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The Vapor Pressures of Vanadium(II) Chloride, Vanadium(III) Chloride, Vanadium(II) Bromide, and Vanadium(III) Bromide by Knudsen Effusion[1a]

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The vapor pressures of crystalline VCl_2, VBr_2, VCl_3, and VBr_3 have been measured by the Knudsen effusion method. Only the simple vaporization was observed for VCl_2 and VBr_2 over the interval 750–950°K. For VCl_3 and VBr_3 vaporization occurred simultaneously with disproportionation or dissociation. However equilibrium pressure data were obtained only for the simple vaporization process. Pressure data derived from the disproportionation and dissociation reactions of VBr_3 were found to be dependent on the orifice size, and it was assumed that nonequilibrium data had been obtained for both VBr_3 and VCl_3.

Introduction

During the course of studies[2] on the vaporization of the vanadium chlorides and bromides in bromine or iodine vapor a knowledge of the vapor pressures of VCl_2, VBr_2, VCl_3, and VBr_3 became necessary. While recently a vapor pressure study of VCl_2 has been reported,[3] there are no previous reports on the vapor pressures of the other compounds mentioned above. Over the temperature intervals pertinent to this work all of the compounds were found to have vapor pressures below *ca.* 0.1 mm. Hence the Knudsen effusion method[4] was chosen for the pressure determinations.

Experimental

Materials.—The vanadium halides used in this work were prepared by reaction of the elemental halogens with high purity vanadium metal.[5] Chlorine was purified by passing the gas through a potassium permanganate solution to remove hydrogen chloride and then through sulfuric acid and over phosphorus(V) oxide to remove moisture. Bromine was vacuum distilled from phosphorus(V) oxide and stored in an evacuated flask connected to the vacuum system by a stopcock lubricated with fluorocarbon grease.

Both VCl_3 and VCl_2 were prepared from VCl_4, the initial product from the reaction of chlorine with vanadium. After preparation of VCl_4, the liquid was refluxed at 160–170° in a stream of nitrogen for preparation of VCl_3.[6] In order to eliminate difficulties arising from handling of the reactive and easily contaminated VCl_4 liquid, both the chlorination of vanadium and the subsequent decomposition of VCl_4 were performed in the same apparatus. The residue of VCl_3 then was heated to 200° *in vacuo* before sealing the apparatus and transferring the solid in the drybox. It was necessary to outgas the solid further under high vacuum at 200° to remove the last traces of VCl_4. Material treated in this way was much less sensitive to hydrolysis. Subsequent reduction of VCl_3 with hydrogen at 475° yielded VCl_2. Further heating of the VCl_2 *in vacuo* at 700° ensured complete removal of the higher vanadium halides.

Anal. Calcd. for VCl_3: V, 32.4; Cl, 67.6. Found: V, 32.2, 32.1, 32.3, 32.3; Cl, 67.7, 67.7, 67.8, 67.5. Calcd. for VCl_2: V, 41.8; Cl, 58.2. Found: V, 41.8, 42.1; Cl, 58.1, 58.0.

Combination of the elements in a sealed, evacuated tube with bromine at room temperature and the vanadium at 400° yielded a deposit of VBr_3 which sublimed from the reaction zone. The VBr_3 was purified by sublimation in a bromine atmosphere at 350 to 400°.

Anal. Calcd. for VBr_3: V, 17.53; Br, 82.47. Found: V, 17.5, 17.6, 17.4; Br, 82.4, 82.5, 82.5.

Hydrogen reduction[7] of VBr_3 at 450° produced VBr_2, which was finally heated at 700° *in vacuo* to decompose the last traces of VBr_3. The pure VBr_2 had a very pale tan color.

Anal. Calcd. for VBr_2: V, 24.18; Br, 75.82. Found: V, 24.1; Br, 75.8.

