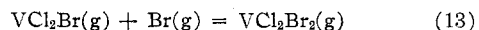


composition of the vanadium(IV) halide vapor. In this reaction no further replacement of chlorine by bromine in the solid VCl_2Br was noticed during the transport experiments. As indicated previously no evidence for the occurrence of undecomposed VCl_4 was found during the transport reactions and thus it is not considered to be an important species in the vapor generated by (12). The heat of this reaction also is consistent with the formation of mixed halides, of which VCl_2Br_2 should be the most important. Because the heat of sublimation of VCl_2Br is not known, a detailed calculation of the type shown for (9), (10), or (11) is not possible. However, if it is assumed that the heat of sublimation of VCl_2Br is intermediate to those of VCl_3 and VBr_3 , then a value for the heat of reaction 13



very close to the value for (10) would be obtained.

In conclusion, it appears that mixed halides of vanadium(IV) are formed in the vapor produced by reaction of bromine with VCl_3 or $\text{VCl}_{3-x}\text{Br}_x$, but the relative abundance of the individual species must await further investigation.

Transport of VCl_2 and VBr_2 in Iodine Vapor.—The reaction of iodine vapor with VCl_2 in a sealed tube under a controlled temperature gradient, where iodine was maintained at 130 to 180° and VCl_2 at 350 to 400°, resulted in the vaporization of VCl_2 and the growth of large green platelets approximately 4 mm. square in a region of the tube at *ca.* 275°. X-Ray patterns of the deposited material showed that the crystals were pure VCl_2 , a result also readily apparent from the characteristic color and shape of the crystals. That a mixed, higher halide of vanadium was formed in the reaction,

and was responsible for the transport of the $\text{VCl}_2(\text{s})$, is certain. The vapor pressure^{3b} of VCl_2 at 400° is estimated to be only *ca.* 1×10^{-6} mm. and thus sublimation could not account for the observed transport of material. Because the vanadium(III) halides also have relatively low vapor pressures in the experimental temperature range it does not seem likely that vanadium(III) halide vapors could account for the observed transport. The most likely explanation lies in the formation of a mixed halide of vanadium(IV) in the reaction, possibly $\text{VCl}_2\text{I}_2(\text{g})$. Such a species should only be stable in the gaseous phase and may account for the fact that only VCl_2 was recovered from the reaction.

In a similar reaction of CrCl_2 with iodine Handy and Gregory¹² obtained the mixed halide CrCl_2I as the stable solid phase. In view of the otherwise close analogy between the mixed halides of vanadium(III) obtained in this work and those of chromium(III) the formation of VCl_2I was expected. If the compound VCl_2I exists its dissociation pressure of iodine must be greater than 1 atm. at *ca.* 275°. A more detailed study of the reaction between VCl_2 and iodine has been undertaken in order to identify the important vapor species.

Under conditions identical with those used for VCl_2 , the reaction of VBr_2 with iodine proceeded to give a deposit of the mixed halide VBr_2I . The structure of VBr_2I has been discussed above and the lattice constants are given in Table I. The argument for the formation of $\text{VBr}_2\text{I}_2(\text{g})$ in order to account for the transport and formation of $\text{VBr}_2\text{I}(\text{s})$ is similar to that given for the formation of $\text{VCl}_2\text{I}_2(\text{g})$.

CONTRIBUTION FROM THE INSTITUTE FOR ATOMIC RESEARCH AND
DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY, AMES, IOWA

Vaporization Reactions of Vanadium(III) Bromide. Dissociation and Disproportionation Equilibria, and the Formation of Vanadium(IV) Bromide^{1a}

