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Vaporization Reactions of Vanadium(III) Bromide. Dissociation and Disproportionation Equilibria, and the Formation of Vanadium(IV) Bromide*

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Abstract

The equilibria (1) $VBr_3(s) = VBr_2(s) + \frac{1}{2}Br_2(g)$ and (2) $2VBr_3(s) = VBr_2(s) + VBr_4(g)$ were studied over the range 644 to 805°K by transpiration in helium. The expressions $\log P_{mm}(Br_2(g)) = -5070/T + 5.02$ and $\log P_{mm}(VBr_4(g)) = -8240/T + 8.47$ were derived from the measurements for (1) and (2), respectively; for (1) $\Delta H^0 = 23.1 \pm 0.9$ kcal/mole and $\Delta S^0 = 9.8 \pm 0.4$ e.u., while for (2) $\Delta H^0 = 37.7 \pm 1.3$ kcal/mole and $\Delta S^0 = 25.5 \pm 0.8$ e.u. Both transpiration in bromine vapor and static pressure measurements using a glass diaphragm gauge showed that $VBr_3(s)$ vaporized as $VBr_4(g)$ in the presence of

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bromine according to (3) $\text{VBr}_3(\text{s}) + \frac{1}{2}\text{Br}_2(\text{g}) = \text{VBr}_4(\text{g})$. Data from the transpiration and diaphragm gauge measurements were in excellent agreement; the transpiration measurements gave for (3) $\log K_p(\text{atm}^{\frac{1}{2}}) = -3455/T + 5.22$ and $\Delta F^\circ = 15.80 \times 10^3 - 23.9T$ for $T = 515-585^\circ\text{K}$.

Solid VBr_4 was isolated by condensation of the vapor at -78°C , and was found to be stable at -45° . At higher temperatures the solid decomposed to $\text{VBr}_3(\text{s})$ and bromine.

Introduction

During a study of the vaporization of vanadium(III) bromide by the effusion method² it was noticed that a volatile vanadium bromide was formed by decomposition of the sample. After escaping from the effusion cell a portion of the vanadium halide vapors was condensed in a trap at -196° along with small amounts of bromine. It thus appeared that in addition to the simple vaporization, vanadium(III) bromide also underwent simultaneous decomposition according to equation 1, and disproportionation according to equation 2.

Observations on the behavior of $\text{VBr}_3(\text{s})$ in vacuo at elevated temperatures supported the occurrence of these reactions since it was possible to completely decompose the sample and obtain a residue of pure VBr_2 . Moreover, it was found that the sublimation of VBr_3 in vacuo, and at ca. 400° was very slow, but that in the presence of bromine vapor the sublimation was rapid. The formation of the volatile $\text{VBr}_4(\text{g})$ according to reaction (3) was indicated.

Equilibrium pressures and thermodynamic data have been derived from transpiration measurements using helium carrier gas for the equilibria (1) and (2). For reaction (3) the equilibrium constants and associated thermodynamic data were obtained from static pressure measurements using a pyrex diaphragm gauge and also from transpiration measurements using bromine as the carrier gas.

The compound VBr_4 has been isolated as a solid at low temperatures by rapid condensation of the vapor at -78° . Although the solid was stable at -45° it decomposed at higher temperatures to yield $\text{VBr}_3(\text{s})$ and bromine.

Experimental

Materials. Reagent-grade bromine was dried over phosphorus(V) oxide and further purified by vacuum distillation. The liquid was stored in an evacuated flask which was attached to the vacuum system through a stopcock lubricated with fluorocarbon grease.

Vanadium metal was obtained from Dr. O. N. Carlson of this laboratory. The metal had been purified by the iodide-crystal bar technique and was of 99.9+ percent purity.

Vanadium(III) bromide was prepared by the combination of bromine vapor and vanadium metal at 400° , as described previously². Further purification of the product was effected by sublimation in a bromine atmosphere at 350 to 400° . The material was stored in sealed glass ampoules until needed for an experiment. Subsequent manipulations always were performed in a glove box under an argon atmosphere having a dew point of ca. -75° .

Transpiration Measurements with Helium as Carrier Gas. In these experiments the helium was purified by flow through a tube of Molecular Sieves (Linde 4A), over uranium turnings at 800° , and finally through a trap at -196° . The difference between atmospheric pressure and that in the system was obtained from a reading of the dibutylphthalate level in a

bubbler located at the front of the gas-purification train.