Effusion Measurements.—The effusion apparatus was similar to that described by Sime and Gregory[8] and consisted of a 20-mm. o.d. sample cell which contained the effusion orifice at one end and a small tube for introduction of the sample at the other. The end containing the orifice was sealed into a larger condensing tube, 25 mm. in o.d., which was provided with a U-tube trap to prevent contamination of the effusing vapors (bromine and VCl_4) with stopcock lubricant and through which the apparatus was evacuated.

For the vapor pressure determination of the materials at a particular temperature the cell and sample were outgassed to a pressure of at least 5×10^{-6} mm. and then a preheated furnace was moved into position around the cell. The furnace had double windings on each end and a $^1/_8$-in. steel liner to reduce temperature gradients. The temperature was measured with two thermocouples which were attached to the effusion cell. A maximum temperature variation of $\pm 1°$ during a determination was obtained through the use of a Brown proportioning controller.

Two cells were constructed, one of Pyrex and one of Vycor. The orifice area for each cell was calculated from the mean of several values of the hole diameter measured on a metallograph. Clausing factors[9] for each cell were determined from vapor pressure measurements of mercury at several different temperatures. The following values were obtained for the orifice area and Clausing factor of each cell: cell 1, Pyrex, 2.76×10^{-2} cm.^{2}, 0.850; cell 2, Vycor, 3.17×10^{-2} cm.^{2}, 0.899.

Fresh samples of the compounds were used in each run to ensure that the activity of the solids remained near unity, since extensive decomposition of both VCl_3 and VBr_3 occurred simultaneously with the simple vaporization process. The vanadium di-

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(1) (a) Contribution No. 1214. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission; (b) this paper was taken in part from 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, J. W. Roddy, and K. O. Berry, *Inorg. Chem.*, **3**, 50 (1964).

(3) M. A. Oranskaya and I. L. Perfilova, *Zh. Neorgan. Khim.*, **6**, 257 (1961).

(4) For a discussion of the Knudsen effusion determination of vapor pressures see: G. Thomson in "Technique of Organic Chemistry," A. Weissberger, Ed., Vol. I, Part I, Second Ed., Interscience Publishers, Inc., New York, N. Y., 1949, pp. 193–195.

(5) The metal was purified by the crystal-bar iodide process and supplied to us through the courtesy of Dr. O. N. Carlson of this laboratory.

(6) J. Meyer and R. Backa, *Z. anorg. allgem. Chem.*, **135**, 177 (1924).

(7) F. Ephraim and E. Ammann, *Helv. Chim. Acta*, **16**, 1273 (1933).

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

(9) P. Clausing, *Ann. physik*, [5] **12**, 961 (1932).

and trihalides condensed in a compact ring at the cool end of the condensing tube, while any decomposition products, *e.g.*, Br_2, VBr_4, and VCl_4, condensed in the trap at −196°. The sublimed material was dissolved in either water or nitric acid after an experiment, and the total vanadium then was determined spectrophotometrically.[10]

After each experiment with VBr_3 in the effusion cell, VBr_4 that had effused into the cold trap was decomposed by allowing the trap to warm to room temperature. Bromine resulting from the reaction

$$VBr_4(s) = VBr_3(s) + {}^1/_2Br_2(g)$$

then was condensed in a side arm at −196°; the arm was sealed off and the elemental bromine determined either by weight determination (for larger amounts) or by spectrophotometric[11] or iodometric analysis. With VCl_3 in the effusion cell, VCl_4 was formed by disproportionation. The VCl_4 was condensed in the trap at −196° and determined by dissolving the deposit in water and analyzing for vanadium.[10]

To calculate the vapor pressure of a particular species from the experimental data the following equation was used.[4]

$$P_{\text{mm}} = \left(\frac{17.1435(g)}{(a)(cf)(t)}\right)\left(\frac{T}{M}\right)^{1/2}$$

In this equation a = orifice area in cm.², cf = Clausing factor, g = grams of material effused, t = time in sec., T = temperature in °K., and M = molecular weight of the vapor species.

