in the experiments was made by Aldrich Co. and was stated to contain at least 99.99% V_2O_3.

Partial vapor pressures of the gaseous species were calculated by the ion-current comparison method, eq 3, using gold as the internal pressure standard.[18]

$$p_1 = \frac{p_2 I_1 T_1 \sigma_2 \gamma_2}{I_2 T_2 \sigma_1 \gamma_1} \qquad (3)$$

In eq 3, I_i is total ion current, T_i is the temperature, σ_i is the ionization cross section, γ_i is the secondary electron multiplier gain factor, which is known to be proportional to the square root of the molecular mass of the corresponding molecule, and p_i is the partial pressure of the species i, while indexes "1" and "2" mean the sample and standard, respectively. Molecular cross sections were obtained by

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the additivity method, with the atomic cross sections being taken from ref 19. Cross sections of VXO_4 and VWO_3 molecules were multiplied by 0.7, according to the suggestion of Guido and Gigli[20] for five and more atomic molecules.

Enthalpies of the reactions under study were calculated using eq 4.

$$\Delta_r H_0^\circ = T\Delta_r \Phi_T^\circ - RT \ln K_p(T) \tag{4}$$

where $\Delta_r H_0^\circ$ and $\Delta_r \Phi_T^\circ$ are the changes of the enthalpy and Gibbs reduced energy of the reaction under consideration at temperatures 0 and T K, respectively, R is the gas constant, and K_p is the equilibrium constant of the reaction. The Gibbs reduced energy of any reaction is defined by eq 5.

$$\Phi_T^\circ \equiv -\frac{G_T^\circ - H_0^\circ}{T} \equiv -\frac{H_T^\circ - H_0^\circ - TS_T^\circ}{T} \tag{5}$$

The values of $\Delta_r H_0^\circ$ were subsequently recalculated to the temperature 298 K.

For the reaction enthalpies to be recalculated from the temperature of experiments to the standard temperature, thermodynamic functions were taken from the reference book[17] for gaseous oxides and were calculated using "rigid rotator−harmonic oscillator" approximation for gaseous vanadium salts under study. Bond lengths and angles along with vibrational frequencies for vanadium salts were obtained as a result of a theoretical study of these molecules.

2.2. Computational Methods. All calculations were performed using the *PC GAMESS* version[21] of the GAMESS(US) quantum chemical package.[22] Energy ordering and equilibrium geometries of possible structures of compounds under investigation (both minima and transition states) in a wide range of spin states were obtained using the restricted open-shell Hartree−Fock (ROHF) method. The SBK effective core potential (ECP) with an associated basis set[23] was used for V, Mo, and W atoms along with full-electron basis set 6-31G for O atoms.[24] The lowest-lying structure for every compound was reoptimized at the B3LYP[25] level with the following basis sets: LanL2TZ(f) basis[26,27] with an associated ECP[28] for Mo and W atoms and full-electron basis sets for V (cc-pVTZ[29]) and O (cc-pVQZ[30]) atoms. The restricted open-shell form of the method was used for the VWO_4 molecule, with the unrestricted form being utilized for $VMoO_4$ and VWO_3 because of convergence problems. Calculations of oxides needed for obtaining theoretical reaction enthalpies were made at the (RO)B3LYP level. All of the optimizations were performed without symmetry constraints.

3. RESULTS

3.1. Experimental Results. In order to synthesize gaseous molybdate $VMoO_4$ and tungstates VWO_3 and VWO_4, V_2O_3 was evaporated from molybdenum and tungsten effusion cells, respectively. While V_2O_3 was evaporating from the molybdenum cell, the concentration of gaseous molybdenum oxide was too low; therefore, vanadium molybdate could not be detected. Hence, silicon dioxide (SiO_2) was added to the cell, and its interaction with the cell material resulted in an increase in the amount of gaseous molybdenum oxide. The scheme of such an interaction is as follows:

$$SiO_2(s) + Mo(s) \rightarrow SiO(g) + MoO_3(g) + MoO_2(g) \tag{6}$$

Interaction between silicon and vanadium oxides can result in the formation of some compounds in the condensed phase, but such processes cannot prevent reaction (6).

