UV-Vis Absorption Spectrum of Vanadium Tetraiodide Vapor and Thermodynamic Properties of the Vanadium Iodides

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Molar absorptivities have been assigned to $VI_4(g)$ for the wavelength interval 230-500 nm. Equilibrium and thermodynamic constants in the range 550-840 K are derived from absorbance data for the following reactions (standard state 1 bar): (1) $2VI_3(s) \rightleftarrows 2VI_2(s) + I_2(g)$ ($\Delta H°/(kJ{\cdot}mol^{-1}) = 93.0(\pm0.8)$, $\Delta S°/(J{\cdot}mol^{-1}{\cdot}K^{-1}) = 113.5(\pm1.3)$); (2) $VI_2(s) + I_2(g) \rightleftarrows VI_4(g)$ ($\Delta H°/(kJ{\cdot}mol^{-1}) = 59.4(\pm0.7)$, $\Delta S°/(J{\cdot}mol^{-1}{\cdot}K^{-1}) = 43.4(\pm1.0)$); (3) $2VI_3(s) \rightleftarrows VI_2(s) + VI_4(g)$ ($\Delta H°/(kJ{\cdot}mol^{-1}) = 152.3(\pm2.9)$, $\Delta S°/(J{\cdot}mol^{-1}{\cdot}K^{-1}) = 156.8(\pm4.5)$; (4) $VI_3(s) + 0.5I_2(g) \rightleftarrows VI_4(g)$ ($\Delta H°/(kJ{\cdot}mol^{-1}) = 104.8(\pm1.8)$, $\Delta S°/(J{\cdot}mol^{-1}{\cdot}K^{-1}) = 98.4(\pm2.7)$.

Following recent work on the vanadium bromide system (*1*), a similar vapor-phase absorbance study of the vanadium iodides has been made. Diaphragm gage experiments have been used by Tolmacheva, Tsintsius, and Andrianova (TTA) (*2*) and by Berry, Smardzewski, and McCarley (BSM) (*3*) to determine equilibrium and thermodynamic constants for reaction 1. BSM (*3*) also report transpiration data used

$$2VI_3(s) \rightleftarrows 2VI_2(s) + I_2(g) \qquad (1)$$

to characterize reaction 2. From their results equilibrium

$$VI_2(s) + I_2(g) \rightleftarrows VI_4(g) \qquad (2)$$

pressures of VI_4, as fixed by equilibrium 3,may be calcu-

$$2VI_3(s) \rightleftarrows VI_2(s) + VI_4(g) \qquad (3)$$

lated: 1 + 2. At temperatures below 633 K partial pressures of $I_2(g)$ and $VI_4(g)$, respectively, given by BSM, *ca.* 3/4 of their observed values, exceed those reported for equilibrium 1 and projected for equilibrium 3 (see Figure 1); i.e., below 633 K $VI_3(s)$ rather than $VI_2(s)$ should be the stable solid phase. BSM do not comment on this discrepancy, but they do observe that the approach to equilibrium for reaction 1 is slow at lower temperatures.

The present work was undertaken to examine the system by an independent method and to include a direct study of reactions 3 and 4. K_4^2 must equal $K_1K_2^2$. Only a cursory

$$VI_3(s) + 0.5I_2(g) \rightleftarrows VI_4(g) \qquad (4)$$

mention of the absorbance spectrum of I_2-VI_4 mixtures has been found in the literature (*4*); quantitative data were not given.