Results and Discussion

Vaporization of VCl_2 and VBr_2.—The experimental vapor pressure–temperature data for VCl_2 are given in Table I for the temperature range 763 to 904°K. Over this range the vapor pressure is given by $\log P_{\text{mm}} = -9804/T + 8.713$, from which $\Delta H° = 44.8 \pm 1.4$ kcal. and $\Delta S° = 26.6 \pm 0.8$ e.u. (standard state of 1 atm.). These calculations were based on the assumption that VCl_2 vaporized as the monomer. Some support for vaporization as the monomer can be found in the good agreement of our results with those of Oranskaya and Perfilova.[3] They obtained $\log P_{\text{mm}} = -9721/T + 8.605$, $\Delta H° = 44$ kcal., and $\Delta S° = 26.2$ e.u. over the interval 1183 to 1373°K. and determined the vapor pressures by the transpiration technique. It is unlikely that vaporization as the dimer or higher polymer would occur over the entire range (763 to 1373°K.) encompassed by the two sets of data.

For VBr_2(s) least squares treatment of the vapor pressure data, which also are given in Table I, yielded $\log P_{\text{mm}} = -10460/T + 9.08$ and $\Delta H° = 47.8 \pm 1.6$, $\Delta S° = 28.3 \pm 0.8$ e.u. over the interval 787 to 989°K. Vaporization as the monomer was assumed.

It should be noted that the entropies of sublimation found for VCl_2 and VBr_2 are somewhat low compared to values reported for other transition metal dihalides. For example, in the interval 800 to 900°K. $\Delta S°$ for sublimation of $TiCl_2$ was found to be 30.7 e.u.[12] Some values of $\Delta S°$ of sublimation which have been reported for closely related dihalides at 298°K. are: $TiCl_2$, 41.2 e.u.[13]; TiI_2, 34 e.u.[14]; $CrCl_2$, 46 e.u.[15]; CrI_2, 58 e.u.[16] A more direct comparison with these values is provided by an estimation of $\Delta S°_{298}$ for sublimation of VCl_2 and VBr_2 given in Table II. These values are comparable with that reported for TiI_2 but are from 7 to 24 e.u. lower than the values given for the other halides. In view of the variation of more than 20 e.u. in the sublimation entropies reported for the above and other dihalides the results given here for VCl_2 and VBr_2 do not seem unreasonable. However, these results do point up the need for more detailed studies of the entropies of the solid and gaseous transition metal halides.

TABLE I

VAPOR PRESSURE DATA[a] FOR SOLID VCl_2 AND VBr_2

T, °K.	t, sec. × 10^{-3}	Wt. of VX_2, mg.	Pressure of VX_2, mm. × 10^4, Obsd.	Calcd.[b]
		VCl_2		
763	18.0	0.86	0.72	0.73
784	15.0	1.66	1.59	1.60
799	12.0	2.15	2.75	2.75
815	12.0	3.72	4.80	4.80
829	10.0	4.85	7.60	7.65
843	9.0	6.65	11.7	12.0
871	7.2	12.4	27.6	28.4
888	6.0	16.9	45.7	46.8
904	3.6	15.9	72.0	73.2
		VBr_2		
793	15.0	1.00	0.78	0.78
826	9.0	1.99	2.63	2.62
847	9.0	4.11	5.49	5.40
873	6.0	6.18	12.6	12.6
902	5.0	12.4	30.9	30.5
947	5.0	43.2	110	109
989	2.0	44.3	288	320
787	15.0	0.98	0.70	0.62

[a] Data taken with cell 2. [b] Calculated from $\log P = -A/T + B$ as given in Discussion.

