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UV–Visible Absorption Spectra and Thermodynamic Properties of Vanadium Bromide Vapors

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A spectrophotometric study has been made of vanadium bromide–bromine and of vanadium oxybromide–bromine vapor mixtures. Although a number of studies of the vanadium chlorides have been published,[1–8] no previous report of the electronic spectra of $VBr_4(g)$ or $VOBr_3(g)$ has been found. Properties of the vanadium bromides have been summarized by a number of workers.[9–22] Diaphragm gage and transpiration studies of reactions 1 and 2 have been reported by two different investigators.[16,17] Results are not in good agreement. In the present work equilibrium and thermodynamic constants for rxs 1 and 2 and for reactions 3 and 4 have been derived from absorbance data. No previous quantitative study of reactions 3 or 4 has been found.

$$VBr_3(s) + 0.5Br_2(g) = VBr_4(g) \qquad (1)$$

$$2VBr_3(s) = VBr_2(s) + VBr_4(g) \qquad (2)$$

$$VOBr_2(s) + 0.5Br_2(g) = VOBr_3(g) \qquad (3)$$

$$VOBr_3(g) + 2VBr_3(s) = 2VBr_4(g) + VOBr(s) \qquad (4)$$

Experimental Section

A Cary 14-H spectrophotometer was used to measure absorbances. Samples, 17, were isolated in 20-mm o.d. cylindrical quartz cells, path lengths 1–5 cm. The furnace assembly has been described previously.[23] Temperatures were measured with chromel–alumel thermocouples, calibrated at the melting points of tin and lead.

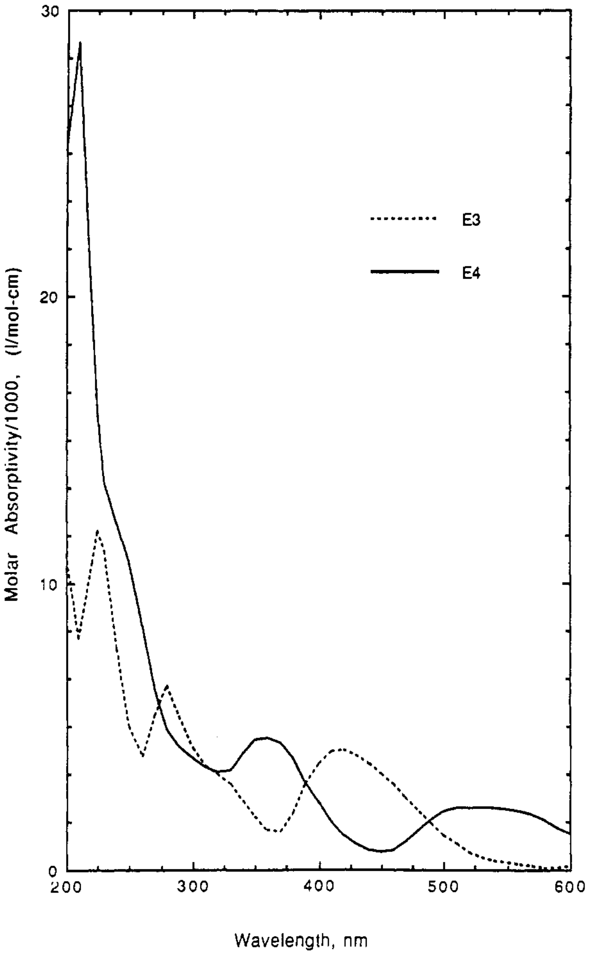

Figure 1. Molar absorptivities at 501 K.

Vanadium bromides were prepared by lightly flaming vanadium powder (Aldrich Chemical, 99.5%) in a bromine (Bakers, Analyzed Reagent) atmosphere in a Pyrex–quartz vacuum system. A brown-black solid, VBr_3,[9] condensed near the reaction zone. Properties reported for the vanadium bromides are summarized in the supplementary material. The extensive studies of Shchukarev et al.[16] and McCarley and Roddy[17] have shown that at temperatures and bromine concentrations of interest in the present study, VBr_4, which on condensation decomposes to $VBr_3(s)$, is the dominant binary vanadium bromide in the vapor phase.