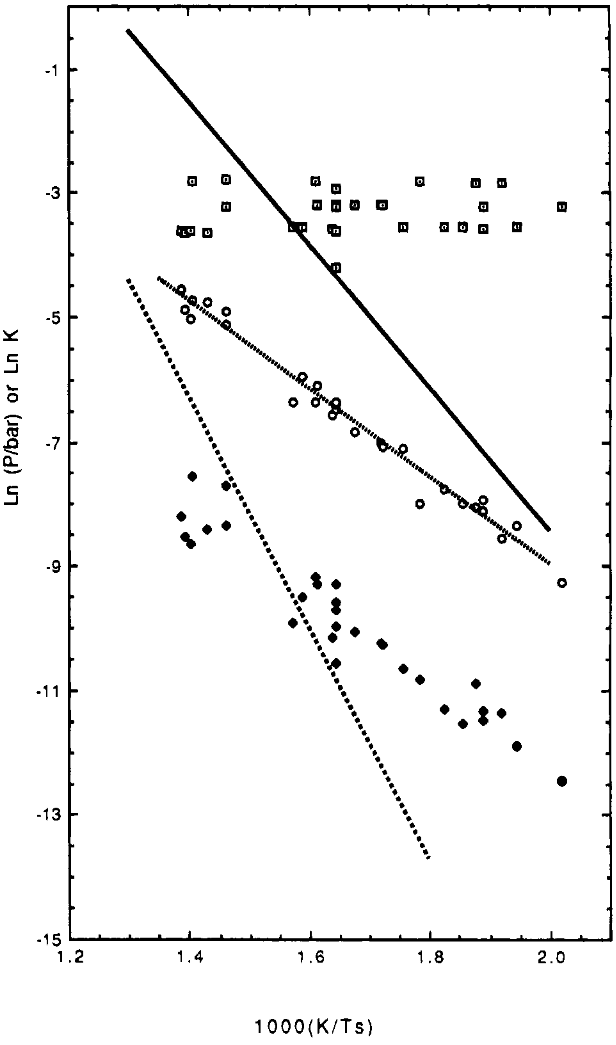

Figure 1. Comparison of BSM (*3*) transpiration pressures with equilibrium constants for reactions 1 and 3: ⊡, ln $P(I_2)$; ◆, ln $P(VI_4)$; ○, ln K_2; ···, LSQ ln K_2; —, ln K_1; •••, 1 + 2, ln K_3.

Experimental Section

A Cary 14-H spectrophotometer was used to measure absorbances. Seven samples, isolated in 20 mm o.d. cylindrical quartz cells, path lengths 1 or 5 cm, were examined. The furnace assembly has been described previously (*5*).

Vanadium iodide mixtures were prepared by reaction of vanadium powder (Aldrich Chemical, 99.5%) and iodine (Baker-Adamson Reagent I_2, 99.8%) in a Pyrex-quartz vacuum system. Typically a few milligrams of vanadium powder and a small excess (over the stoichiometric amount needed to form VI_4) of iodine crystals were introduced into a 6 mm o.d. vertical Pyrex tube, connected to the vacuum line and to a graded seal attached at the center of the side of a quartz absorbance cell. The system was evacuated (*ca.* 10^{-8} bar), pumping for several minutes, and then sealed off by collapsing the tubing with a natural gas-oxygen flame.

Vanadium iodides were generated in a thermal gradient as recommended by BSM (*3*). The micaceous crystals (VI_3)

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Table 1. Molar Absorptivities for $VI_4(g)$, Based on Concentrations Derived Using BSM (*3*) Equilibrium Constants for the Reaction $VI_2(s) + I_2(g) \rightleftarrows VI_4(g)$ ($\epsilon_{\lambda,T} = a + b(T/K)$ (range 570–850 K))

λ/nm	a/ (10^3 L·mol^{-1}·cm^{-1})	b/ (L·mol^{-1}·cm^{-1}·K^{-1})	$\epsilon_{\lambda,700}$/ (10^3 L·mol^{-1}·cm^{-1})
230	38.9	−24.7	21.6
240	41.5	−21.7	26.2
250	42.0	−21.0	27.3
260	36.4	−16.9	24.6
270	29.5	−12.1	21.0
280	28.3	−12.9	19.3
290	25.8	−12.0	17.4
300	19.3	−6.37	14.9
310	17.4	−6.25	13.0
320	16.2	−6.45	11.7
330	15.8	−7.07	10.8
340	16.3	−8.49	10.4
350	15.3	−8.04	9.67
360	14.6	−7.90	9.07
370	15.4	−9.33	8.87
380	13.8	−7.72	8.40
390	14.5	−8.98	8.21
400	14.0	−8.64	7.95
410	15.4	−10.7	7.91
420	15.1	−10.7	7.61
430	12.9	−8.44	6.99
440	11.9	−7.52	6.64
450	15.3	−12.0	6.90
460	4.97	−0.84	4.92
470	15.6	−12.8	6.64
480	14.7	−11.3	6.79
490	11.6	−7.37	6.43
500	23.7	−21.4	8.72