By ROBERT E. MCCARLEY AND JAMES W. RODDY^{1b}

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The equilibria $\text{VBr}_3(\text{s}) = \text{VBr}_2(\text{s}) + \frac{1}{2}\text{Br}_2(\text{g})$ (1) and $2\text{VBr}_3(\text{s}) = \text{VBr}_2(\text{s}) + \text{VBr}_4(\text{g})$ (2) were studied over the range 644 to 805°K. by transpiration in helium. For (1) $\Delta H^\circ = 23.1 \pm 0.9$ kcal./mole and $\Delta S^\circ = 10.6 \pm 0.4$ e.u., while for (2) $\Delta H^\circ = 37.7 \pm 1.3$ kcal./mole and $\Delta S^\circ = 34.7 \pm 1.2$ e.u. Both transpiration in bromine vapor and static pressure measurements using a glass diaphragm gage showed that $\text{VBr}_3(\text{s})$ vaporized as $\text{VBr}_4(\text{g})$ in the presence of bromine according to $\text{VBr}_3(\text{s}) + \frac{1}{2}\text{Br}_2(\text{g}) = \text{VBr}_4(\text{g})$ (3). The transpiration measurements gave for (3) $\Delta F^\circ = 15.80 \times 10^3 - 23.9T$ for $T = 515\text{--}585^\circ\text{K}$. Solid VBr_4 was isolated by condensation of the vapor at -78° and was found to be stable at -45° . At higher temperatures the solid decomposed to $\text{VBr}_3(\text{s})$ and bromine.

Introduction

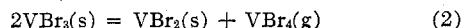
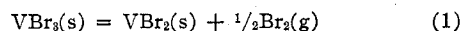
During a study of the vaporization of vanadium(III) bromide by the effusion method² it was noticed that a

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

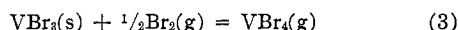
(1) (a) Contribution No. 1213. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission; (b) a portion of a thesis submitted by J. W. Roddy to the Iowa State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) R. E. McCarley and J. W. Roddy, *Inorg. Chem.*, **3**, 80 (1964).

simple vaporization, vanadium(III) bromide also underwent simultaneous decomposition according to eq. 1 and disproportionation according to eq. 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 decompose the sample completely 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.



As a result of the foregoing observations the pressure studies reported below were undertaken in order to obtain quantitative information about the vaporization equilibria of VBr_3 .

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+ % purity.

Vanadium(III) bromide was prepared by the combination of bromine vapor and vanadium metal at 400° , as described elsewhere.² 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 dibutyl phthalate 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 Werner.³ Figure 1 (a) 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. 1 (b). Purified helium entered the cell at A (Fig. 1 (a)), 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. 1 (b)), while bromine and VBr_4 were collected in the trap 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% 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 $\frac{1}{8}$ -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

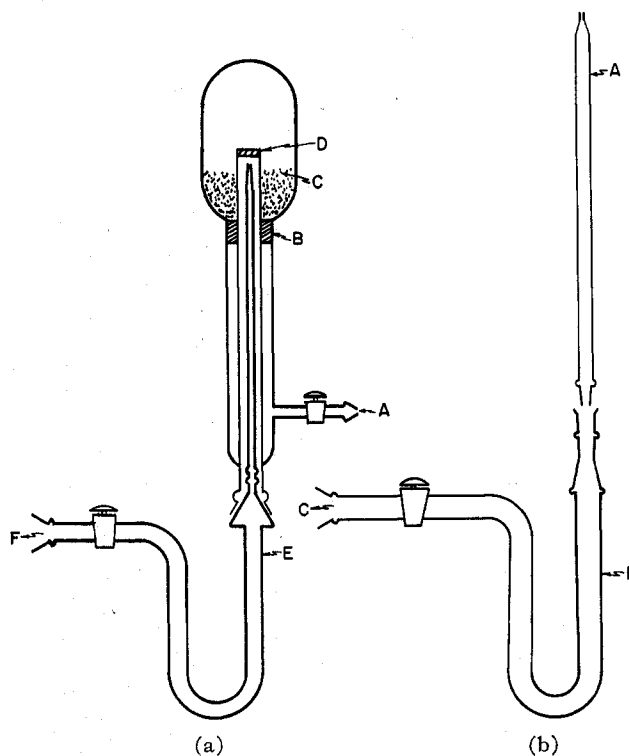


Fig. 1.—(a) Transpiration cell and condenser: A, carrier gas inlet; B, glass wool support; C, solid whose vapor pressure is to be determined; D, coarse fritted-glass disk; E, condenser; F, gas exit. (b) Condenser: A, condenser for VBr_3 ; B, cold-trap condenser for Br_2 and VBr_4 ; C, gas exit.

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. pressure 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./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 vanadium.⁴ 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 gage, 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. pressure 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

(3) W. Treadwell and W. Werner, *Helv. Chim. Acta*, **36**, 1436 (1953).

(4) E. Wright and M. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **9**, 251 (1937).