VO^+, VO_2^+, XO_2^+, XO_3^+, and VXO_4^+ (X = Mo, W) ions were detected in the mass spectra of vapor in the temperature range 1900−2100 K. For X = Mo, a SiO^+ ion was also observed. Relative intensities of ion currents varied depending on the temperature. In order to determine the vapor composition, the appearance energies of the ions were measured using the vanishing current method with gold as the energy standard, the ionization energy of which is known to be 9.2 eV.[31] The appearance energies obtained were (±0.3 eV) as follows: 6.5 (VO^+), 10.5 (VO_2^+), 9.5 (MoO_2^+), 12.1 (MoO_3^+), 10.0 (WO_2^+), 11.6 (WO_3^+), 11.0 ($VMoO_4^+$), and 10.5 (VWO_4^+). Comparing these values with literature data concerning the ionization energies of the oxides[13,31,32] and chromium molybdates and tungstates[33] allowed us to conclude that the vapor over V_2O_3−SiO_2−Mo and V_2O_3−W systems consists of vanadium and molybdenum (tungsten) oxides VO, VO_2, XO_2, and XO_3, along with vanadium molybdate or tungstate VXO_4.

When determining the molecular precursors, we did not limit ourselves to measurement of the appearance potentials of all ions of a mass spectrum but used also some complementary methods of identification. In particular, for all ions of the mass spectrum, we analyzed the shapes of the ionization efficiency curves in order to find out if there were any inflection points indicating the existence of two or more precursors of an ion. Not a single ionization curve has demonstrated this singularity. Such characteristic bends of the ionization efficiency curves can be found when the relative content of either the molecular or fragment ion is not less than 20%. In addition, we lowered the ionization voltage from 25 V to its threshold values and then measured the ratios of the VO^+/VO_2^+, MoO_2^+/MoO_3^+, and WO_2^+/WO_3^+ ion currents. Every time the ionization voltage dropped to 15 V and lower the values of these ratios increased. On the contrary, the processes of dissociative ionization of the VO_2, MoO_3, and WO_3 molecules proceed according to the following respective schemes:

$$VO_2 + e^- = VO^+ + O + 2e^- \tag{7}$$

$$MoO_3 + e^- = MoO_2^+ + O + 2e^- \tag{8}$$

$$WO_3 + e^- = WO_2^+ + O + 2e^- \tag{9}$$

These ratios had to decrease because the appearance potentials of the fragment ions in this case are 4−5 eV higher than the ones for the molecular ions of the same mass. According to our estimates, the errors of the ion-current measurements caused by inadequate account of the processes of dissociative ionization of the molecules present in the vapor do not exceed 20% and may result in an error of 2−3 kJ when the enthalpy of the reactions is calculated using eq 4.

During one of the experiments, we managed to increase the sensitivity of our mass spectrometer; hence, we were able to detect VWO_3^+ in addition to VO^+, VO_2^+, WO_2^+, WO_3^+, and VWO_4^+ ions. Unfortunately, the intensity of VWO_3^+ was too low to measure an exact value of its appearance energy, but it was determined to be lower than the appearance energy of the VWO_4^+ ion. With this fact, combined with an increase of the ratio of intensities VWO_3^+/VWO_4^+ as the temperature increases, the molecular origin of the VWO_3^+ ion was proven.

Unfortunately, we failed to obtain gaseous molybdate $VMoO_3$. Having been heated to a relatively high temperature for a more reliable measurement of the $VMoO_3^+$ ion current, the effusion orifice was clogged by melt.