In two cases, after the initial reaction mixtures were cooled to room temperature, vapors which absorbed strongly between 200 and 300 nm were observed. The bromine absorbance is small in this range,[26] and appreciable concentrations of the binary vanadium bromides are not expected in the vapor at room temperature.[16,17] The absorbing compound has been assumed to be $VOBr_3(g)$. $VOBr_3$ has been well characterized by a number of workers.[9,19–21] It forms a red liquid, fp −59 °C and bp 170 °C,[9] which decomposes, very slowly at room temperature and rapidly around its boiling point, to $VOBr_2(s)$ and bromine.[19,20] $VOBr_3(g)$ may be stabilized by a bromine atmosphere. It is assumed to have been formed in the present work by reaction of traces of V_2O_5, or lower oxides, on the metal powder, with VBr_4 and Br_2,

$$V_2O_5(s) + 3VBr_4(g) + 1.5Br_2(g) = 5VOBr_3(g) \qquad (5)$$

and/or by reaction of vanadium bromides with traces of H_2O (present as an impurity, possibly scavenged from the quartz walls) and Br_2.

$$VBr_4 + H_2O + 0.5Br_2 = VOBr_3 + 2HBr \qquad (6)$$

Similar reactions in the chloride system have large negative standard free energy changes.[11–15] From the small amounts of $VOBr_3$ formed, only small concentrations of HBr are expected. The spectral fit for samples 3–5, in the range 200–240 nm,[24] was slightly improved by assuming HBr

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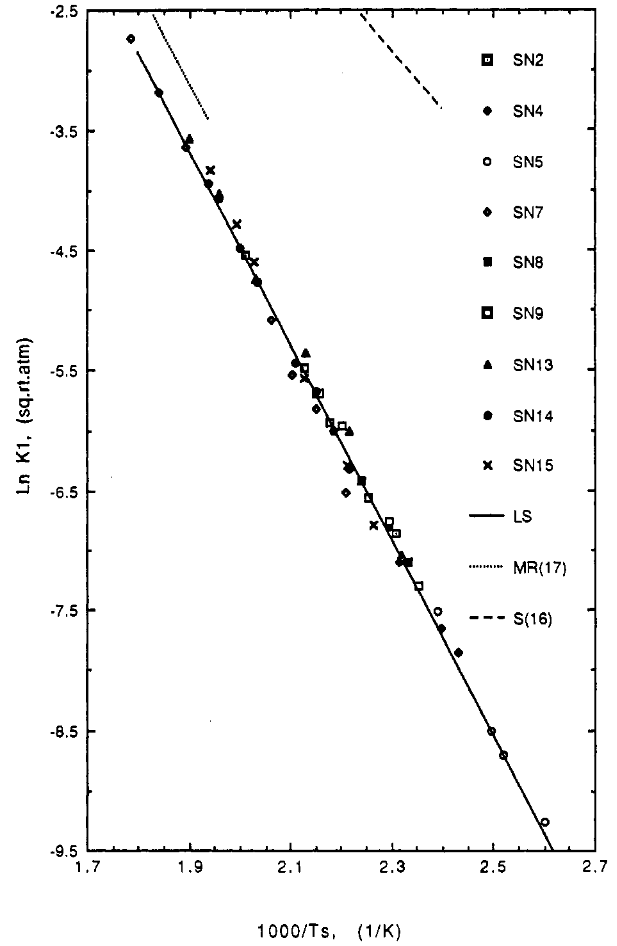

Figure 2. Equilibrium constants for reaction 1.

concentrations of 0.78, 0.18, and 0.80 mM, respectively; otherwise no spectral evidence for the presence of HBr was found.

In the two cases, SN3 and SN10 (SN, abbreviation for sample number), the material volatile at room temperature was examined. The other samples were generated from the brown-black solid. A description of the various samples is given in supplementary material.