(5) F. Binkley, *J. Biol. Chem.*, **173**, 403 (1948).

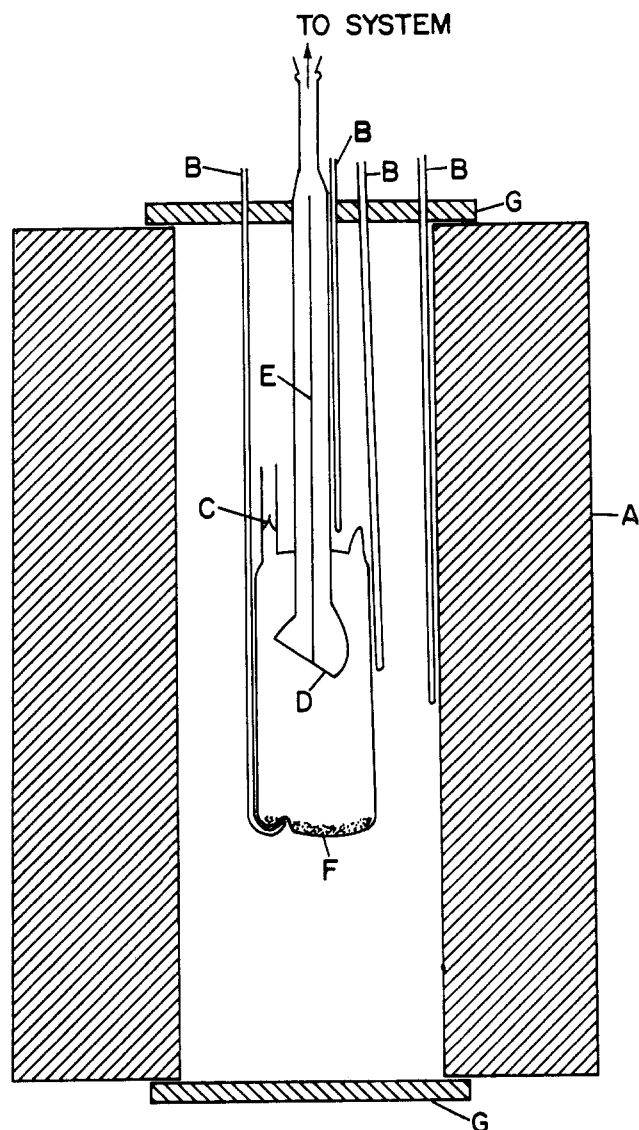


Fig. 2.—Diaphragm gage: A, Marshall furnace with external taps to furnace windings; B, thermocouples; C, fragile glass break-seal; D, glass diaphragm; E, null point indicator; F, solid VBr_3 .

Gregory and MacLaren.⁶ Prior determinations of the apparent $\text{VBr}_3(\text{g})$ pressures as a function of the bromine flow rate⁷ at each temperature indicated that flow rates between 30 and 60 cc./min. were sufficient for equilibrium conditions. Vanadium which was transported from the cell was determined as indicated previously.

Diaphragm Gage Measurements.—The reaction of bromine with VBr_3 was studied by static equilibrium pressure measurements using an all-glass diaphragm gage as a null indicating instrument. An illustration of the experimental arrangement of the cell is given in Fig. 2. The gages used in this investigation exhibited sensitivities of 0.2 mm. deflection per mm. pressure change when viewed with a telescope having a magnification of 17 $\times$. The gages 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.

Initially, each cell was outgassed at 450° for 12–15 hr. at 10^{-6} mm. pressure. The vanadium(III) halide then was transferred to the gage in the glove box and subsequently outgassed for at least 6 hr. at 150–200°. At higher temperatures some decomposition of the vanadium(III) halide was noticeable, hence the

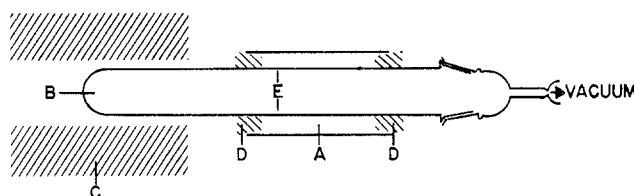


Fig. 3.—Apparatus for preparation of VBr_4 : A, solid CO_2 ; B, solid VBr_3 ; C, furnace; D, cork rings; E, condenser.

higher outgassing temperatures could not be employed. Finally, bromine vapor at the desired pressure was conducted into the gage, condensed at -78° , and the gage was re-evacuated and sealed from the vacuum system.