The equilibrium constants of gas-phase reactions (10)−(14) were measured in order to determine the standard formation enthalpies of the gaseous salts under consideration.

$$VO + XO_3 = VXO_4 \tag{10}$$

$$VO_2 + XO_2 = VXO_4 \tag{11}$$

$$VO + WO_2 = VWO_3 \quad (12)$$

$$VWO_4 + VO = VO_2 + VWO_3 \quad (13)$$

$$VWO_4 + WO_2 = WO_3 + VWO_3 \quad (14)$$

The partial pressures and reaction enthalpies obtained are listed in Tables S1−S3 (Supporting Information).

3.2. Theoretical Results. Nowadays, we have a rather well-established concept of the structures of gaseous salts of oxygen acids based on both experimental data (gas electronography, IR spectroscopy of molecules isolated in inert matrixes, etc.) and quantum chemical calculations and referring in most cases to a model of the ion pair (cation−anion). The majority of the salts with the formula M_mXO_n (M is a cation, X is an anion-forming element, and m = 1 or 2) have a closed cyclic structure, and the most probable location of the cation is a point on a perpendicular to a triangle side or to a tetrahedron edge with a bidentate bond cation−anion. The gaseous salt structures are not rigid; the cation M has a considerable degree of freedom in its rotation around the relatively rigid anion group XO_n.

The structures investigated are shown in Figure 1. One can divide them according to the following classification: VXO_n (Figure 1a−c,i−k), $(VO)XO_{n-1}$ (Figure 1d−f,m,n), and XVO_n (Figure 1f−h,k−m) (n = 3 or 4), as well as groups with monodentate (Figure 1b,d,h,j,l,n), bidentate (Figure 1a,e,g,i,m), and tridentate (Figure 1c,f,k) binding of the cation part.

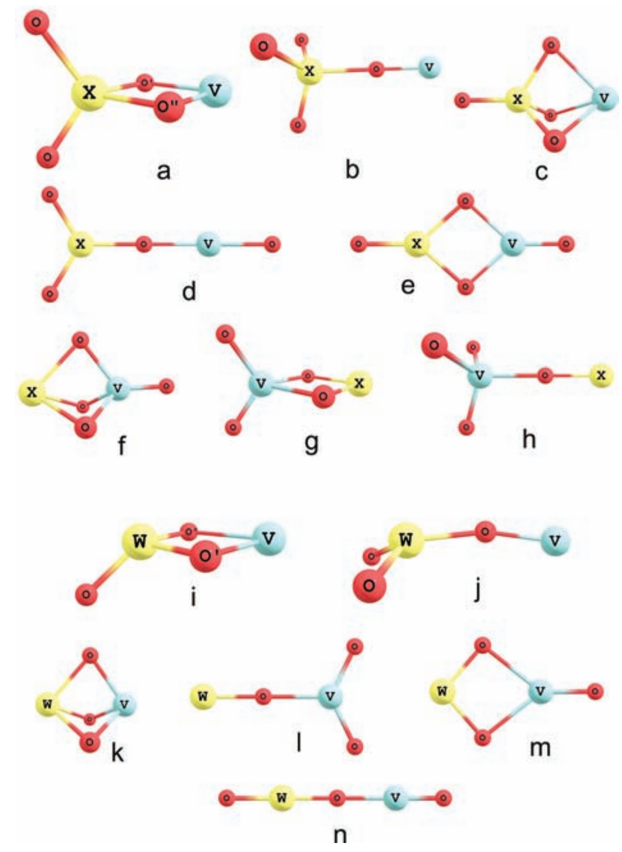

Figure 1. Possible isomers of $VMoO_4$, VWO_4, and VWO_3.

The "bidentate" structures of the VXO_4 type (Figure 1a) with quartet spin states turned out to be the ones with the lowest-lying energy. Special attention should be paid to the fact that at the ROHF level the structures with C_{2v} symmetry were higher by 172 and 22 kJ/mol for $VMoO_4$ and VWO_4, repectively, than similarly distorted ones.