which collected on the reactor tube walls were easily dislodged and transferred into the cell body by shaking. Excess iodine was condensed by cooling the reaction tube, which also contained some unreacted vanadium and VI_2, in liquid nitrogen. The reaction tubes were then sealed off to isolate VI_3–VI_2 mixtures in the absorbance cells. When mixtures of VI_3 and I_2 were desired, the iodine in the cooled reactor was allowed to warm to give the desired iodine concentration before the seal-off.

Generally samples were equilibrated overnight before the absorbance was measured. To prevent condensation of solid on the windows, vapors in the cell body were held at a temperature, T_g, above that of any condensed phase (in the cell side arm at T_s). Temperatures were measured with chromel–alumel thermocouples; thermocouple readings were checked using the melting points of tin and lead.

Results and Discussion

Vapor-phase absorbances were measured in the wavelength (λ) range 230–500 nm. Spectra were fit satisfactorily assuming iodine and one other (VI_4) absorbing vapor. To obtain measurable contributions from $VI_4(g)$, substantial concentrations of iodine must be present. Iodine vapor absorptivities have been reported by Sulzer and Wieland (*6*) (350–500 nm) and by Passchier (*7*) (230–350 nm). As an initial approximation, refined later to give the best spectral fit, the concentration (c) of iodine was derived from iodine molar absorptivities and absorbances measured at temperatures low enough so that the contribution of $VI_4(g)$ could be neglected.

For sample 2 with T_s > 640 K, $c(VI_4)$ appeared to be fixed by equilibrium 2, and trial values were calculated using equilibrium constants, $K_2 = c(VI_4)/c(I_2)$, given by BSM (*3*), and the equation $c_0(I_2) = c(I_2) + c(VI_4)$; $c_0(I_2)$ represents the concentration of $I_2(g)$ when $c(VI_4)$ is 0. Molar absorptivities for $VI_4(g)$, $\epsilon_\lambda(VI_4)$, were then derived, at 10 nm intervals for the range 230–500 nm, by subtracting the iodine absorbance from the total and dividing the difference by the cell path length and $c(VI_4)$. The temperature dependences of the molar absorptivities were expressed in empirical equations of the form $\epsilon_{\lambda,T} = a_\lambda + b_\lambda T_g$; a_λ and b_λ, derived by a least-squares fit, were assumed to be constants for each selected wavelength. Values, adjusted slightly in some cases to improve the overall spectral fit, are listed in Table 1.