The gage was centered in a vertical, 12-in. 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 gage to measure the sample temperature, another located in contact with the gage wall mid-way between the top and bottom, and the third at the top of the gage. 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 gage 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 gage 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 15° intervals on both heating and cooling of the sample. Sufficient time for equilibrium to be established was ascertained by holding the sample at a given temperature until no further change in the pressure was noted.

VBr_4 Isolation and Characterization.—Using the apparatus shown in Fig. 3 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, solid CO_2 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. The results of three experiments are given in Table I.

TABLE I
ANALYTICAL DATA FROM VBr_4 PREPARATIONS

Expt.	Br_2 , mmoles $\times 10^2$	VBr_3 , mmoles $\times 10^2$	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

(6) N. W. Gregory and R. O. MacLaren, *J. Phys. Chem.*, **59**, 110 (1955).

(7) For a more detailed description of these experiments see the doctoral thesis of J. W. Roddy.

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 .

Results and Discussion

Transpiration Measurements in Helium.—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. 1 (b)) 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 0.5 mole of bromine on decomposition.

Equilibrium pressures observed for both reactions 1 and 2 are given in Table II. Least squares treatment of the data for (2) gave the expression $\log P_{\text{mm}}(\text{VBr}_4) = -8240/T + 10.47$ for the temperature range 644 to 805°K . The maximum error in the equation is approximately 4%. For a standard state of 1 atm., $\Delta H^\circ = 37.7 \pm 1.3$ kcal./mole and $\Delta S^\circ = 34.7 \pm 1.2$ e.u. is calculated for the reaction over the indicated temperature range.

TABLE II
TRANSPARATION OF VBr_3 IN HELIUM

Sample no.	Temp., $^\circ\text{K}$.	Obsd. pressure, mm. $\times 10^2$		Calcd. pressure, ^a mm. $\times 10^2$	
		VBr_4	Br_2	VBr_4	Br_2
1	805	170	8.16	170	7.95
2	775	66.5	4.54	69.1	4.55
3	758	40.5	3.43	39.8	3.24
4	736	18.3	2.04	18.8	2.05
5	718	10.1	1.42	9.86	1.38
6	700	4.96	0.92	5.00	0.91
7	689	3.28	0.71	3.24	0.69
8	680	2.19	0.55	2.25	0.56
9	644	0.47	0.22	0.47	0.21

^a Calculated from the expression $\log P = -B/T + A$ as given in the text.

Equilibrium pressures for (1) are given by the expression $\log P_{\text{mm}}(\text{Br}_2) = -5070/T + 5.20$. The heat and entropy calculated from this expression are 23.1 ± 0.9 kcal./mole and 10.6 ± 0.4 e.u., respectively, for the temperature range 644 to 805°K . and a standard state of 1 atm.

After this work was completed it came to the attention of the authors that Shchukarev, *et al.*,⁸ also have obtained equilibrium data for (2) by static pressure measurements. They found $\Delta H^\circ = 38 \pm 2$ kcal./

mole and $\Delta S^\circ = 41.5 \pm 2$ e.u. over the slightly higher temperature interval of 763 to 923°K . While the values of ΔH° are in good agreement, the values of ΔS° differ by an amount outside of our experimental error. One factor contributing to the higher entropy value found by the above authors may be their failure to correct the pressure data for the small pressure of bromine resulting from (1). They argue that bromine resulting from the dissociation reaction (1) was not present in their experiments because in a preliminary examination of the reaction products transported by the gas saturation method they found a Br:V ratio of 4 in the limited range 773 to 813°K . They also took optical absorption data over this same range for the gases over VBr_3 and obtained an approximately constant ratio of absorbance to pressure at a wave length which is not clear in our translation. The relative constancy of the latter ratio was also used by these authors as an indication that only reaction 2 was important in their work.

The data in Table II indicate that in the range 773 to 813°K . the bromine pressure from (1) is only *ca.* 4 to 6% of the total vapor pressure over VBr_3 . Consequently rather careful analysis of the products resulting from transport in the gas stream is needed to detect an appreciable departure from the Br:V ratio of 4. For example, in the experiment at 805°K . reported in Table II the products obtained were VBr_4 , 0.272×10^{-3} mole, and bromine, 0.026×10^{-3} g.-atom, for an overall Br:V ratio of 4.10.