TABLE II

ESTIMATED THERMODYNAMIC DATA FOR VAPORIZATION OF VANADIUM HALIDES

Compound	$\Delta H°_0$, kcal.	I	$\Delta H°_{298}$, kcal.	$\Delta S°_{298}$, e.u.
VCl_2	50.6	−80.6	48.5	33.8
VBr_2	52.8	−81.4	50.7	34.6
VCl_3	50.0	−108.2	47.6	54.7
VBr_3	52.9	−117.0	50.5	63.5

To estimate the heats and entropies of sublimation of VCl_2 and VBr_2 at 298°K. σ-function plots were derived from the data according to the method of Brewer and Searcy.[17] In order to calculate σ a ΔC_p of −7 cal. deg.⁻¹ for sublimation of both VCl_2 and VBr_2 was used as a reasonable value by comparison with similar metal halides.[15] The results are given in Table II.

The value of $\Delta H°_{298}$ can be used to estimate the average V–X bond energy for the gaseous dihalides as shown in Table III.

Equations 1 and 2 yield 120 and 112 kcal., respectively, for the average V–Cl and V–Br bond energy. Even with the rather large uncertainty of *ca.* 15 kcal. in these bond energies, resulting primarily from the uncertainty in the heats of formation of the halides,

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

[11] F. Binkley, *J. Biol. Chem.*, **173**, 403 (1948).

[12] M. Farber and A. J. Darnell, *J. Chem. Phys.*, **25**, 526 (1956).

[13] D. Altman, M. Farber, and D. M. Mason, *ibid.*, **25**, 531 (1956).

[14] A. Herczog and L. M. Pidgeon, *Can. J. Chem.*, **34**, 1687 (1956).

[15] H. Doerner, U. S. Bur. Mines Bulletin 577, 1937.

[16] T. L. Allen, *J. Am. Chem. Soc.*, **78**, 5476 (1956).

[17] L. Brewer and A. Searcy, *J. Chem. Educ.*, **26**, 548 (1949).

TABLE III

	Reaction	ΔH°_{298}, kcal.	Reference
	$VCl_2(g) = VCl_2(s)$	−48.5	This work
	$VCl_2(s) = V(s) + Cl_2(g)$	108	[a]
	$V(s) = V(g)$	122	[b]
	$Cl_2(g) = 2Cl(g)$	58	[c]
(1)	$VCl_2(g) = V(g) + 2Cl(g)$	239.5	
	$VBr_2(g) = VBr_2(s)$	−50.7	This work
	$VBr_2(s) = V(s) + Br_2(l)$	100	[a]
	$V(s) = V(g)$	122	[b]
	$Br_2(l) = 2Br(g)$	53.4	[c]
(2)	$VBr_2(g) = V(g) + 2Br(g)$	224.7	

[a] "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500, 1950. [b] L. Brewer, "Heats of Sublimation of the Elements," U. S. Atomic Energy Commission Report UCRL-2854, 1955. [c] T. Cottrell, "The Strengths of Chemical Bonds," Butterworths Scientific Publications, London, 1958.

the bond energy is considerably higher than that calculated from Pauling's equation[18]

$$D(\text{V–X}) = {}^1/_2[D(\text{V–V}) + D(\text{X–X})] + 23(X_x - X_v)^2$$

In this equation the dissociation energies and electronegativities of the halogens and vanadium were those listed above and in Pauling's book. The V–V single bond energy was taken as one-sixth of the heat of atomization of vanadium.[19] Values of 84 and 69 kcal. were calculated for the V–Cl and V–Br bond energies, respectively, using Pauling's equation and his value of 1.6 for the electronegativity of vanadium.

By substituting the V–Cl bond energy of 120 kcal. into Pauling's equation an electronegativity of 1.2 is obtained for V(II). This lower value is more consistent with values that have been determined from data for other metal halides. For example, Pauling lists a value of 1.7 for the electronegativity of iron, but Allen[20] has calculated more recently a value of 1.3.

Vaporization of VCl_3 and VBr_3.—The vaporization of both VCl_3 and VBr_3 was accompanied by decomposition *via* disproportionation and dissociation of elemental halogen, the latter occurring only in the case of VBr_3. It was possible to determine the vapor pressures of the solids because the vapors resulting from the separate processes condensed at widely separated regions of the apparatus. An attempt was made to determine the dissociation and disproportionation pressures also, but particularly in the case of VBr_3, it did not appear that equilibrium pressures were obtained owing to a low condensation coefficient for the vapor in the effusion cell.