To prevent cell window deposits, solids were condensed in the cell side arm and kept at a temperature, T_s, below that of the vapor, T_v, in the cell body. Samples were usually equilibrated overnight before recording the absorbance. At higher temperatures, and for fully vaporized samples, shorter periods wer sufficient.

Amounts of vanadium in five of the samples which could be fully vaporized were determined using an ICP atomic emission spectrometer, Model 955, Plasmo Atomcorp.

Results and Discussion

In the range 200–300 nm vapors of SN3 and SN10 showed absorbance maxima at 280 and 225 nm and minima at 260 and 210 nm. The absorbance rose rapidly as the wavelength was reduced from 210 to the lower limit of the instrument, 190 nm. In contrast vapors from SN 7, 9, and 11–16 showed only a single peak at 208 nm after which the absorbance fell rapidly as the wavelength was reduced to 190 nm. The other samples gave spectra which appeared to be combinations of these extremes. Considering the manner in which the samples were prepared, properties reported by others, and spectra reported for the chlorides,[1-7] it has been assumed that VOBr$_3$(g) molecules generate the peaks at 280 and 225 nm and that VBr$_4$(g) is responsible for the peak at 208 nm. The associated electronic state transitions have been discussed by others.[1-8]

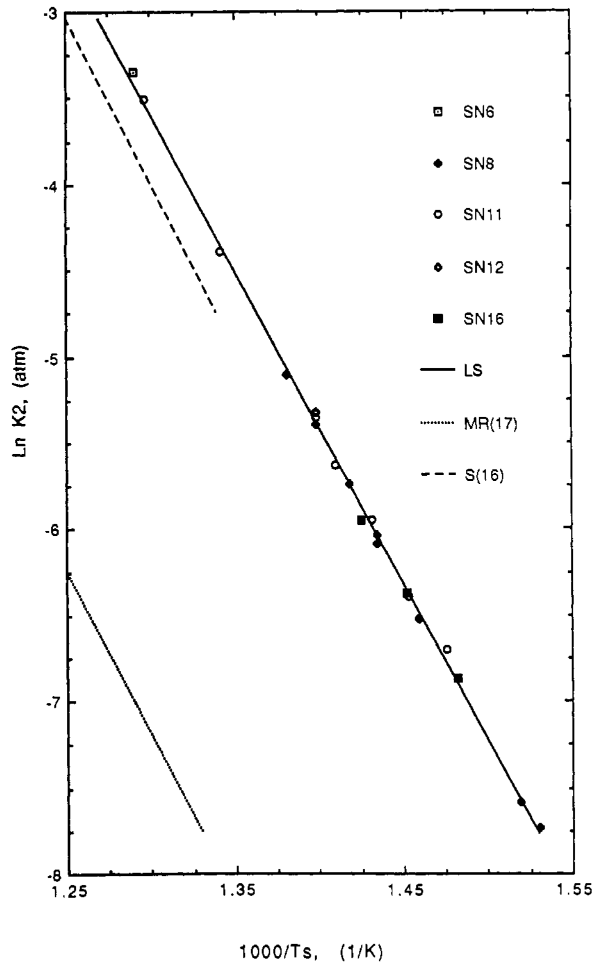

Figure 3. Equilibrium constants for reaction 2.

Molar Absorptivities. VOBr$_3$(g). Absorbances of SN3, between 493 and 700 K, and of SN10, between 378 and 528 K, did not change appreciably as T_s was changed, taken as evidence that the samples were fully vaporized. Hence molar absorptivities for VOBr$_3$, $\epsilon3_{\lambda,n}$ (λ, the wavelength; n, the temperature), between 200 and 300 nm, were taken as $A_{\lambda,n}/\text{C3}$ ($A_{\lambda,n}$ is the observed absorbance divided by the cell path length). C3, the concentration of VOBr$_3$(g), was calculated from the amount of vanadium in the cell and the cell volume.