From the equation given by Shchukarev, *et al.*,⁸ for (2), $\log P(\text{atm.}) = -8325/T + 9.125$, we calculate pressures which are more than an order of magnitude too high when compared to our data. The reason for this difference is difficult to assess. However, because we find good agreement between our results for (1) and (2) with those reported below for (3) we believe our results to be the more reliable.

At 650°K ., the pressures of $\text{Br}_2(\text{g})$ from (1), of $\text{VBr}_4(\text{g})$ from (2), and of $\text{VBr}_3(\text{g})$ from previous work² are, respectively, 2.5×10^{-3} , 6.3×10^{-3} , and 3.5×10^{-4} mm. Thus all three vaporization processes are of comparable magnitude over the indicated temperature range with disproportionation and formation of $\text{VBr}_4(\text{g})$ 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 ⁹ and CrBr_3 ¹⁰; therefore unit activity for the solids VBr_3 and VBr_2 was assumed for all experiments.

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

(8) S. A. Shchukarev, T. A. Tolmacheva, and V. M. Tsintsius, *Zh. Neorgan. Khim.*, **7**, 1505 (1962); *Chem. Abstr.*, **57**, 9445 (1962).

(9) E. H. Hall and J. M. Blocher, Jr., *J. Phys. Chem.*, **63**, 1525 (1959).

(10) R. J. Sime and N. W. Gregory, *J. Am. Chem. Soc.*, **82**, 93 (1960).

TABLE III
 RESULTS OF MEASUREMENTS ON THE REACTION OF VBr_3 WITH BROMINE IN THE DIAPHRAGM GAGE

Reading no.	Temp., °K.	Av. cell temp., °K.	P_t , mm. ^a	P_{Br_2} , mm.	P_{VBr_4} , mm.	$K_{\text{obsd.}}$, atm. ^{1/2}	$K_{\text{calcd.}}$, atm. ^{1/2}
Initial $P_{\text{Br}_2} = 124.0$ mm. at 295°K.							
1	531.2	540.2	241.00	212.82	28.18	0.070	0.054
2	558.8	563.3	259.80	213.42	46.38	0.115	0.177
3	584.0	591.2	289.95	206.71	83.24	0.210	0.207
4	572.4	581.4	277.20	211.24	65.96	0.164	0.157
5	602.4	612.6	320.80	193.84	126.96	0.331	0.313
6	593.2	598.9	302.50	200.64	101.86	0.261	0.256
7	620.0	628.2	352.15	175.61	176.54	0.438	0.456
8	609.2	615.4	328.70	188.30	140.40	0.371	0.364
9	631.6	638.2	373.40	162.76	210.64	0.599	0.577
10	656.3	658.0	424.75	128.03	296.72	0.951	0.927
11	645.0	644.8	395.90	145.62	250.28	0.752	0.750
12	666.4	669.3	450.65	111.63	339.02	1.164	1.11
13	657.2	660.6	429.70	125.28	304.42	0.986	0.942
14	684.8	690.8	503.35	76.99	426.36	1.762	1.535
15	681.6	681.7	483.30	89.40	393.90	1.511	1.456
16	710.0	712.2	547.50	50.82	496.68	2.527	2.323
17	700.5	698.9	525.10	61.38	463.72	2.146	1.991
18	720.6	721.7	570.00	36.30	533.70	3.213	2.735
Initial $P_{\text{Br}_2} = 163.0$ mm. at 293.5°K.							
3	520.7	532.3	309.80	281.04	28.76	0.062	0.040
4	562.4	568.8	346.50	284.86	61.64	0.132	0.126
5	591.2	594.1	390.35	269.09	121.26	0.268	0.252
6	575.2	583.3	366.30	281.16	85.14	0.184	0.173
7	599.8	612.3	410.25	269.39	140.86	0.311	0.306
8	614.6	625.8	440.20	254.42	185.78	0.422	0.421
9	625.0	635.6	460.85	244.65	216.20	0.501	0.522
10	644.2	655.6	516.20	211.50	304.70	0.760	0.766
11	637.0	645.4	489.90	226.48	263.42	0.635	0.665
12	666.2	675.1	577.35	171.99	405.36	1.121	1.151
13	658.4	664.0	547.10	189.92	357.18	0.944	1.000
14	680.0	693.6	640.25	129.63	510.62	1.627	1.469
15	670.7	681.1	606.65	149.35	457.30	1.357	1.247
16	685.7	700.2	666.30	110.90	555.40	1.913	1.618
17	717.7	731.4	744.10	67.74	676.36	2.981	2.723
18	701.2	720.3	702.55	96.97	605.58	2.230	2.094