Calculations by the (RO)B3LYP method conserved the distorted structure for VWO_4, while the (U)B3LYP method gave the symmetric structure for $VMoO_4$ even after optimization was started from the distorted one. The latter result agrees with the results of Mann et al.,[34] who had found the same structure to be the lowest-energy isomer using the (U)B3LYP method with another basis set. $\langle S^2 \rangle$ in our (U)B3LYP calculation was equal to 3.76 (while the expected value was 3.75).

The "monodentate" isomer with vanadium as the cation (Figure 1j) had the lowest energy in the VWO_3 group, with the "bidentate" isomer (Figure 1i) lying nearly 24 kJ/mol higher at the ROHF level. Both of the isomers mentioned had sextet spin states. We examined both of them at the B3LYP level, and the "bidentate" isomer turned out to have lower energy (opposite to the ROHF results). $\langle S^2 \rangle$ values were near 8.76 (the expected value was 8.75). We also mention that Mann et al.[34] showed a similar "bidentate" structure with a sextet spin state to be the lowest-energy isomer for the $VMoO_3$ molecule.

The equilibrium geometry parameters and vibrational frequencies obtained at the B3LYP level for the molecules under study are summarized in Table 1. A summary concerning all of the structures obtained is given in the Supporting Information.

Table 1. Equilibrium Geometry Parameters and Vibrational Frequencies Calculated at the B3LYP Level for the Ground States of $VMoO_4$, VWO_3, and VWO_4 Molecules

	$VMoO_4$ [Figure 1a (quartet)]	VWO_3 [Figure 1l (sextet)]	VWO_4 [Figure 1a (quartet)]
r(V−O′), Å	1.871	2.106	1.852
r(V−O″), Å	1.871		1.915
r(X−O′), Å	1.889	1.778	1.903
r(X−O″), Å	1.889		1.869
r(X−O), Å	1.700	1.710	1.713
∠VO′X	94.21	90.41	92.65
∠VO″X	94.23		91.71
∠OXO	110.23		111.70
∠VWO		137.12	
frequencies, cm^{-1}	117, 230, 244, 281, 303, 365, 548, 611, 673, 729, 984, 1001	108, 222, 242, 249, 318, 419, 835, 864, 1002	107, 210, 252, 262, 301, 333, 436, 615, 691, 728, 975, 1015

The total energies of two spin states were compared for each of the oxides involved in reactions (10)−(14): singlet and triplet or doublet and quartet for the systems with even or odd numbers of electrons, repectively. The states with lower energy are quartet for VO, doublet for VO_2, triplet for MoO_2, and singlet for WO_2, WO_3, and MoO_3. All of the results are in agreement with reference data.[35]

4. DISCUSSION

Combining the average values of the enthalpies of reactions (10)−(14), recalculated to the temperature 298 K, with the standard formation enthalpies of gaseous oxides VO (148.6 ± 10.0), VO_2 (−232.6 ± 15.0), MoO_2 (−15.6 ± 15.0), MoO_3 (−364.4 ± 15.0), WO_2 (29.1 ± 15.0), and WO_3 (−319.7 ± 15.0), taken from the book in ref 17, allows us to calculate the standard formation enthalpies and the standard atomization enthalpies of gaseous vanadium molybdate and tungstates. Initially, the standard formation enthalpies of VXO_4, calculated from eqs 10 and 11, turned out to differ by 50−60 kJ. However, we mention right away that the discrepancy was resolved after reconsideration of the enthalpies of formation of the oxides participating in reactions (10) and (11). The standard formation enthalpies from the reference book[17] of both molybdenum and tungsten di- and trioxides (along with the corresponding values for chromium oxides) had been used previously[33] when the thermodynamic properties of gaseous chromium molybdates and tungstates had been investigated. The standard formation enthalpies of $CrXO_4$, obtained from equations similar to eqs 10 and 11, had been very close to each other. Therefore, in order to explain the discrepancy in the current work, we carefully analyzed the data in refs 17 and 36 about the standard formation enthalpies of gaseous V_2O_3 and found these values to be very inconsistent. So, we examined publications[37−39] cited in the reference books[17,36] and some more recent publications[40−43] concerning the formation enthalpies of gaseous vanadium monoxide and dioxide.