The transpiration cell was a modification of that used by Treadwell and Werner³. Fig. 1a shows the complete cell, while the condenser for the vanadium(III) bromide and the trap for bromine and VBr_4 vapor are shown in Fig. 1b. Purified helium entered the cell at A (Fig. 1a), became saturated with the halide vapors by passing vertically through the solids C, and left the cell by passing through the coarse, fritted-disk D. After leaving the cell vanadium(III) bromide condensed in A (Fig. 1b) and the bromine (formed by dissociation of the VBr_3 in the cell or by dissociation of VBr_4 in the condenser) was condensed in B. Subsequently the helium passed through a drying tube (to prevent back-diffusion of water vapor) into a water saturator and finally into a Precision wet-test meter for measurement of the total gas volume. The wet-test meter was calibrated to within 1 to 2 percent by prior determination of the vapor pressure of water by the transpiration technique.

A resistance furnace containing double windings at the ends to prevent heat loss, and a 1/8 in. thick, stainless steel liner to reduce temperature gradients, was used to maintain the cell temperature. An on-off, time proportioning

electrical controller was used to maintain a constant cell temperature to within $\pm 1^{\circ}$. The cell temperature was measured with a chromel-alumel thermocouple which had been calibrated at the boiling point of sulfur and the melting point of lead.

In a typical experiment the filled cell was mounted in place and connected to the gas-purification train. The system was evacuated to at least 5×10^{-4} mm. Hg and filled with purified helium. The furnace was brought to temperature in a position above the cell, after which it was lowered around the cell. Thermal equilibrium was established before the helium flow was started. The desired flow rate had been estimated previously by noting the flow rate through the bubbler located at the front of the train.

Determination of the pressures as a function of the helium flow-rates showed that flow-rates from 20 to 50 cc. per min. gave constant values for the pressures. Thus a flow-rate of ca. 30 cc/min was chosen for all of the measurements.

At the end of an experiment, the furnace was lifted away from the cell which was allowed to cool. The condenser was removed and the amount of tribromide determined by

spectrophotometric analysis of the vanadium⁴. Bromine was determined either iodometrically (for the larger samples) or by a spectrophotometric method according to Binkley⁵ (for small samples).

Transpiration in Bromine Vapor. Additional transpiration experiments were performed with vanadium(III) bromide using bromine as the carrier gas. A similar transpiration cell was used for these measurements, but the gas purification train was replaced by a bromine reservoir. The pressure of bromine, which was determined by balancing the pressure across a pyrex diaphragm gauge, was controlled by immersing the reservoir in a water thermostat or one of several low-temperature slush-baths.

The cell was evacuated to 10^{-3} mm. Hg and allowed to reach thermal equilibrium. Bromine then was passed over the sample and all volatile products were condensed in a trap at liquid nitrogen temperature. The amount of bromine was determined and the flow rate calculated according to the method of Gregory and MacLaren⁶. On the basis of a prior determination of the apparent $VBr_4(g)$ pressure as a function of the bromine flow-rate⁷, flow-rates between 30 and 60 cc. per min. were chosen for the measurements. Vanadium which

was transported from the cell was determined as indicated previously.

Diaphragm Gauge Measurements. The reaction of bromine with VBr_3 was studied by static equilibrium pressure measurements using an all glass diaphragm gauge as a null indicating instrument. An illustration of the experimental arrangement of the cell is given in Fig. 2. The gauges used in this investigation exhibited sensitivities of 0.2 mm. deflection per mm. pressure change when viewed with a telescope having a magnification of 17X. The gauges could be heated to 450° with no apparent change in the null-point. Pressures were obtained from the manometer which was read with a precision cathetometer having a sensitivity of 0.05 mm. Hg.

Initially, each cell was outgassed at 450° for 12-15 hr. at 10^{-5} mm. Hg. The vanadium(III) halide then was transferred to the gauge in the glove box and subsequently outgassed for at least 6 hr. at $150-200^\circ$. At higher temperatures some decomposition of the vanadium(III) halide was noticeable, hence the higher outgassing temperatures could not be employed. Finally, bromine vapor at the desired pressure was conducted into the gauge, condensed at -78° , and the gauge was re-evacuated and sealed from the vacuum system.

The gauge was centered in a vertical, twelve inch Marshall furnace insulated at each end with a covering of transite and asbestos. Three thermocouples were located on the cell: one recessed in the bottom of the gauge to measure the sample temperature, another located in contact with the gauge wall midway between the top and bottom, and the third at the top of the gauge. Each of the thermocouples was calibrated using the boiling point of sulfur (444.6°) and the melting point of lead (327.3°) as reference standards. The three thermocouples were used to measure the temperature gradient along the cell. Since it was necessary to prevent condensation of solids on the glass diaphragm the top of the gauge was maintained at a higher temperature than that of the sample. By adjusting the external furnace taps a gradient of 3 to 6° was obtained at 400° with the top of the gauge at the higher temperature. The furnace temperature was controlled to within $\pm 1^{\circ}$ by an electronically proportioning controller used in conjunction with a Raytheon voltage stabilizer on the furnace power supply.