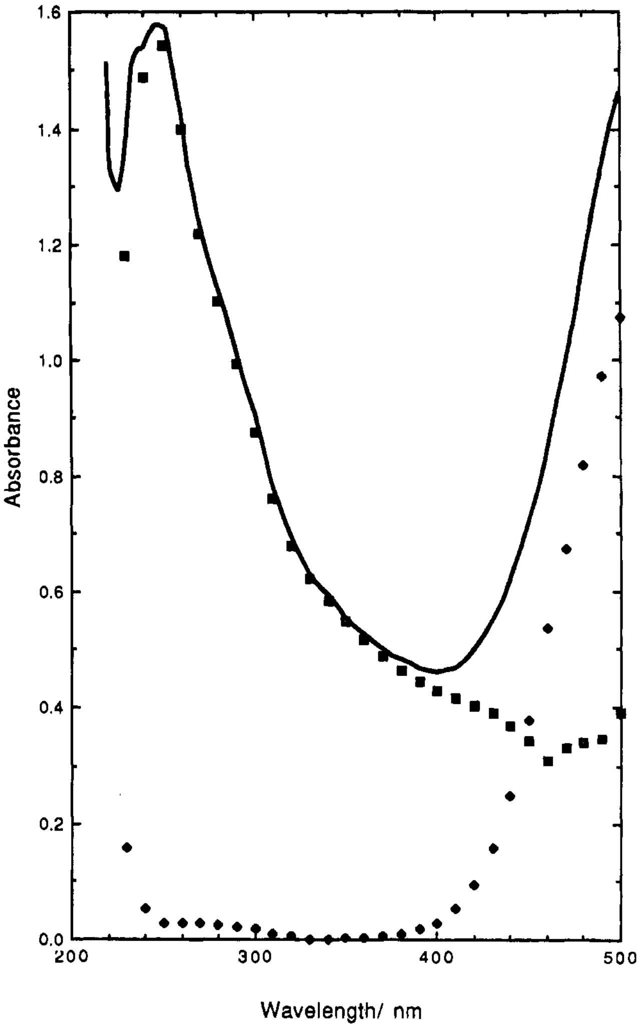

Figure 2. Absorbances for a mixture formed by sample 3, with T_g = 811 K, T_s = 800 K, $c(I_2(g))$ = 2.50 mM, and $c(VI_4(g))$ = 62.1 μM, as compared with calculated contributions from $I_2(g)$ and $VI_4(g)$: —, absorbance, mixture; ◆, absorbance, I_2; ■, absorbance, VI_4.

The absorbances observed for a representative mixture (from sample 3) and values calculated for iodine vapor and $VI_4(g)$ are shown in Figure 2. The VI_4 spectrum shows two strong overlapping peaks with maxima of *ca.* 240 and 250 nm and a slight indication of an unresolved peak(s?) on the broad shoulder at *ca.* 300 nm. Iodine absorbs strongly at wavelengths above 450 and below 220 nm (*6*, *7*).

The derived concentrations are listed for each sample, in the order in which scans were taken, in Table 2. The reaction numbers (RN) for which concentrations were used to calculate equilibrium constants are identified in the RN column. The "fit" column indicates the spectral fit by listing the number of absolute values of ΔA, $\Delta A = (A_{obs} - A_{calc})$, which exceeded 0.016, taken as an estimate of absorbance uncertainty. The maximum possible number for each mixture is 28 (less when the absorbance was off scale near a peak maximum).

Fifteen of the 77 mixtures, identified by the letter v in the RN column, appeared to be fully vaporized; i.e.,

Table 2. T_g, Vapor Temperature; T_s, Condensed Phase Temperature; c, Vapor Concentrations; RN, Reaction Number for Which Equilibrium Constant Calculated (v Indicates Sample Fully Vaporized); and fit, Number of Wavelengths for Which abs ($A_{obs} - A_{calc}$) > 0.016