TABLE IV

VAPOR PRESSURE DATA FOR SOLID VCl_3 AND VBr_3

Cell	T, °K.	t, sec. × 10^3	VX_3, wt., mg.	VX_4 wt., mg.	Obsd. press., mm. × 10^4 VX_4	Obsd. press., mm. × 10^4 VX_3	Calcd. P_{mm} VX_3 (× 10^4)
				VCl_3			
1	624	14.0	0.33	21.3	2.00	0.34	0.34
1	648	10.0	0.88	44.6	5.92	1.31	1.29
1	659	8.2	1.27	54.7	9.00	2.32	2.31
1	682	7.2	3.50	127	24.2	7.40	7.31
1	696	5.0	4.55	147	41.0	14.0	14.2
1	719	3.0	7.78	212	100	40.7	40.0
1	742	2.0	12.9	301	218	103	105
2	655	7.2	1.14	50	7.7	1.95	1.87
2	674	5.0	2.01	80	18.0	5.02	4.94
2	707	2.5	4.92	150	69.6	25.1	23.5
				VBr_3			
1	594	13.1	0.19	1.74	0.123	0.151	0.150
1	634	6.0	0.84	4.61	0.733	1.53	1.52
1	664	2.1	1.42	6.60	3.06	7.46	7.21
1	616	7.5	0.40	2.63	0.330	0.568	0.558
1	675	2.0	2.18	7.47	3.68	12.1	12.3
1	697	1.8	5.40	14.8	8.22	34.0	34.1
2	629	8.0	1.04	5.48	0.537	1.15	1.16
2	655	5.0	2.38	9.12	1.46	4.27	4.59
2	685	3.0	6.17	17.1	4.64	19.0	19.7

The vapor pressure data for VCl_3 and VBr_3 are given in Table IV. Data taken with either cell 1 or cell 2, which had different orifice diameters, gave essentially the same results. Thus the condensation coefficients for the simple vaporization processes were assumed to be near unity and the measured pressures near the equilibrium vapor pressures. In the absence of any direct evidence for extensive dimerization or polymerization of the vapors, the vapor pressures were calculated for vaporization as the monomers.

By least squares treatment of the data the vapor pressure equations and thermodynamic information given in Table V were derived. Further treatment of the data according to the method of Brewer and Searcy[17] gave the results for VCl_3 and VBr_3 in Table II. There are no other data available with which to compare these results.

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(18) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960.

(19) D. D. Eley, *Discussions Faraday Soc.*, **8**, 34 (1950).

(20) T. L. Allen, *J. Chem. Phys.*, **26**, 1644 (1957).

TABLE V

VAPORIZATION CHARACTERISTICS OF VCl_3 AND VBr_3

Compd.	Process	log P_{mm}	$\Delta H°$, kcal.	$\Delta S°$, e.u.	T, °K.
VCl_3	Subl.	$-9777/T + 11.20$	44.7 ± 1.4	38.0 ± 0.8	625–740
	Dispropn.[a]	$-7801/T + 9.84$	36 ± 1	32 ± 1	625–740
	Dispropn.[b]	$-8350/T + 11.58$	38 ± 1	39.6 ± 1	700–900
VBr_3	Subl.	$-9470/T + 11.12$	43.3 ± 1.2	37.7 ± 1	590–700

[a] This work. [b] Data derived from ref. 21.

Disproportionation pressures for the reaction

$$2VCl_3(s) = VCl_2(s) + VCl_4(g)$$

are also given in Table IV and were derived from measurements with both cell 1 and cell 2. A comparison of the results derived from this work and those of Oranskaya, *et al.*,[21] is given in Table V; the latter authors utilized the transpiration technique to measure the disproportionation pressure. As indicated the agreement of these results is poor.