Pressure readings were taken at 10 to 15⁰ intervals on both heating and cooling of the sample. Sufficient time for equilibrium to be established was ascertained by holding the

sample at temperature until no further change in the pressure was noted.

Results and Discussion

The transpiration measurements using helium as the carrier gas gave data on the equilibrium pressures of $\text{VBr}_4(\text{g})$ and $\text{Br}_2(\text{g})$ over $\text{VBr}_3(\text{s})$. In these measurements it was possible to distinguish between the $\text{VBr}_4(\text{g})$ and $\text{VBr}_3(\text{g})$ which were both carried in the gas stream by the location of the deposited material. The $\text{VBr}_3(\text{g})$ deposited in A (Fig. 1b) immediately on leaving the hot zone of the furnace while $\text{VBr}_4(\text{g})$ was deposited in the cold trap B, along with bromine formed by reaction (1). On warming the cold trap the VBr_4 decomposed to form a deposit of $\text{VBr}_3(\text{s})$ and additional bromine. Total bromine was determined and corrected for the amount of bromine liberated by decomposition of the VBr_4 in order to obtain the amount of bromine formed by (1). The correction was made on the basis of the vanadium determination (from VBr_4) and the fact that each mole of VBr_4 yielded one-half mole of bromine on decomposition.

The equilibrium $\text{VBr}_4(\text{g})$ pressures for (2) are given in Fig. 3. Least squares treatment of the data gave the expres-

sion $\log P_{\text{mm}}(\text{VBr}_4(\text{g})) = -8240/T + 8.47$ for the temperature range 644 to 850°K. The maximum error in the equation is approximately four percent. For a standard state of one atmosphere, $\Delta H^\circ = 37.7 \pm 1.3$ kcal/mole and $\Delta S^\circ = 25.5 \pm 0.8$ e.u. is calculated for the reaction over the indicated temperature range.

Equilibrium pressures for (1) are given in Fig. 4 and the data are given by the expression $\log P_{\text{mm}}(\text{Br}_2(\text{g})) = -5070/T + 5.02$. The heat and entropy calculated from this expression are 23.1 ± 0.9 kcal/mole and 9.8 ± 0.4 e.u., respectively, for the temperature range 644 to 805°K and a standard state of 1 atm.

At 650°K, the pressures of $\text{Br}_2(\text{g})$ from (1), $\text{VBr}_4(\text{g})$ from (2) and of $\text{VBr}_3(\text{g})$ from previous work² are respectively 1.7×10^{-3} , 9.0×10^{-5} and 3.5×10^{-4} mm. Thus all three vaporization processes are of comparable magnitude over the indicated temperature range with decomposition and formation of $\text{Br}_2(\text{g})$ the most important. The equilibrium pressures measured in this work were not found to be dependent upon the extent of dissociation of the sample as had been reported for corresponding work on TiBr_3 ⁸ and CrBr_3 ⁹.

Diaphragm Gauge Measurements. Reactions of $\text{VBr}_3(\text{s})$ with bromine were performed at five different initial bromine pressures in the diaphragm gauge. The only reaction that was considered to be occurring in the gauge was (3). Simple vaporization of the tribromide was unimportant since the vapor pressure of $\text{VBr}_3(\text{s})^2$ was less than 4×10^{-3} mm. at 700°K , the maximum temperature obtained in any of these experiments. Also the temperatures were sufficiently low that the dissociation of molecular bromine could be neglected¹⁰.

The equilibrium constant for reaction (3) is given by

(4),

$$(4) \quad K_p = P_{\text{VBr}_4} / P_{\text{Br}_2}^{\frac{1}{2}}$$

and was determined in the following manner. If the original bromine pressure in the gauge was P'_{Br_2} at T_1 , then after equilibrium had been established in the gauge at T_2 , the total pressure was given by (5),

$$(5) \quad P_t = (T_2/T_1)P'_{\text{Br}_2} + \frac{1}{2}P_{\text{VBr}_4}$$

assuming the gases exhibited ideal behavior. The pressure of $\text{VBr}_4(\text{g})$ was calculated by rearranging (5) to

$$(6) \quad P_{\text{VBr}_4} = 2 \left[P_t - (T_2/T_1)P'_{\text{Br}_2} \right]$$

The actual pressure of bromine then was calculated from equation (7)

$$(7) \quad P_{\text{Br}_2} = (T_2/T_1)P'_{\text{Br}_2} - \frac{1}{2}P_{\text{VBr}_4}$$