We adopt $\Delta_f H^\circ(298.15) = 135 \pm 10$ kJ/mol for VO(g) and -185 ± 15 kJ/mol for VO_2(g). These values are the average values of the second law results from Berkowitz et al.,[37] Coopens et al.,[38] Killingbeck,[40] and Frantseva and Semenov,[41] the third law results from Farber et al.,[39] and the second and third law results from Ranchorndhevakul et al.,[42] Balducci et al.[43] and Aristov and Armentrout.[44] The values from these studies show good agreement. The information is summarized in Table 2.

Table 2. Selective Standard Formation Enthalpies of Gaseous Vanadium Mono- and Dioxide

reference data	$-\Delta_f H^\circ_{298}$(VO), kJ/mol	$-\Delta_f H^\circ_{298}(VO_2)$, kJ/mol
ref17 (reference book)	148.6 ± 10.0	−232.6 ± 15.0
ref 36 (reference book)	127.6 ± 20.9	−232.6 ± 41.8
ref 43, average value	133.2 ± 8.5	−174 ± 11.0
ref 42, average value	119.0 ± 10.0	−189.9 ± 10.0
ref 39, third law results	146.9 ± 16.7	−184.0 ± 16.7[a]
ref 41, second law results		−188.5 ± 12.6[a]
ref 41, third law results		−233.6 ± 8.4[b]
ref 40, average value		−187 ± 27
ref 37, second law results	133.4 ± 10.0[a]	
ref 38, second law results	138.8 ± 11.0[a]	
ref 38, second law results	136.2 ± 11.0[b]	
ref 44, collision-induced dissociation	138.3 ± 33.8[c]	
adopted value	135 ± 10	−185 ± 15

[a] The original value was recalculated using reference data from ref 17. [b] The original value was recalculated using reference data from ref 36. [c] The original value was recalculated using reference data from refs 32 and 36.

In order to test new values of VO and VO_2 formation enthalpies, we used our experimental data to determine the equilibrium constant and enthalpy for the gas-phase reaction (15).

$$VO + WO_3 = VO_2 + WO_2 \tag{15}$$

The experimental enthalpy of this reaction was found to be 21 ± 4 kJ, with the calculated one being equal to 29 ± 28 kJ. One can see these values to agree within the error limits.

Consequently, we used adopted values of the formation enthalpies of gaseous vanadium monoxide and dioxide for obtaining standard formation enthalpies of gaseous $VMoO_4$, VWO_3, and VWO_4. Then, $\Delta_f H^\circ(VXO_4)$, calculated from eqs 10 and 11, did agree within the experimental errors and so did the formation enthalpies of VWO_3, calculated from eqs 12−14. The results obtained are summarized in Tables 3 and 4.

Table 3. Standard Formation Enthalpies and Standard Atomization Enthalpies of Gaseous Vanadium Molybdate $VMoO_4$ and Tungstate VWO_4

substance		$VMoO_4$	VWO_4
$-\Delta_f H^\circ(298)$, kJ/mol	eq 10	677 ± 24	710 ± 21
	eq 11	675 ± 27	703 ± 23
	weighted average	676 ± 27	706 ± 23
$\Delta_{at} H^\circ(298)$, kJ/mol		2848 ± 28	3071 ± 24

Table 4. Standard Formation Enthalpies and Standard Atomization Enthalpy of Gaseous Vanadium Tungstate VWO_3

substance		VWO_3
$-\Delta_f H^\circ(298)$, kJ/mol	eq 12	322 ± 19
	eq 13	341 ± 29
	eq 14	329 ± 31
	weighted average	331 ± 29
$\Delta_{at} H^\circ(298)$, kJ/mol		2447 ± 30

We also calculated the theoretical enthalpies of the reactions under investigation to check the accuracy of the B3LYP method for reactions involving open-shell gaseous oxides and salts.