Both bromine and VOBr$_3$ absorb in the range 310–600 nm. Between 406 and 440 K, C3, for SN3, appeared controlled by equilibrium 3 (when vapors were not supercooled). Cb$_o$, Cb$_o$ = Cb + 0.5 C3, the Br$_2$(g) concentration expected if none of the VOBr$_2$ had been converted to VOBr$_3$, was determined using molar absorptivities of bromine[26] and absorbances at low temperatures where C3 is small. C3 = $A_{280,n}/\epsilon3_{280,n}$. Values of $\epsilon3_{\lambda,n}$ at 10-nm intervals over the 310–600-nm range were then calculated from Cb, ϵb, C3, and Beer's Law. Results were tested with data from SN10 and adjusted to give the best overall fit for the two samples. Empirical equations, $\epsilon3_{\lambda,n} = a_\lambda + b_\lambda T$ or $\epsilon3_{\lambda,n} = a_\lambda + b_\lambda T_v + c_\lambda T_v^2$, with a_λ, b_λ, and c_λ assumed constants for each selected wavelength, were derived by least-squares; see Table 1S (supplementary material). The linear form was adequate for most wavelengths. The VOBr$_3$ spectrum, Figure 1, shows maxima at 225, 280, and 420 nm and minima at 210, 260, and 360 nm.

VBr$_4$(g). Molar absorptivities for VBr$_4$(g), $\epsilon4_{\lambda,n}$, were derived in a similar way from SN 7, 9, and 11–17 absorbances. In addition to bromine, most contained some VOBr$_3$; see Table 2S. When

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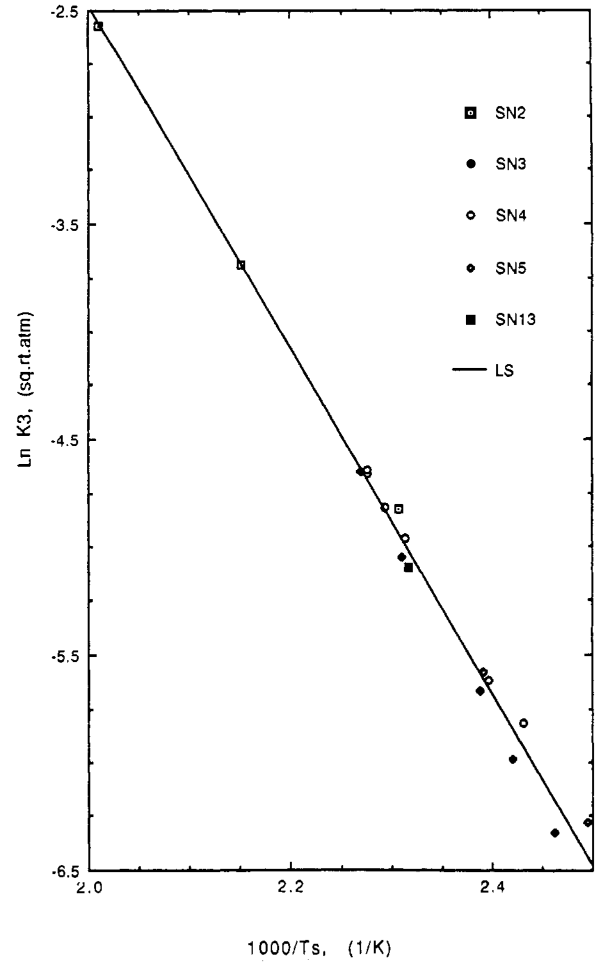

Figure 4. Equilibrium constants for reaction 3.