An experimental difficulty arose when the pressure in the gauge at the end of a set of measurements was found to be from 3 to 6 mm. greater than the initial pressure. The increase in pressure was assumed to be the result of hydrogen bromide formed by slight, unavoidable hydrolysis of the sample. Consequently, all values of the pressure were corrected for this increased increment, which was estimated by either of two methods. In the first method the bromine was condensed at -63° and the residual pressure was measured directly. In the second method, the gauge was heated to a temperature sufficient to cause hydrolysis but not high enough for reaction (3) to commence (ca. 200°), and the increase in pressure was noted. Using this procedure good agreement of the results was obtained for the five sets of measurements.

The equilibrium constants calculated from two sets of measurements where the initial bromine pressures were 124.0 mm. and 163.0 mm. are given in Fig. 5. In Table I are given the expressions for the equilibrium constants calculated by least squares treatment of each set of data. The average of these results for (3) is given by $\log K_p(\text{atm}^{\frac{1}{2}}) = -3465/T + 5.23$, which corresponds to $\Delta F^\circ = \Delta H^\circ - T\Delta S^\circ = 15.85 \times 10^3 - 23.9T$ over the range 555 to 720°K .

Table I

Equilibrium Constants and Enthalpies for the VBr_3 -Bromine
Reaction from 555 to 720°K

Initial P_{Br_2} , mm.	$\log K$, $\text{atm}^{\frac{1}{2}}$	ΔH° , kcal/mole
43.6	$-3494/T + 5.23$	16.0 ± 1.5
88.0	$-3463/T + 5.22$	15.8 ± 1.5
107.0	$-3447/T + 5.22$	15.8 ± 1.5
124.0	$-3454/T + 5.23$	15.8 ± 1.5
163.0	$-3470/T + 5.27$	15.9 ± 1.5

In order to prove the formation of $\text{VBr}_4(\text{g})$ by reaction (3) and to confirm the results of the measurements with the diaphragm gauge, equilibrium pressures were obtained by the transpiration measurements in bromine vapor. The method was the same as that used by Sime and Gregory⁹ in their study of the $\text{CrBr}_3(\text{s})$ - $\text{Br}_2(\text{g})$ reaction.

For determination of the equilibrium constant (4) the equilibrium pressure of $\text{VBr}_4(\text{g})$ was determined as a function of the bromine pressure at three temperatures. A plot of the quantity P_{VBr_4} vs. the square root of the bromine pressure

at the temperatures 515, 551 and 585°K is given in Fig. 6. The linear relationship is that predicted by reaction (3) and equation (4), while the intercept of the lines at the origin shows that vaporization of $VBr_3(g)$ was negligible in these experiments. The equilibrium constants were calculated from the slope of the lines at each temperature and are given in Fig. 7. This data gave the equations $\log K_p(\text{atm.}^{\frac{1}{2}}) = -3455/T + 5.22$ and $\Delta F^0 = 15.80 \times 10^3 - 23.9T$, which are in excellent agreement with the results from the measurements with the diaphragm gauge.

A check on the consistency of the results of this work is provided by the following calculation. If equation (1) is subtracted from equation (2) the equation for (3) is obtained. Subtraction of ΔH for (1) from that for (2) gives a value of 14.6 kcal for (3). This compares favorably (within the uncertainty in ΔH) with the value 15.8 kcal determined from the diaphragm cell and transpiration in bromine.

Oranskaya, et al.¹¹ have recently determined the disproportionation equilibrium for $VCl_3(s)$, and their data may be compared with our results. Thus, for the reaction

the heat and entropy changes at 700°K are, respectively, 38.2

and 37.7 kcal and 26.6 and 25.5 e.u. for $X = \text{Cl}$ and $X = \text{Br}$. A reaction of $\text{VCl}_3(\text{s})$, comparable to (1) for $\text{VBr}_3(\text{s})$, apparently has not been observed.

Some data for the reaction of $\text{VCl}_3(\text{s})$ with chlorine is also available for comparison with our data for (3), although not over the same temperature interval. Simons and Powell¹² found $\Delta H = 6.9$ kcal for $X = \text{Cl}$ at 433-453°K, and we find $\Delta H = 15.8$ kcal for $X = \text{Br}$ at 515°K, in the reaction

The increment in ΔH for this reaction, $\Delta H (X = \text{Br}) - \Delta H (X = \text{Cl})$, is 8.9 kcal; it is very nearly the same as the increment in ΔH for the corresponding reactions of CrCl_3 ¹³ and CrBr_3 ⁹, i.e. 8.4 kcal. A collection of thermodynamic data for these reactions is given in Table II.