The enthalpies of reaction (10) are −372 and −438 kJ as well as −408 and −504 kJ for reaction (11) for molybdenum and tungsten compounds, respectively. Other results are −337, 168, and 102 kJ for reactions (12)−(14), respectively. Unfortunately, one can see that these results differ considerably from the experimental values, which are equal to (in the same order) −446 ± 16, −523 ± 10, −472 ± 16, −346 ± 9, −485 ± 5, 49 ± 2, and 26 ± 2 (see Tables S1−S3 in the Supporting Information). Although the calculations at the B3LYP level proved to be not enough for reproducing the experimental reaction enthalpies, we expect this level to be enough for determination of the structures.

In the isocation series of gaseous oxyacid salts, the atomization enthalpy of gaseous salts has been shown[45] to be linearly dependent on the atomization enthalpy of gaseous anion-forming oxides, with the dependence being represented by the following equation:

$$\begin{aligned}&\Delta_{at}H^\circ(\text{salt, gas, } 298)\\ &\quad = k\Delta_{at}H^\circ(\text{anion-forming oxide, gas, } 298) + b\end{aligned} \tag{16}$$

We recalculated the values given in ref 14 using new standard formation enthalpies of gaseous vanadium monoxide and dioxide.

Such a dependence is plotted (Figure 2) for the isocation series of vanadium salts, with the atomization enthalpies of vanadium molybdate and tungstates having been taken from the present work, whereas the atomization enthalpies of vanadium phosphates were taken from ref 14 and recalculated using adopted values of the formation enthalpies of VO and VO_2.

Coefficients of eq 16 are $k = 1.08 \pm 0.04$ and $b = 992 \pm 54$, and the correlation coefficient r is 0.998. Taking into account

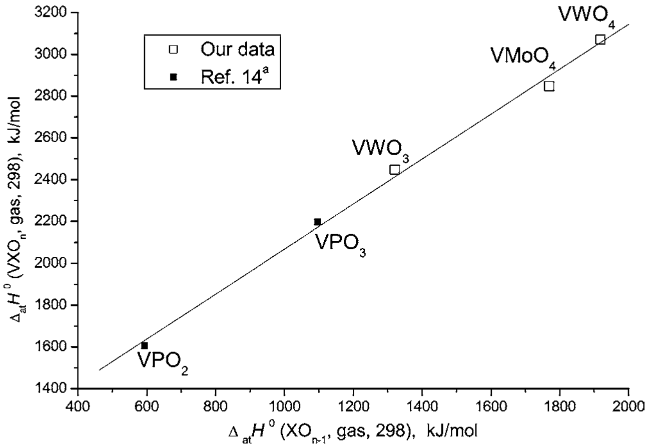

Figure 2. Atomization enthalpies of gaseous vanadium salts versus the atomization enthalpies of the corresponding gaseous anion-forming oxides. The sizes of the symbols represent the uncertainties of the atomization enthalpies.

the high correlation coefficient, we can expect our results to be reasonable.

Atomization and then the formation enthalpies of other vanadium salts can also be estimated from eq 16 using the coefficients obtained; for example, the formation enthalpy of $VMoO_3$ was calculated to be −318 kJ/mol. We estimate the accuracy of this value to be near 40 kJ/mol.

Finally, we emphasize the ability of molybdenum to reduce V_2O_3 being much lower than the corresponding ability of tungsten. The partial pressures of tungsten oxides and vanadium tungstate were much higher than the partial pressures of molybdenum oxides and vanadium molybdate at the same temperature. Molybdenum does not react with V_2O_3 to a considerable degree; hence, molybdenum cells, unlike tungsten ones, were concluded to be applicable in the investigation of V_2O_3 vaporization under nearly neutral conditions.