T_g/K	T_s/K	$c(I_2)/\mu M$	$c(VI_4)/\mu M$	RN	fit
Sample 1, 5 cm Cell					
611	599	1414	0.693	4	0
644	625	1413	2.31	4	11
696	678	1490	9.31	1−4	8
Sample 2, 5 cm Cell					
670	652	409	1.35	2	0
691	673	436	1.97	2	0
710	692	435	2.58	2	0
765	746	433	5.32	2	0
846	825	425	12.9	2	0
754	735	433	4.61	2	0
724	708	434	3.48	2	0
859	841	423	15.3	2	3
795	779	430	8.17	2	1
658	639	301	0.82	2	0
632	613	167	0.30	1−4	0
597	577	66.7		1	1
581	561	35.5		1	0
595	576	62.5		1	0
574	554	29.9		1	0
655	643	430	1.18	1−4	0
606	592	102		1	0
679	665	423	1.58	2	0
577	557	39.2		1	1
835	808	420	11.8	2	0
720	694	435	3.09	2	0
665	644	420	1.10	1−4	0
642	623	246	0.49	1−4	0
644	632	332	0.82	1−4	0
598	587	89.1		1	0
596	586	86.7		1	0
597	586	87.4		1	0
600	589	92.5		1	0
Sample 3, 1 cm Cell					
735	724	2583	24.4	1−4	0
714	705	1964	15.4	1−4	0
750	737	2530	29.4	2	0
769	756	2521	38.0	2	0
690	690	1369	8.04	1−4	0
661	655	621	1.70	1−4	0
811	800	2497	62.1	2	0
793	783	2507	52.4	2	1
662	645	473	1.46	1−4	0
Sample 3, 1 cm Cell					
681	665	1269	3.87	4	0
677	651	540	1.64	1−4	0
Sample 4, 1 cm Cell					
824	808	2784	77.2	2	0
842	826	2769	91.6	2	0
767	755	2821	40.4	2	0
720	707	2574	19.5	4	0
690	677	2339	8.34	4	0
669	658	2341	4.36	4	1
861	840	2747	114.2	2	1
659	640	2342	2.31	4	1
Sample 5, 5 cm Cell					
795	812	3839	21.6	v	3
772	767	3839	21.1	v	0
757	752	3840	20.5	v	1
710	670	3846	8.61	4	2
716	686	3844	12.6	4	1
551	548	3850			2
422	414	3850			4
Sample 6, 5 cm Cell					
822	805	5386	19.7	v	7
706	683	5390	12.5	4	5
758	757	5387	19.0	v	4
739	736	5387	18.4	v	4
715	712	5387	17.6	v	4
669	639	5394	3.50	4	2
630	564	5396	0.30	4	2
583	533	5396			2
513	474	5396			0
459	422	5396			0
404	399	5395			2
513	477	5396			1
Sample 7, 5 cm Cell					
826	847	1733	28.9	v	1
863	860	1733	28.1	v	0
795	805	1734	25.1	v	1
807	815	1734	25.4	v	1
825	830	1734	25.4	v	0
843	848	1735	24.7	v	0
844	847	1735	23.9	v	0
804	816	1736	22.5	v	1

Table 3. Thermodynamic Constants for Reactions 1−4

RN	A	B	$\Delta H°/(kJ \cdot mol^{-1})$	$\Delta S°/(J \cdot mol^{-1} \cdot K^{-1})$	T/K range	ref
1	−11 190	13.656	93.0(±0.8)	113.5(±1.3)	550−725	
1	−11 504	13.601	91.9(±4.2)	113.1(±4.2)	591−804	2
1	−11 423	14.476	95.0(±0.6)	120.3(±0.8)	672−746	3
2	−7 142	5.224	59.4(±0.7)	43.4(±1.0)	610−840	
2	−7 001	5.020	58.2(±1.7)	41.7(±2.5)	495−722	3
3	−18 324	18.858	152.3(±2.9)	156.8(±4.5)	610−725	
4	−12 603	11.832	104.8(±1.8)	98.4(±2.7)	560−725	

absorbances were found to change only slightly as temperatures were increased. In 22 cases both $VI_2(s)$ and $VI_3(s)$ appeared to be present; i.e., the iodine concentrations correlated as expected for equilibrium 1. For 10 of these, the VI_4 contributions were not large enough to measure; i.e., absorbances were attributed entirely to iodine. For the other 12, $c(I_2)$ and $c(VI_4)$ were used to derive values of each of the four equilibrium constants, K_1, K_2, K_3, and K_4. For 21 other scans $VI_2(s)$ appeared to be the only solid phase present; i.e., $c(VI_4)/c(I_2)$ values correlated as K_2, but the concentrations did not give satisfactory values of K_1, K_3, or K_4. The 21 + 12 values gave a total of 33 values of K_2. By a similar criterion $VI_3(s)$ appeared to be the only solid phase present for 19 other scans; for 7 of these the VI_4 contribution was too small to measure, leaving a total of 24 values of K_4. The correlations are shown in Figure 3. The least-squares constants, based on the equation $\ln K = AT_s^{-1} + B$, standard state 1 bar, are listed in Table 3. Standard deviations are shown in parentheses. Values from refs 2 and 3 are listed for comparison.