Table II

Thermodynamic Data for the Reactions

M	X	ΔH° , (kcal)	ΔS° , e.u.	T° , K	Reference
V	Cl	6.9	----	453	(12)
Cr	Cl	28.0	25.4	800	(13)
V	Br	15.8	23.8	515	this work
Cr	Br	36.4	27.8	800	(9)

Isolation of VBr_4 . Using the apparatus shown in Fig. 8 vapors of VBr_4 were produced at B by heating $\text{VBr}_3(\text{s})$ in vacuo to ca. 325° . The $\text{VBr}_4(\text{g})$ was condensed at E which was cooled to -78° by powdered $\text{CO}_2(\text{s})$ in the jacket A. Under these experimental conditions any $\text{VBr}_3(\text{g})$ produced at B was removed from the vapor by condensation on the tube walls before reaching the condenser E. Bromine vapor, also formed in the experiment, passed through E since the partial pressure generated by the reaction was less than the vapor pressure of bromine at -78° , i.e. ca. 0.05 mm. Thus only the VBr_4 vapors were retained in E.

The collection of VBr_4 was continued for several hours until enough material for an analysis was obtained. At the termination of the experiment the tube was removed from the furnace, and the condenser E was allowed to warm slowly to room temperature. Decomposition of the VBr_4 produced a deposit of VBr_3 and bromine, which was collected by condensation at -196° and subsequently determined iodometrically. The entire deposit of VBr_3 in the condenser was dissolved in water and analyzed for total vanadium. Results of three experiments are given in Table III.

Table III

Analytical Data from VBr_4 Preparations

Experiment	Br_2 $\text{mmole} \times 10^2$	VBr_3 $\text{mmole} \times 10^2$	molar ratio Br_2/VBr_3	atom ratio Br/V
1	4.57	9.10	0.502	4.01
2	18.6	37.1	0.502	4.02
3	35.9	72.2	0.498	3.98

The pure solid VBr_4 was magenta colored at -78° but darkened at higher temperatures. The solid was stable at -45° but slowly decomposed at -23° to VBr_3 and bromine. It was noticed that $\text{VBr}_4(\text{g})$ diffused over long distances in the vacuum systems at room temperature without decomposition. Hence the decomposition of VBr_4 must be kinetically slow; its behavior in this respect is similar to that of VCl_4 .

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Figure Captions

- Fig. 1a. Transpiration Cell and Condenser. A. Carrier gas inlet. B. Glass wool support. C. Solid, whose vapor pressure is to be determined. D. Coarse fritted-glass disk. E. Condenser. F. Gas exit.
- Fig. 1b. Condenser. A. Condenser for VBr_3 . B. Cold-trap condenser for Br_2 and VBr_4 . C. Gas exit.
- Fig. 2. Diaphragm Gauge. A. Marshall furnace with external taps to furnace windings. B. Thermocouples. C. Fragile glass break-seal. D. Glass diaphragm. E. Null point indicator. F. Solid VBr_3 .
- Fig. 3. Disproportionation Pressure of $\text{VBr}_3(\text{s})$.
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- Fig. 6. Isotherms for the Reaction of Bromine with VBr_3 .
- Fig. 7. Equilibrium Constants for the Reaction of Bromine with VBr_3 by Transpiration.
- Fig. 8. Apparatus for Preparation of VBr_4 . A. Solid CO_2 . B. Solid VBr_3 . C. Furnace. D. Cork rings. E. Condenser.

Fig. 1a. Transpiration Cell and Condenser. A. Carrier gas inlet. B. Glass wool support. C. Solid, whose vapor pressure is to be determined. D. Coarse fritted-glass disk. E. Condenser. F. Gas exit.

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Fig. 3. Disproportionation Pressure of $\text{VBr}_3(\text{s})$.

Fig. 4. Dissociation Pressure of Bromine over VBr_3 .

Fig. 5. Equilibrium Constants for the Reaction of Bromine with VBr_3 in the Diaphragm Gauge.

Fig. 6. Isotherms for the Reaction of Bromine with VBr₄.

Fig. 7. Equilibrium Constants for the Reaction of Bromine with VBr_3 by Transpiration.

Fig. 8. Apparatus for Preparation of VBr_4 . A. Solid CO_2 .
 B. Solid VBr_3 . C. Furnace. D. Cork rings.
 E. Condenser.

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