fixed by equilibrium 1, C4, the concentration of $VBr_4(g)$, at low temperatures and relatively low bromine concentrations, was small and neglected, and approximate values of C3 and Cb were derived from the observed absorbances. Both SN9 and SN17 were fully vaporized at their four highest scan temperatures, where C4 was taken as CV − C3; CV represents the total concentration of vanadium, determined by analysis. With the relationship Cb_o = Cb + 0.5(C3 + C4), with Cb_o and C3 different constants for each sample, Beer's Law was used to derive values of $\epsilon 4_{\lambda,n}$. Initial estimates of C3 and Cb_o were adjusted by successive approximations until the two samples gave consistent values of $\epsilon 4_{\lambda,n}$, at 360 nm, a peak maximum. For the range 425–680 K, results were fit by least squares to the empirical equation $\epsilon 4_{360} = a + bT_v$. Cb, C3, C4, ϵb, ϵ3, and $A_{\lambda,n}$ values were then used to calculate $\epsilon 4_{\lambda,n}$ at 10-nm intervals over the 200–600 nm range. For the wide temperature range, 410–790 K, needed to include all samples, results were correlated in the form $\epsilon 4_{\lambda,n} = a_\lambda + b_\lambda T_v + c_\lambda T_v^2$; see Table 1S. The derived VBr_4 spectrum at 501 K, Figure 1, shows maxima at 208, 360, and 530 nm and minima at 320 and 445 nm.

Concentrations in the other samples were derived from molar absorptivities, Table 1S, by least squares, using absorbances at 10-nm intervals over the range 280–500 nm: $A_{\lambda,n}$ = C3($\epsilon 3_{\lambda,n}$) + C4($\epsilon 4_{\lambda,n}$) + Cb($\epsilon b_{\lambda,n}$). The spectral fit was tested by calculating values of ΔA: ΔA = ($A_{\lambda,n}$(obs) − $A_{\lambda,n}$(calc))PL; $A_{\lambda,n}$(calc) = C3($\epsilon 3_{\lambda,n}$) + C4($\epsilon 4_{\lambda,n}$) + Cb(ϵb_{λ},*n*), and PL is the path length. The least-squares concentrations were adjusted slightly to improve the fit. For each sample, temperatures, concentrations, and the number of ΔA values exceeding 0.015, taken as a reasonable uncertainty, are listed in Table 2S in the order in which scans were taken.

Equilibrium Constants and Thermodynamic Properties. Selected sets of concentrations were found to correlate by assuming the vapor composition to be fixed by equilibrium reactions identified by numbers in column K, Table 2S. Thermodynamic properties, derived from the equilibrium constants, are given in Table 3S.

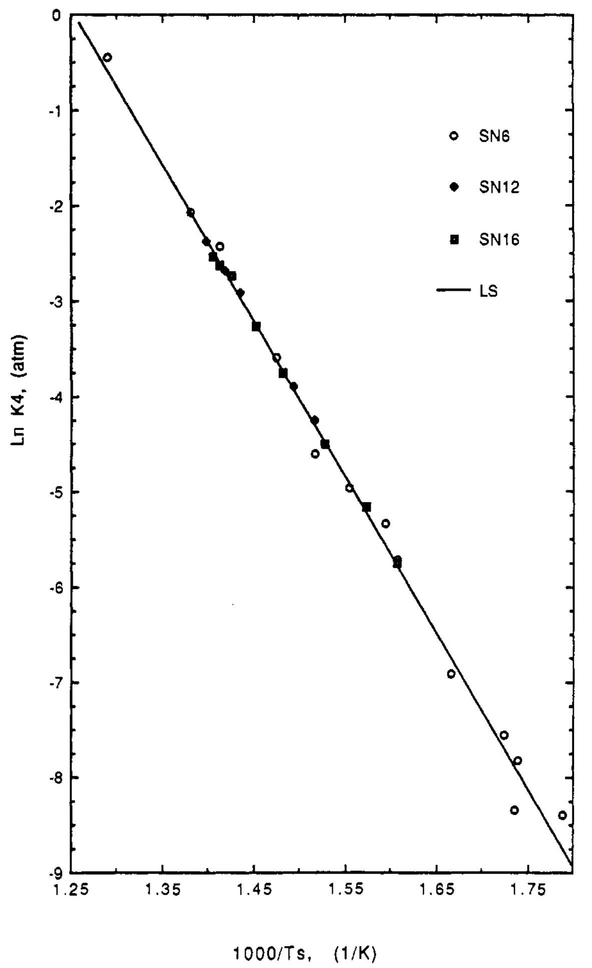

Figure 5. Equilibrium constants for reaction 4.