The results of a number of previous investigations concerning vaporization of V_2O_3 have been described and discussed in detail by Wang et al.[46] The authors have also given their own results of the evaporation of V_2O_3 from tungsten cells. The vaporization process has been described by eq 17, and the dependences of the partial pressures of vanadium monoxide and dioxide on temperature have been found to be determined by eqs 18 and 19, respectively, in the temperature range 1839–2105 K.

$$V_2O_3(s) = xVO_2(g) + (2 - x)VO(g) + (1 - x)O(g) \tag{17}$$

$$\log p(VO, Pa) = -(31422 \pm 575)/T + (14.55 \pm 0.29) \tag{18}$$

$$\log p(VO_2, Pa) = -(24846 \pm 703)/T + (11.39 \pm 0.36) \tag{19}$$

One can see that, as the temperature increases, the greater becomes the relative content of VO in vapor and the x value decreases.

We studied the vaporization of the same sample, i.e., V_2O_3, from molybdenum cells. The dependences of the partial pressures of VO and VO_2 on the temperature were found to be

$$\log p(VO, Pa) = -(33842 \pm 1138)/T + (16.98 \pm 0.98) \tag{20}$$

$$\log p(VO_2, Pa) = -(35665 \pm 1337)/T + (17.42 \pm 0.68) \tag{21}$$

in the temperature range 1845–2069 K.

According to these results, the line of vanadium monoxide lies higher than the line of VO_2.

However, we point out here that the absolute values of the partial pressures being calculated using the ion-current comparison method (eq 3) depend on the ionization cross-sectional values being used. Many researchers still traditionally use the ionization cross sections of Mann[19] and the additivity rule. Both eqs 18 and 19 and eqs 20 and 21 were obtained using the ionization cross sections from ref 19 and the additivity rule.

Nevertheless, the additivity rule and its modifications are known to give incorrect results sometimes. For example, the ratio $\sigma(VO_2)/\sigma(VO)$ calculated using the additivity rule is equal to 1.14, although this value has been reported to be 0.33 in ref 47. This review[47] provides experimentally determined ionization cross sections both for atoms and for some molecules. The information is presented in the form of ratios that allowed us to obtain $\sigma(Au)/\sigma(VO)$ and $\sigma(Au)/\sigma(VO_2)$ values, which are the multipliers in eq 3. Using these data allowed us to represent the dependences of the partial pressures of vanadium monoxide and dioxide on the temperature by eqs 22 and 23 (the temperature range is 1845–2069 K).

$$\log p(VO, Pa) = -(33842 \pm 1138)/T + (17.34 \pm 0.98) \tag{22}$$

$$\log p(VO_2, Pa) = -(35665 \pm 1337)/T + (18.34 \pm 0.68) \tag{23}$$

Figure 3 shows a graphic comparison of eqs 18–23.

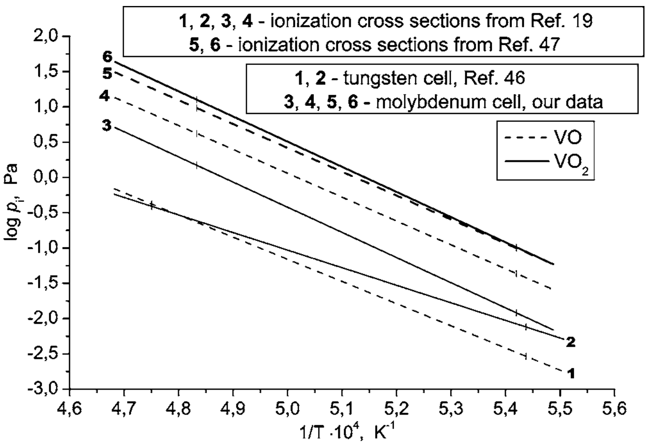

Figure 3. Temperature dependencies of the vapor pressures of V_2O_3. Lines 3–6 are based on 28 data points each.