The results derived in the present work are found to be self-consistent; i.e., constants derived directly from the absorbance data for reactions 3 and 4 are, within experimental error, the same as the sums 1 + 2 and 0.5 (1) + 2, respectively. Furthermore, the relationship $K_2 = K_3 = K_4$ is required when $P(I_2) = 1$ bar. The extrapolation of the least-squares lines, Figure 3, shows this behavior. Also, as may be seen from values in Table 2, $P(I_2) < K_1$ when equilibrium 2 alone determines the concentrations and $P(I_2) > K_1$ when equilibrium 4 alone determines the concentrations.

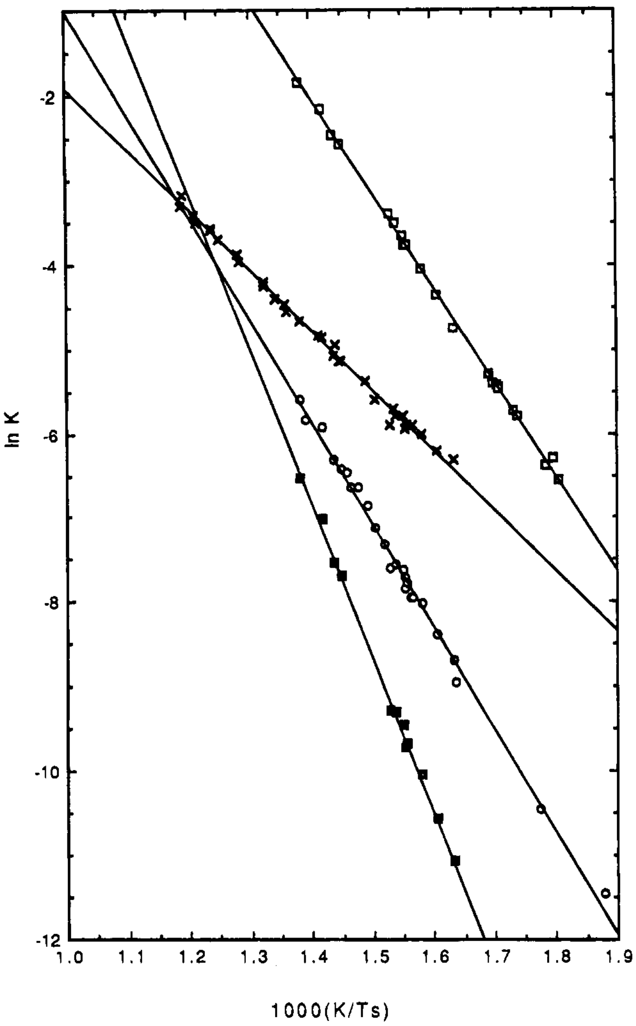

Figure 3. Calculated values of ln K_1, ln K_2, ln K_3, and ln K_4, and least-squares lines: □, ln K_1; ×, ln K_2; ■, ln K_3; ○, ln K_4. Samples, temperatures, and concentrations are listed in Table 2.

The absorbance K_1 values correspond closely with those observed by TTA (*2*) at their four highest and four lowest temperatures. Their values are somewhat higher at midrange. BSM (*3*) K_1 values are higher by a factor *ca.* 1.6. Since the absorbance data appear consistent with the values of K_2 derived by BSM, one concludes that the recombination reactions $VI_2(s) + 0.5I_2(g) \rightleftharpoons VI_3(s)$ and $VI_2(s) + VI_4(g) \rightleftharpoons 2VI_3(s)$ are sufficiently slow and the forward and reverse reactions of equilibrium 2 sufficiently fast that the transpiration study (*3*) gave satisfactory results for equilibrium 2 even when $c(I_2) > K_1$ and $c(VI_4) > K_3$.