^a Corrected for the pressure of HBr resulting from slight, unavoidable hydrolysis as indicated in the text.

the temperatures were sufficiently low that the dissociation of molecular bromine could be neglected.¹¹

The equilibrium constant for reaction (3) is given by

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

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

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

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

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

The actual pressure of bromine then was calculated from eq. 7.

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

An experimental difficulty arose when the pressure in the gage 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 gage 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 obtained from two sets of measurements where the initial bromine pressures were 124.0 and 163.0 mm. are given in Table III. In Table IV are given the expressions for the equilibrium constants calculated by least squares treatment of the five sets of data. The average of these results for (3) is given by $\log K_p (\text{atm.}^{1/2}) = -3465/T + 5.23$, 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 . A comparison of the equilibrium constants calculated from this expression with the observed, experimental values is also given in Table III.

Transpiration Measurements in Bromine Vapor.—In order to prove the formation of $\text{VB}_4(\text{g})$ by reaction 3

(11) T. DeVries and W. Rodebush, *J. Am. Chem. Soc.*, **49**, 656 (1927).

TABLE IV

EQUILIBRIUM CONSTANTS AND ENTHALPIES FOR THE $\text{VBr}_3\text{--Br}_2$ REACTION FROM 555 TO 720°K.

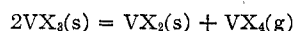
Initial P_{Br_2} , mm.	$\log K$, atm. ^{1/2}	ΔH° , kcal./mole
43.6	$-3494/T + 5.23$	16.0 ± 1.5
88.0	$-3463/T + 5.22$	15.8 ± 1.5
107.0	$-3447/T + 5.22$	15.8 ± 1.5
124.0	$-3454/T + 5.23$	15.8 ± 1.5
163.0	$-3470/T + 5.27$	15.9 ± 1.5

and to confirm the results of the measurements with the diaphragm gage, equilibrium pressures were obtained by the transpiration measurements in bromine vapor. The method was the same as that used by Sime and Gregory¹⁰ 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; the results are given in Table V. A plot of the quantity P_{VBr_4} vs. the square root of the bromine pressure at 515, 551, and 585°K. gave a straight line at each temperature. The linear relationship is that predicted by reaction 3 and eq. 4, while the intercept of the lines at the origin showed that vaporization of $\text{VBr}_3(\text{g})$ was negligible in these experiments, as expected.² The equilibrium constants were calculated from the slope of the lines at each temperature and are given as K_{obsd} in Table VI. These data gave the equations $\log K_p$ (atm.^{1/2}) = $-3455/T + 5.22$ and $\Delta F^\circ = 15.80 \times 10^3 - 23.9T$, which are in excellent agreement with the results from the measurements with the diaphragm gage.

Using the data obtained for (1) and (2) only, we calculate for (3) $\Delta H^\circ = 14.6 \pm 2.2$ kcal./mole and $\Delta S^\circ = 24.1 \pm 1.6$ e.u. These results are in satisfactory agreement with the experimental results for (3) since the data for (1) and (2) were obtained over a slightly higher temperature interval. Shchukarev, *et al.*,¹² also obtained data for (3) which we believe to be in error. From diaphragm gage measurements only, they report for (3) and the temperature range 523 to 873°K., $\Delta H^\circ = 19 \pm 1$ kcal./mole and $\Delta S^\circ = 33 \pm 1$ e.u. The excellent agreement between our results from the five sets of diaphragm gage measurements and those from the transpiration in bromine vapor lends support to the higher reliability of our data.

Oranskaya, *et al.*,¹³ have recently determined the disproportionation equilibrium for $\text{VCl}_3(\text{s})$, 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 34.7 e.u. for $\text{X} = \text{Cl}$ and $\text{X} = \text{Br}$. A reaction of $\text{VCl}_3(\text{s})$, comparable to (1) for $\text{VBr}_3(\text{s})$, apparently has not been observed.