Equilibrium 1. A total of 47 sets, with bromine concentrations varying from 115 to 6210 μM, gave values of C4(RT_v/Cb)$^{0.5}$, which correlate as K_1, equilibrium constants for reaction 1. The line shown (Figure 2) represents the least-squares fit (standard deviation shown in parentheses); ln K_1(atm)$^{0.5}$ = −8128(1.1%)T_s^{-1} + 11.80(1.7%). Within the combined uncertainties the absorbance $\Delta H°$ and $\Delta S°$ values agree with those given in ref 17. However their equilibrium constants (see Figure 2) are higher by a factor ca. 1.7. If values of $\epsilon 4_{\lambda,n}$ are reduced by a factor of 1.7 so as to increase C4 correspondingly, an unsatisfactory spectral fit results. Reference 16 results differ widely; Figure 2 shows an extrapolation of their equation.

Equilibrium 2. A total of 20 values of C4(RT_v) correspond to equilibrium constants for reaction 2, K_2. The least-squares line, ln K_2(atm) = −18194(0.9%)T_s^{-1} + 20.06(1.1%), is shown in Figure 3. With $VBr_3(s)$ and $VBr_2(s)$ in equilibrium, Cb must be fixed by equilibrium 7 (eq 7 = eq 2 − eq 1). However, as predicted

$$\mathrm{VBr_3(s) = VBr_2(s) + 0.5Br_2(g)} \qquad (7)$$

from Cb values calculated from K_1 and C4, Cb is too small to confirm this by measuring the bromine absorbance.

Reference 16 $\Delta H°$ and $\Delta S°$ values agree with the absorbance result, as does the $\Delta H°$ value from ref 17. However the ref 17 $\Delta S°$ is much lower, giving C4 values *ca.* $^1/_{42}$ of the absorbance values.

Equilibrium 3. A total of 17 observed values of C3(RT_v/Cb)$^{0.5}$ correlate as expected for K_3, equilibrium constants for reaction

3. In this set Cb varies from 881 to 6210 μM. The least-squares line is shown in Figure 4; ln $K_3(\mathrm{atm})^{0.5} = -8002(2.3\%)T_s^{-1} + 13.53(3.2\%)$. Several observations from SN4 and SN5 gave equilibrium constants for both reactions 1 and 3 (see Table 2S). The K_3 values appear consistent with the qualitative behavior observed for $VOBr_3$,[15-17] as summarized in the supplementary material. The relatively high concentrations of $VOBr_3(g)$ observed at room temperature in some samples are attributed to supercooling, i.e., kinetic rather than thermodynamic stability.

Equilibrium 4. A total of 26 observations gave values of $(C4)^2(RT/C3)$ corresponding to K_4. The least-squares line is shown in Figure 5: ln $K_4 = -16360(1.5\%)T_s^{-1} + 20.53(1.8\%)$. The behavior of SN6 in particular provides evidence for reactions 4 and 6 (see supplementary material).

Remarks. In general the spectral fit for all samples was satisfactory when Br_2, $VOBr_3$, and VBr_4 were assumed to be the only absorbing species. However the presence of low concentrations of other related molecules cannot be ruled out. Some irregularities in three of the samples (see supplementary material) were noted. The very good correlation of the derived concentrations in terms of the various equilibrium reactions and the reasonable values of thermodynamic constants adds to confidence that the data have been interpreted correctly. Although the least-squares standard deviations were in the range 1–3%, the uncertainty of the absolute values of the molar absorptivities, based on scatter observed and analytical uncertainty, is estimated to be *ca.* 10%.

Supplementary Material Available: Text describing the preparation of samples, relevant properties of vanadium bromides and projections based on K_3, reactions 4 and 6, and irregularities; Table 1S, molar absorptivity equations for $VOBr_3(g)$ and $VBr_4(g)$, Table 2S, temperatures, concentrations, and ΔA values for all samples, and Table 3S, thermodynamic properties (10 pages). Ordering information may be found on any current masthead page.