There are relatively few data in the literature to compare with those in Table 3. Values of $S°(MI_4(g)) - S°(MI_2(s))$, for various metals (M), evaluated at 600 K from the compilation edited by Knacke, Kubaschewski, and Hesselmann (*9*) are: (Ge) 311; (Hf) 347; (Mo) 320; (Pb) 311; (Ti) 324; (Zr) 303 J·mol^{-1}·K^{-1}. The present work gives 330 J·mol^{-1}·K^{-1} for V. $\Delta S°$ values at 600 K for reactions 1−4, respectively, for the titanium iodides are 108, 37, 145, and 91 J·mol^{-1}·K^{-1} (*9*), for the vanadium bromides (*1*) 137, 28, 167, and 98 J·mol^{-1}·K^{-1}. $\Delta H°$ (298 K) for reaction 1, based on the compilation by Wagman et al. (*10*), is 101 kJ·mol^{-1}.

An unsuccessful attempt was made to verify the absolute values assigned to the molar absorptivities of $VI_4(g)$ using absorbances of fully vaporized samples and an analytical determination of the amount of vanadium in the cell. As may be seen in Table 2, the derived values of $c(VI_4)$ in the fully vaporized mixtures for samples 6 and 7 decrease in successive scans. A similar decrease was not observed when solid phases, $VI_2(s)$ and/or $VI_3(s)$, were present. On thermodynamic grounds (*2*, *8*) a significant reaction of $VI_4(g)$ and $I_2(g)$ with quartz to form $SiI_4(g)$ and $V_2O_5(s)$ is not expected. Analysis of solutions of the contents of the cells, by ICP atomic emission spectrometry, did not show the presence of significant amounts of silicon. Possibly at the higher temperatures VI_4 scavenges water from the quartz, forming HI and vanadium oxides or oxyiodides. In contrast to the behavior of the bromide system (*1*), no spectral evidence was found for the presence of significant amounts of volatile oxyhalides. Absorptivities calculated from the analytically determined amounts of vanadium in samples 5−7 were not in mutual agreement; derived values for sample 5 were appreciably lower (*ca.* 1/4) than those listed in Table 1, suggesting that some of the vanadium may have been converted to a soluble (in 2% HNO_3) but nonvolatile or volatile but nonabsorbing compound.

Literature Cited

(1) Gregory, N W. *Inorg. Chem.* **1994**, *33*, 3014.
(2) Tolmacheva, T. A.; Tsintsius, V. M.; Andrianova, L. V. *Russ. J. Inorg. Chem.* **1963**, *8* (3), 281; *Zh. Neorg. Khim.* **1963**, *8*, 553.
(3) Berry, K. O.; Smardzewski, R. R.; McCarley, R. E. *Inorg. Chem.* **1969**, *8* (9), 1994.
(4) Nakahira, M.; Ohtani, T.; Nakamura, H. In *Reactivity of Solids*; Dyrek, K., Haber, J., Nowotny, J., Eds.; Material Science Monographs 10; Elsevier: New York, 1982; Vol. 1, p 321.
(5) Hilden, D. L. Ph.D. Thesis, University of Washington, Seattle, WA, 1971.
(6) Sulzer, P.; Wieland, K. *Helv. Phys. Acta* **1952**, *25*, 653.
(7) Passchier, A. A. Ph.D. Thesis, University of Washington, Seattle, WA, 1968. Passchier, A. A.; Gregory, N. W. *J. Phys. Chem.* **1968**, *72*, 2697.
(8) Chase, M. W., Jr.; Davies, C. A.; Downey, J. R.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *JANAF. Thermochemical Tables*, 3rd Ed.; American Chemical Society and American Institute of Physics: New York, 1986.
(9) Knacke, O.; Kubaschewski, O.; Hesselmann, K. *Thermochemical Properties of Inorganic Substances*, 2nd ed.; Springer-Verlag: New York, 1991.
(10) Wagman, D. D.; et al. *J. Phys. Chem. Ref. Data* **1982**, *11*, Suppl. 2, 2−206.

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