(12) S. A. Shchukarev, T. A. Tolmacheva, and V. M. Tsintsius, *Zh. Neorgan. Khim.*, **7**, 679 (1962).

(13) M. A. Oranskaya, Yu. C. Lebedev, and I. L. Perfilova, *ibid.*, **6**, 259 (1961).

TABLE V

TRANSPIRATION OF VBr_3 IN BROMINE VAPOR

Sample no.	Temp., °K.	Br_2 flow rate, ml./min.	Br_2 press., atm. $\times 10^2$	Quantity transported Moles Br_2 ($\times 10^3$)	Moles V ($\times 10^3$)	VBr_4 press., ^a (atm. $\times 10^2$)
3	561	30	1.58	0.79	0.625	1.25
4	561	45	1.58	0.46	0.381	1.31
5	561	21	1.58	0.36	0.335	1.35
7	561	45	8.8	2.53	0.957	3.34
8	561	62	8.9	1.98	0.742	3.31
9	561	9	8.8	4.23	1.91	3.97 ^b
10	561	33	8.8	3.18	1.22	3.38
11	561	27	11.1	3.02	1.04	3.80
12	561	38	11.1	4.66	1.59	3.77
13	561	107	11.2	8.31	2.72	3.61 ^b
14	561	11	11.1	5.14	1.81	3.90 ^b
15	561	22	21.7	7.38	1.86	5.45
16	561	67	21.6	9.52	2.34	5.30
17	561	98	21.7	11.37	2.78	5.26 ^b
18	561	38	21.7	10.51	2.60	5.35
20	587	52	1.58	1.03	1.77	2.72
22	587	47	11.1	3.71	2.41	7.17
23	587	30	21.9	12.79	5.86	10.2
25	515	46	1.58	0.43	0.112	0.41
26	515	35	11.1	2.78	0.272	1.08
27	514	28	22.0	9.93	0.673	1.51

^a Calculated from the expression $P_{\text{VBr}_4} = nP_{\text{Br}_2}/1 - n$, where n is the mole fraction vanadium (as VBr_4) in the vapor.

^b Not considered to be equilibrium pressures because of high or low value of flow rate during the experiment.

TABLE VI

EQUILIBRIUM CONSTANTS FOR THE $\text{Br}_2\text{--VBr}_3$ REACTION BY TRANSPIRATION IN BROMINE

T , °K.	K_{obsd}	K_{calcd}^a
515	0.0316	0.0324
561	0.113	0.115
587	0.211	0.216

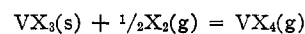
^a Calculated from the expression $\log K_p$ (atm.^{1/2}) = $-3455/T + 5.22$.

TABLE VII

THERMODYNAMIC DATA FOR THE REACTIONS

$\text{MX}_3(\text{s}) + \frac{1}{2}\text{X}_2(\text{g}) = \text{MX}_4(\text{g})$					
M	X	ΔH° , kcal.	ΔS° , e.u.	T , °K.	Ref.
V	Cl	6.9	...	453	14
Cr	Cl	28.0	25.4	800	15
V	Br	15.8	23.9	515	This work
Cr	Br	36.4	27.8	800	10

Some data for the reaction of $\text{VCl}_3(\text{s})$ with chlorine are also available for comparison with our data for (3), although not over the same temperature interval. Simons and Powell¹⁴ found $\Delta H^\circ = 6.9$ kcal. for $\text{X} = \text{Cl}$ and 433–453°K., and we find $\Delta H^\circ = 15.8$ kcal. for $\text{X} = \text{Br}$ at 515°K., in the reaction



The increment in ΔH° for this reaction, $\Delta H^\circ (\text{X} = \text{Br}) - \Delta H^\circ (\text{X} = \text{Cl})$, is 8.9 kcal.; it is very nearly the same as the increment in ΔH° for the corresponding reactions of CrCl_3 ¹⁵ and CrBr_3 ¹⁰, *i.e.*, 8.4 kcal. A collection of thermodynamic data for these reactions is given in Table VII.

(14) J. H. Simons and M. G. Powell, *J. Am. Chem. Soc.*, **67**, 75 (1945).

(15) H. Doerner, U. S. Bureau of Mines Bulletin 577 1937.