On the one hand, one can see that the lines describing the vaporization of V_2O_3 from the tungsten cell are lower than the corresponding lines describing the vaporization of V_2O_3 from the molybdenum cell. This is due to the fact that V_2O_3 interacts with tungsten to a considerable degree, while the conditions of V_2O_3 vaporization from the molybdenum cell are close to those of the neutral ones.

On the other hand, eqs 22 and 23 (lines 5 and 6 in Figure 3) seem to describe the vaporization process more correctly than eqs 20 and 21 (lines 3 and 4) because the experimentally measured cross sections VO and VO_2 were used. Choosing another ionization cross-sectional value caused it to approach the lines of VO and VO_2 and the x value from eq 17 to tend toward 1. The latter fact means that the partial pressure of oxygen is insignificant when V_2O_3 vaporizes from the molybdenum cell, which agrees with the experimentally obtained partial pressures of molybdenum oxides. These can also explain the need for using special conditions to synthesize gaseous vanadium molybdates.

We emphasize that, although the selection of the cross-sectional values of the molecules affects the partial pressure values to a considerable degree, it can change the enthalpies of the reactions under investigation by no more than 2 kJ according to our estimations. Unfortunately, the ionization cross sections of molybdenum and tungsten oxides as well as vanadium salts have not been published by Drowart et al.;[47] therefore, we cannot perform exact calculations.

If the conditions during vaporization of V_2O_3 from the molybdenum cell are supposed to be close to the neutral ones, the activity of V_2O_3 in the V_2O_3−W system can be calculated using eq 24.

$$a(V_2O_3) = \frac{p(VO)\,p(VO_2)}{p^0(VO)\,p^0(VO_2)} \tag{24}$$

The numerator contains the partial pressures of V_2O_3 forming during vaporization of V_2O_3 from the tungsten cell, with the partial pressures in the denominator being taken from vapor above V_2O_3 being evaporated from the molybdenum cell.

Temperature dependence of the activity is shown in Figure 4. Such a dependence can be represented as

$$\log a(V_2O_3) = (13237 \pm 13)/T - (8.46 \pm 0.01) \tag{25}$$

The temperature range is 1845−2069 K.

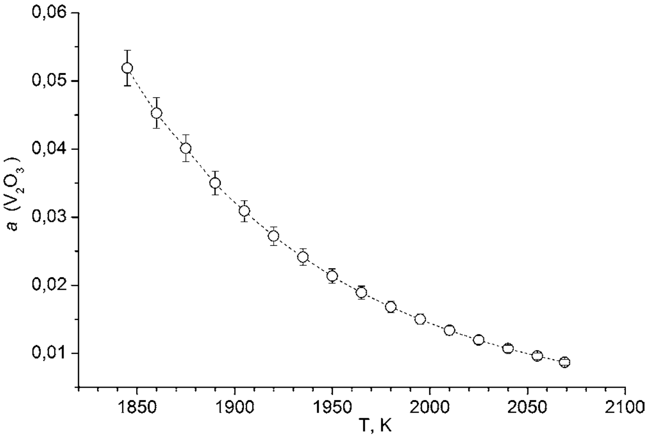

Figure 4. Activity of V_2O_3 in the V_2O_3−W system as a function of the temperature.

As the temperature is increased from 1845 to 2069 K, the activity of V_2O_3 decreases from 5.0×10^{-2} to 8.7×10^{-3} correspondingly and the greater becomes interaction of V_2O_3 with tungsten.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Equilibrium data for the gas-phase reactions (10)−(14) (Tables S1−S3), and optimized structures, their energies, and the number of imaginary frequencies for a number of isomers of $VMoO_4$, VWO_3, and VWO_4 molecules. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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