Although the results from the cells of different orifice areas were in good agreement for disproportionation of VCl_4, the results of measurements to determine the equilibrium pressures from the reactions

$$VBr_3(s) = VBr_2(s) + {}^1/_2Br_2(g)$$

and

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

showed a definite dependence on the orifice area. This was taken to indicate that in reactions of this type the condensation coefficients may be much less than unity, and thus equilibrium pressures were not obtained. Therefore, in spite of the agreement between the data from the two cells, it is probable that nonequilibrium pressures were obtained for the disproportionation of VCl_3. Consequently it is likely that the previous workers' results on the disproportionation of VCl_3 are the more reliable. Equilibrium pressures for the reactions of VBr_3 given above have been determined by the transpiration technique and are the subject of another paper.[22]

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[21] M. A. Oranskaya, Yu. S. Lebedev, and I. L. Perfilova, *Zh. Neorgan, Khim.*, **6**, 259 (1961).

[22] R. E. McCarley and J. W. Roddy, *Inorg. Chem.*, **3**, 54 (1964).

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Crystal and Molecular Structure of Indium(III) Iodide (In_2I_6)[1]

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Indium(III) iodide exists in the crystals as dimers, In_2I_6, according to a determination of the structure by single-crystal X-ray diffraction. The crystals are monoclinic, space group $P2_1/c$, with $a = 9.837 \pm 0.004$, $b = 6.102 \pm 0.004$, $c = 12.195 \pm 0.009$ Å., $\beta = 107.69 \pm 0.05°$, $Z = 2$, $d_x = 4.72$ g./cc. Twinning is common. Iodine atoms are approximately in cubic closest packing. Indium atoms are in adjacent tetrahedral holes so that the structure consists of pairs of tetrahedra sharing edges. The In–I bond distances are 2.84 Å. for the bridge bonds and 2.64 Å. for the terminal bonds. The In–In distance in the molecule is 3.88 Å. Bond angles are 93.7° for I–In–I (bridge bonds) and 125.1° for I–In–I (terminal bonds).

Introduction

Most crystalline metallic trihalides exist as structures which are infinite complexes in one, two, or three dimensions.[2] Only a few (*e.g.*, monomeric SbF_3[3] and $SbCl_3$[4] and dimeric Al_2Br_6[5] and Au_2Cl_6[6]) are known to have structures consisting of discrete molecules, although dimeric molecular structures are very common for trihalides in the liquid and gaseous states. Dimers exist also in the solid triiodides of aluminum, gallium, and indium according to iodine nuclear quadrupole spectra reported by Segel and Barnes.[7] This fact is confirmed for the indium compound by the crystal structure determination reported in the present paper. According to X-ray powder diagrams[8] it is likely that the aluminum and gallium iodides have the same crystal structure as In_2I_6.

This substance was originally investigated in this laboratory as part of a search for trihalides with structures like rare earth halides. Because of unrecognized twinning in the first samples, we thought at one time that the structure was triclinic with a unit cell containing 64 atoms in the primitive unit. In trying to

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[1] Work done under the auspices of the U. S. Atomic Energy Commission.

[2] A. F. Wells, "Structural Inorganic Chemistry," Clarendon Press, Oxford, England, 1962, p. 353.

[3] A. Byström and A. Westgren, *Arkiv Kemi Mineral. Geol.*, **17B**, No. 2, 1 (1943).

[4] I. Lindqvist and A. Niggli, *J. Inorg. Nucl. Chem.*, **2**, 345 (1956).

[5] P. A. Renes and C. H. MacGillavry, *Rec. trav. chim.*, **64**, 275 (1945).

[6] E. S. Clark, D. H. Templeton, and C. H. MacGillavry, *Acta Cryst.*, **11**, 284 (1958).

[7] S. L. Segel and R. G. Barnes, *J. Chem. Phys.*, **25**, 578 (1956).

[8] E. L. Amma, private communication, 1963.